



UNIVERSIDAD AUTÓNOMA DEL ESTADO DE MÉXICO

INSTITUTO INTERAMERICANO DE TECNOLOGÍA Y CIENCIAS DEL AGUA

**"REVISIÓN CRÍTICA DE LOS PRINCIPALES TRATAMIENTOS DE
POLIFENOLES Y DERIVADOS"**

TESIS

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MAESTRÍA EN CIENCIAS DEL AGUA

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RESUMEN

Los efluentes industriales son una de las fuentes más importantes de contaminación del agua, debido a que contienen diversos contaminantes orgánicos como tintes sintéticos, plaguicidas, productos farmacéuticos y polifenoles, estos son solo algunos de muchos otros compuestos detectados a niveles traza en el agua residual; que por su complejidad en sus estructuras químicas son resistentes a la degradación biológica y química.

En esta tesis se llevó a cabo una revisión de los diferentes tratamientos aplicados para eliminar polifenoles del agua residual y evaluar las tecnologías más favorables, además de discernir los principales factores limitantes. Los tratamientos evaluados fueron: procesos de oxidación avanzados (POA) y adsorción.

Diversos métodos se han utilizado para el tratamiento del agua residual en los últimos años, uno de los más investigados son los procesos de oxidación avanzada (POA) por su efectividad para degradar contaminantes orgánicos mediante la generación de un poderoso agente oxidante como lo es el radical hidroxilo.

En el proceso de adsorción, se evaluó el potencial de los diferentes materiales adsorbentes, ya que su eficiencia depende de las propiedades fisicoquímicas de los contaminantes, pH, las características del agua y las condiciones de operación.

En la última parte de esta tesis, están propuestas las tecnologías más adecuadas, sus ventajas, áreas de oportunidad y futuras tendencias para el tratamiento del agua residual con altas concentraciones de polifenoles.

ABSTRACT

Industrial effluents are one of the most important sources of water pollution, as they contain various organic pollutants such as synthetic dyes, pesticides, pharmaceuticals, and polyphenols, these are just some of the many other compounds detected at trace levels in wastewater; that due to their complexity in their chemical structures are resistant to biological and chemical degradation.

In this thesis, a review of the different treatments applied to eliminate polyphenols from wastewater was carried out and the most favorable technologies evaluated, in addition to discerning the main limiting factors. The treatments evaluated were advanced oxidation processes (AOP) and adsorption.

Various methods have been used to treat wastewater in recent years, one of the most investigated is advanced oxidation processes (AOP) for their effectiveness in degrading organic pollutants through the generation of a powerful oxidizing agent such as the hydroxyl radical.

In the adsorption process, the potential of the different adsorbent materials was evaluated, since their efficiency depends on the physicochemical properties of the pollutants, the pH, the characteristics of the water and the operating conditions.

In the last part of this thesis, the most suitable technologies, their advantages, areas of opportunity and future trends for the treatment of wastewater with high concentrations of polyphenols are proposed.

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Lista de abreviaciones

Al	Aluminio
AT	Ácido tánico
CPC	Colector parabólico compuesto
Da	Dalton
DBO₅	Demanda bioquímica de oxígeno
DHHDP	Deshidrohexitolhidroxifenilo
DQO	Demanda química de oxígeno
DRX	Difracción de rayos X
E°	Potencial de oxidación
EDS	Espectroscopia de rayos X de energía dispersiva
Fe	Hierro
Fe²⁺	Ion ferroso
Fe³⁺	Ion férrico
H⁺	Hidrógeno (ion hidrógeno)
H₂O₂	Peróxido de hidrógeno
HO₂·	Radical perhidroxilo
LDHs	Hidroxidos dobles en capas
LDPE	Polietileno de baja densidad
LLDPE	Polietileno de baja densidad lineal
M_w	Peso molecular
nm	Nanómetro
nZV	nano cero-Valente
OD	Oxígeno disuelto
OH·	Grupo hidroxilo
pH	Potencial de hidrógeno
POA	Proceso de oxidación avanzada
SEM	Microscopio electrónico de barrido
sp.	Especie
TDAH	Trastorno por déficit de atención e hiperactividad
Tg	Transición vítrea
TQ	Tanino de Quebracho
TT	Tanino de Tara
UV	Ultravioleta
UV-Vis	Ultravioleta –visible
ZVAl	Aluminio cero-valente
ZVM	Metales cero-valente
PP	Polifenoles

INTRODUCCIÓN

Los polifenoles son metabolitos secundarios sintetizados exclusivamente por plantas vasculares (García et al., 2016), comprenden una gran diversidad de moléculas cuya estructura se caracteriza por al menos dos anillos fenólicos unidos a uno o más grupos hidroxilo (Belščak-Cvitanović et al., 2018). La clasificación general de los polifenoles incluye a los flavonoides, ácidos fenólicos, estilbenos, lignanos y taninos (Singla et al., 2019). Estos últimos, los taninos; son biomoléculas con alto peso molecular de hasta 20000 Da (Khanbabaee & van Ree, 2001) y puede formar complejos fuertes con diversas macromoléculas (Das et al., 2020).

Estos compuestos se clasifican en taninos hidrolizables y taninos condensados (Kalyanaraman et al., 2015), debido a su amplia diversidad estructural y características químicas se consideran como unos de los polifenoles más importantes por sus diferentes aplicaciones industriales como adhesivos para madera (Baltes et al., 2018), curtido de piel (Thankappan et al., 2015), anticorrosivos (Shirmohammadli et al., 2018), etc. Además, se han desarrollado productos a base de extractos de plantas ricos en taninos con propiedades terapéuticas, medicinales, farmacológicas y antioxidantes (Oćwieja, Adamczyk, & Morga, 2015).

Los taninos son solubles en agua (Yan et al., 2020) y por su naturaleza recalcitrante se han convertido en un problema importante en el agua residual, porque no pueden ser eliminados de manera efectiva mediante tratamientos convencionales debido a su persistencia y resistencia a la degradación microbiana (Bardi et al., 2017). La presencia de estos compuestos contribuye al aumento de la Demanda Química de Oxígeno (DQO); sumado a su toxicidad generan efectos adversos que causan alteraciones en flora, fauna acuática y salud humana (Grandclément et al., 2017).

Los procesos de oxidación avanzada (POA) han demostrado ser efectivos en la remoción de estos contaminantes orgánicos mediante la generación de radicales hidroxilo o especies reactivas oxidantes (Zhuan & Wang, 2020), aunque se generan subproductos tóxicos en presencia de cloro y bromo (Giannakis et al., 2020; Gonçalves et al., 2019) o como los ácidos húmicos al degradarse los taninos (Tang et al., 2014).

En este sentido, el objetivo principal de esta investigación fue hacer una revisión sobre la remoción de polifenoles, en particular los taninos y ácidos húmicos en el agua residual a través de las diferentes tecnologías existentes como: ozonización, procesos basados en UV, Fenton, foto-Fenton, fotocátalisis, tratamiento hidrotermal, procesos electroquímicos avanzados de oxidación (EAOP) y adsorción.

1. ANTECEDENTES

Los metabolitos producidos por organismos vivos se clasifican como primarios o secundarios. Los metabolitos primarios son esenciales para el mantenimiento celular y su concentración dentro del organismo depende sólo de su estado fisiológico. Las proteínas, ácidos nucleicos, carbohidratos y los lípidos son ejemplos importantes de metabolitos primarios (García et al., 2016). Por otra parte, los metabolitos secundarios no participan directamente en el metabolismo fotosintético o respiratorio, pero son importantes porque juegan un papel decisivo en la supervivencia de las plantas (Chiquee et al., 2015), actuando como protección frente a diferentes amenazas biológicas, sequedad, rayos UV y radicales libres (Shirmohammadli et al., 2018).

Existen cinco principales clases de metabolitos secundarios que se encuentran en la naturaleza definidos por su estructura química: compuestos nitrogenados (alcaloides, aminoácidos no proteinogénicos, lectinas y cianógenos), isoprenoides (terpenos y esteroides), policétidos, ácidos grasos y fenoles (cumarinas, flavonoides, lignina, taninos) (Huang et al., 2009). En este contexto, el grupo denominado taninos cuyo nombre se deriva del francés "tanin" (sustancia de curtido), es usado como referencia de polifenoles naturales (Khanbabaee & van Ree, 2001), su estructura con más de un grupo –OH es la clase más grande de metabolitos en plantas vasculares y su biosíntesis se deriva de la vía shikimato-cinamato (Figura 1).

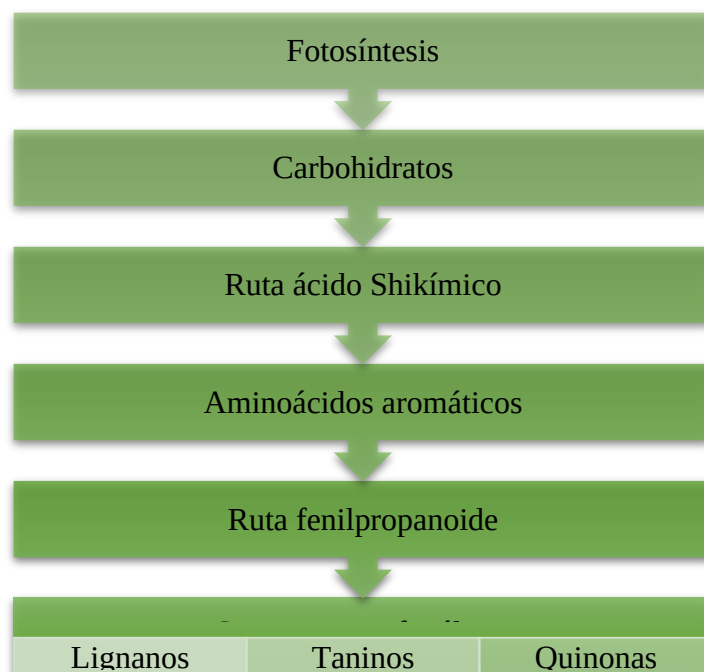


Figura 1. Biosíntesis de diversos compuestos fenólicos a partir de un conjunto de aminoácidos formado por la vía del ácido Shikímico (Ramawat et al., 2009).

Los polifenoles son sintetizados exclusivamente en plantas vasculares y en una amplia variedad de especies (por ejemplo, monocotiledóneas, dicotiledóneas, helechos y coníferas) y tejidos vegetales (por ejemplo, hojas, madera, etc.). En las plantas vasculares, los taninos son el tercer grupo más abundante de metabolitos secundarios después de los dos principales componentes de madera como carbohidratos estimulantes (en forma de celulosa y hemicelulosa) y lignina. A pesar de que la lignina es el biopolímero aromático más distribuido en la naturaleza, los taninos en términos de propiedades fisicoquímicas, su reactividad, la diversidad biológica, alto contenido de $-OH$ /monómero y versatilidad tiene ventajas reconocidas para el desarrollo de biomateriales. Además, en tejidos blandos como hojas, tallos y corteza de plantas leñosas, la abundancia de taninos puede exceder en comparación con la lignina (García et al., 2016).

En la naturaleza los taninos se encuentran en todo el mundo, en muchas familias de plantas superiores como en madera de castaño y roble (*Quercus sp*) (Khanbabaee & van Ree, 2001), Dividivi, pino (*Pinus radiata*), mimosa (*Acacia mearnsii*), entre otras (Shirmohammadli et al., 2018). Altas concentraciones de taninos se encuentran en casi todas las partes de la planta

como la corteza, hojas, frutos, raíces y semillas (Khanbabaee & van Ree, 2001). Dependiendo de su origen y su amplia variedad química, estos compuestos tienen una masa molar entre 300 y 3000 Da (g mol^{-1}); sin embargo, recientemente se han aislado moléculas con una masa molar de hasta 20000 Da (Sieniawska & Baj, 2017). Estos polifenoles contienen una gran cantidad de grupos hidroxilo y otros grupos funcionales (1 a 2 por 100 Da), y por lo tanto son capaces de formar enlaces cruzados con proteínas y otras macromoléculas (Chung et al., 1998).

El aumento en la concentración de taninos en la planta se relaciona con alguna enfermedad, se asume que la función de los taninos es para protección contra la luz (rayos UV y radicales libres) y como mecanismo de defensa en el caso de diferentes amenazas biológicas (animales, insectos, hongos y bacterias) (Khanbabaee & van Ree, 2001). También se les conoce como agentes protectores contra la deshidratación en algunas plantas, mediante mecanismos moleculares. Los taninos se pueden obtener como subproducto de desechos agrícolas como el té y café (Shirmohammadli et al., 2018). También se han encontrado taninos en una variedad de alimentos como sorgo, mijo, cebada, frijoles, habas, guisantes, algarrobas, gandules, y otras legumbres; también las frutas contienen gran cantidad de taninos como ejemplos los arándanos, moras, manzanas, plátanos, dátiles, uvas, espinos, melocotones, peras, caquis, ciruelas, frambuesas y fresas (Chung et al., 1998).

Por otra parte, se sabe que los taninos tienen la capacidad de curtir o convertir la piel de los animales en cuero, precipitar alcaloides, gelatinas y otras proteínas (Jordan lloyd, 1934). Desde la antigüedad, las tribus prehistóricas sabían sobre el curtido de pieles, las protegían con material cerebral y la grasa de los animales muertos (Khanbabaee & van Ree, 2001).

1.1 Tipos de taninos

Debido a la enorme diversidad estructural y propiedades químicas, los taninos se clasifican en dos grupos principalmente: taninos hidrolizables y taninos condensados (Khanbabaee y van Ree, 2001).

1.1.1 Taninos hidrolizables

Los taninos hidrolizables son combinaciones de fenoles simples, como ácido gálico elágico (Figura 2) y de ésteres de un azúcar, principalmente glucosa; pueden fraccionarse hidrolíticamente por ácidos, bases o ciertas enzimas para producir carbohidratos y ácidos fenólicos (Shirmohammadli et al., 2018). A su vez se dividen en productos después de la hidrólisis en galotaninos y elagitaninos (Pizzi, 2019).

Los galotaninos, una vez hidrolizados liberan ácido gálico y glucosa, se encuentran principalmente en las nueces de agallas, es decir, en los brotes de algunos árboles (particularmente en *Quercus infectoria* y *Rhus semialata*) y en las vainas de tara (*Caesalpinia spinosa*). A la vista, tienen un color amarillo o blanco-crema. Al gusto, se siente un sabor astringente y amargo a la vez. Ejemplos importantes de galotaninos son ácido tánico, tanino turco, tanino tara, tanino acer y tanino hamamelis (Sieniawska & Baj, 2017).

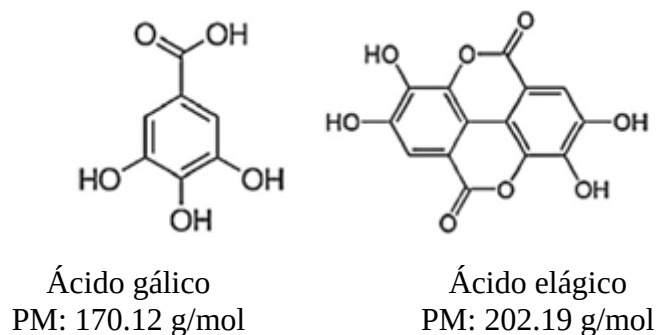


Figura 2. Representación esquemática de una molécula de taninos hidrolizables (Shirmohammadli et al., 2018).

El ácido tánico es el más conocido de los taninos hidrolizables (Pizzi, 2019). Su estructura química se expresa como $C_{76}H_{52}O_{46}$, que corresponde a una molécula central de glucosa y diez grupos galoil (Figura 3); los grupos galoil pueden variar de 2 hasta 12 por molécula (dependiendo de la fuente vegetal utilizada para la extracción del ácido tánico). El ácido tánico generalmente se extrae de *Caesalpinia spinosa* (Tara), *Rhus semialata*, *Rhus coriaria* L. y *Quercus infectoria* (Zhang et al., 2019).

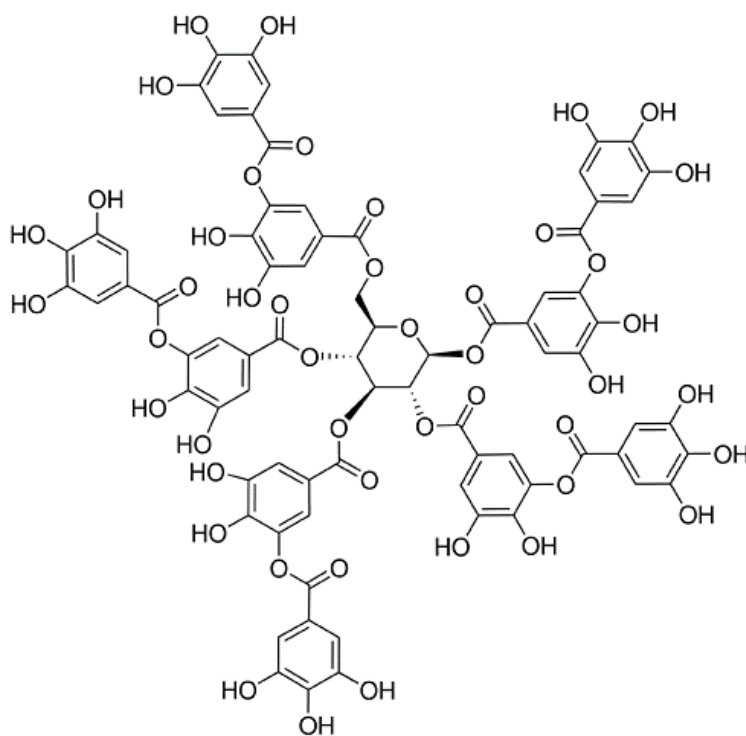
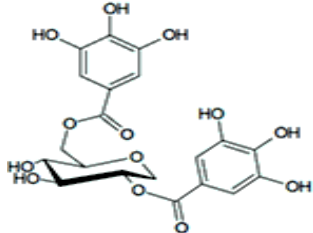
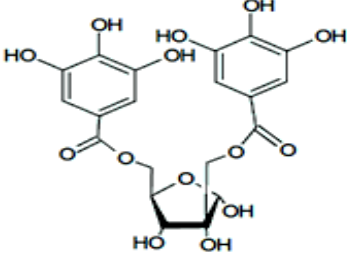
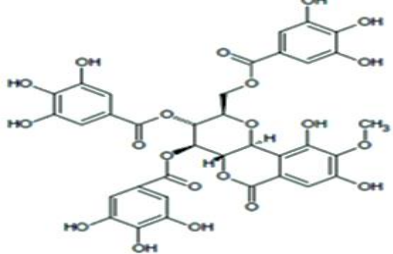
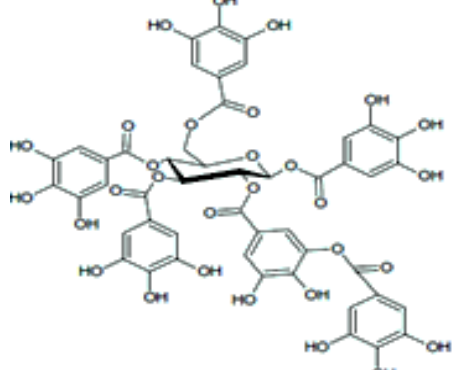


Figura 3. Estructura química del ácido tánico (Sieniawska & Baj, 2017).

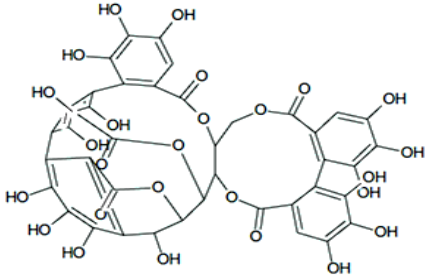
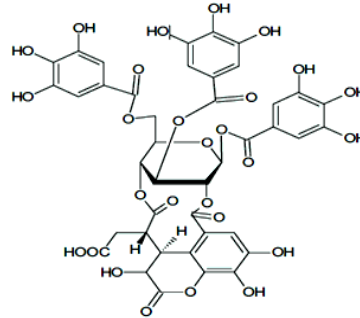
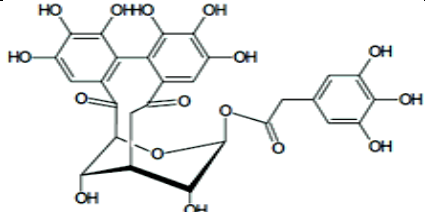
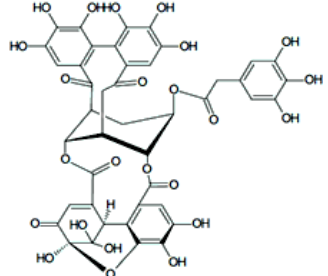
La distribución de los taninos hidrolizables es limitada comprende sólo algunas especies dicotiledóneas y se pueden extraer de árboles de castaño (*Castanea sp.*), Mirabolanos (*Terminalia y Phyllanthus sp.*), Dividivi (*Caesalpinia sp.*), Roble (*Quercus sp.*), Eucalipto (*Eucalyptus sp.*) y *Asian Myrica sp.*, ejemplos de estos taninos se muestran en la tabla 1 (García et al., 2016).

Tabla 1. Ejemplos de galotaninos

Nombre	Estructura	Fuente
Acer tanino 6-digaloil-1,5- anhidro-Dglucitol, compuesto cristalino		<i>Acer ginnala</i>
Tanino hamameli Digaloil-hamamelose		Especies de <i>Hamamelis</i> , <i>Castanea</i> , y <i>Sanguisorba</i>
3,4,11-tri-O-galoi lbergenina Galotanino C- glicosídico		<i>Mallotus japonicas</i>
2-O-digaloil-1,3,4,6- tetra- O-galoil-b- glucopiranososa hexagaloil		<i>Paeonia suffruticosa</i>

Los elagitaninos con más de 500 productos naturales caracterizados hasta el momento, constituyen el grupo más grande de taninos conocidos, se forman a partir de los galotaninos por acción oxidativa acoplado de al menos dos unidades galoil (compuestos de unidades de biarilo y glucosa). Ejemplos de elagitaninos se describen en la tabla 2 y 3.

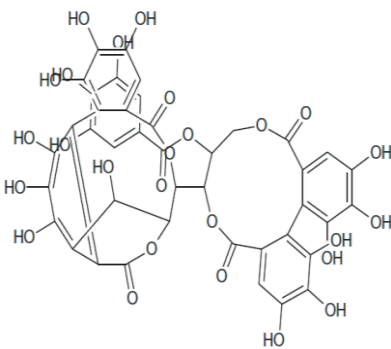
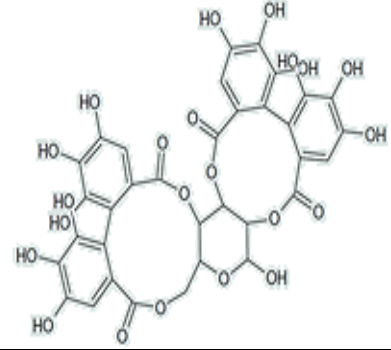
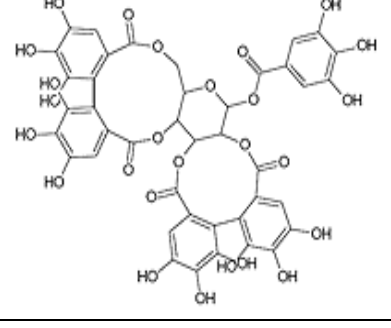
Tabla 1. Ejemplos de elagitaninos

Nombre	Estructura	Fuente
Castalagin		Está presente en madera de roble y castaño
Ácido chebulínico tiene un grupo polifenólico que se considera un producto de la oxidación del grupo Deshidrohexahidroxidifenilo (DHHDP).		<i>Terminaria chebula</i>
Corilagin, parte primaria de las estructuras de varios elagitaninos y deshidroellagitaninas		<i>Caesalpinia coriaria</i> y <i>Punica granatum</i>
Geraniin deshidroellagitanino, compuesto cristizable		Especies de <i>Euphorbiaceae</i> <i>Ac alyphea</i> <i>Hippomaneae</i> y geranio

Fuente: Sieniawska & Baj, 2017

Los elagitaninos experimentan una amplia variedad de modificaciones posteriores al acoplamiento, la apertura del anillo de glucosa con la formación de un enlace C-glucosídico, así como un resto flavogalonilo. Los compuestos *elagitaninos C-glucosídicos* son los más abundantes que se encuentran en la naturaleza (Tabla 3).

Tabla 3. Ejemplos de elagitaninos *C-glucosídicos*

Nombre	Estructura	Fuente
Casuarinin, isómero de casuarictina		<i>Pericarpio de punica granatum L.</i> , especies de <i>Casuarina</i> y <i>Stachyurus</i> , <i>Alnus sieboldiana</i> Matsum
Pedunculagin formado a partir de casuarictina y la pérdida de un grupo galato		Especies de <i>Casuarina</i> y <i>Stachyurus</i>
Potencilina		<i>Agrimonia japonica</i>

1.2 Taninos condensados

Los taninos condensados son estructuralmente más complejos que los taninos hidrolizables, se conocen comúnmente como proantocianidinas o más ampliamente, como poliflavonoides. Los flavonoides son un grupo de metabolitos basado en un sistema de anillo heterocíclico derivado de fenilalanina (B) y biosíntesis de policétidos (A), su estructura flavonoide, las letras estándar se usan para identificar los anillos y el sistema de numeración sistemática de átomos de carbono se muestra en la Figura 4; todos los taninos condensados derivan de

oligómeros polihidroxi-flavan-3-ol unidos entre sí principalmente por enlaces C-C entre los anillos A de las unidades de flavanol y los anillos de pirano de otras unidades de flavanol.

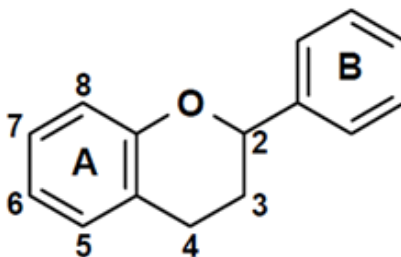


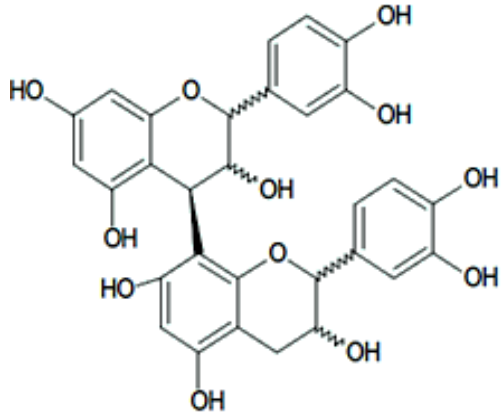
Figura 4. Estructura flavonoide (Jordan lloyd, 1934).

Los taninos condensados constituyen más del 90% de la producción mundial total de taninos comerciales (> 220.000 toneladas por año), son química y económicamente más interesante como biopolímero. Son muy abundantes en las cortezas y maderas de leguminosas (*Acacia* sp., *Lotus* sp. y *Serícea* sp.), coníferas (*Tsuga* sp. y *Pinus* sp.), abedul (*Betula* sp.), gambier (*Uncaria* sp.), manglares (*Rhizophora* sp.), madera de *Schinopsis* sp. (Quebracho) (Tabla 4) (García et al, 2016). Además, están ampliamente distribuidos en frutas, verduras, forrajes, plantas, cacao, vino tinto y ciertos alimentos como sorgo, mijo y legumbres (Chung et al., 1998).

Los polifenoles vegetales (taninos condensados, taninos hidrolizables y florotaninos), representan el cuarto polímero orgánico más abundante en biomasa y el segundo, después de la lignina, considerando solo polímeros aromáticos (Billerach et al., 2019).

Tabla 4. Ejemplos de taninos condensados

Nombre	Estructura	Fuente
Proantocianidina A1		Pieles de maní
Proantocianidina A2		<i>Aesculus hippocastanum</i> <i>Vaccinium oxycoccos</i>
Proantocianidina C1		<i>Vitis vinifera</i>
Nombre	Estructura	Fuente

Procianidina B2		<i>Crataegus monogyna</i> <i>Vitis vinifera</i> <i>Cinchona pubescens</i>
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Fuente: Sieniawska & Baj, 2017

1.2 Propiedades fisicoquímicas de los taninos

En general, los taninos son oligómeros/polímeros sólidos amorfos, no cristalinos, de color amarillo pálido, ligeramente marrón, de baja densidad. Numerosos taninos son ópticamente activos, mientras que su estereoquímica está muy influenciada por la secuencia C15. Los extractos de taninos secos son higroscópicos y exhiben una fuerte absorción en la región UV-Vis con varios máximos (λ_{max} : 250 y 290 nm). A temperatura ambiente son solubles en agua, su propiedad recalcitrante los hace tan persistentes y requieren de mucho tiempo para degradarse en condiciones naturales, además puede bioacumularse en organismos vivos y ecosistemas (Nguyen et al., 2020). Producen un ambiente ácido con un fuerte sabor "astringente", así como coloides en el agua donde forman soluciones viscosas debido al puente de hidrógeno formado entre los grupos -OH y las moléculas de agua. La viscosidad depende de la concentración de taninos, la dispersión, la topología y la proporción de dominios hidrófilos/hidrófobos (García et al., 2016).

Además, son compuestos termolábiles y UV-lábiles propensos a la oxidación, sin embargo, el comportamiento térmico está fuertemente asociado con el peso molecular (M_w) y la estructura química. La temperatura de transición vítrea (T_g) está fuertemente asociada con peso molecular (M_w), el grado de pureza y el contenido de humedad. La T_g del tanino nativo oscila entre 120 y 180 °C (García et al., 2016).

1.3 Aplicaciones de taninos en diversas industrias

Actualmente diferentes industrias están explorando nuevos biopolímeros naturales como el quitosano, lignina y taninos para reemplazar polímeros a base de hidrocarburos (Singh & Kumar, 2020). Los taninos son uno de los materiales más interesantes ya que se pueden obtener de las plantas, y debido a sus diferentes características químicas y estructuras tienen un amplio rango de aplicaciones que se describen brevemente a continuación (Shirmohammadli et al., 2018).

1.3.1. Industria del cuero

La industria del curtido del cuero utiliza una técnica a base de cromo para obtener una piel suave, ligera y versátil que es difícil de lograr con otros métodos de fabricación; pero en la actualidad el curtido del cuero es el principal uso industrial de los taninos vegetales y puede ser un sustituto del cromo en el procesamiento del cuero (Sharma et al., 2019). El curtido a base de taninos proporciona al cuero fuerza, suavidad, resistencia a los productos químicos, estabilidad térmica y propiedades antimicrobianas (Shirmohammadli et al., 2018).

1.3.2. Industria de la madera

La madera contiene ácidos orgánicos, taninos y material lignocelulósico que son más susceptible a agentes de descomposición biológicos, químicos y físicos, por tanto, se requiere productos químicos como adhesivos, antitermita y otros materiales de revestimiento para su protección (P. Singh & Kumar, 2020a). Estos productos contienen compuestos fenólicos sintéticos, resinas amínicas y formaldehído que son sustancias cancerígenas. Como alternativa para este problema se están investigando materiales naturales de origen vegetal o animal, como los taninos en la producción de adhesivos para madera convirtiéndose en la segunda aplicación más importante después de la fabricación del cuero (Pizzi, 2019).

1.3.3. Industria de alimentos

1.3.3.1 Bebidas

En los vinos, los taninos se agregan por varias razones: para proporcionar olor, estabilidad de color, protección contra la oxidación, ya que pueden afectar el sabor, el olor y el color del vino; además se agregan para precipitación de material proteico, mejorar la sensación en la boca, el sabor y actúa como conservante natural (Shirmohammadli et al., 2018). Otra aplicación en bebidas es para aclarar la cerveza y jugos de frutas (Sharma et al., 2019), y proporcionar antioxidantes (Singh and Kumar, 2020).

1.3.3.2 Empaque de alimentos

La mayoría de los alimentos están envueltos o empacados en plástico polietileno de baja densidad (LDPE) y polietileno lineal de baja densidad (LLDPE) para protegerlos de la contaminación, aumentar la vida útil, prevenir daños físicos y deterioro a causa de los contaminantes ambientales. Pero estos materiales son peligrosos para el medio ambiente y la salud; por lo tanto, se están investigando nuevos materiales de envoltura a partir de fuentes biológicas como quitosano, almidón, gelatina, taninos y metilcelulosa. Actualmente, se están utilizando envases activos como una alternativa para proteger los alimentos los cuales usan taninos junto con otros polímeros naturales como la nano-celulosa para fabricar empaques con propiedades antioxidantes, biodegradables, con estructuras hidrófobas y resistente al calor aplicados en alimentos, medicamentos, ingeniería de tejidos, apósitos para heridas (P. Singh & Kumar, 2020b).

1.3.3.3. Alimento para animales

Actualmente se utilizan varios medicamentos para el control de parásitos en rumiantes. Algunas investigaciones han demostrado que el uso de plantas con alta concentración de taninos condensados para alimentación animal, mejoran la absorción de aminoácidos en el intestino delgado y la digestión de las proteínas; protegiéndose contra la eliminación bacteriana e inhibe la hinchazón en el rumen del ganado. Por el contrario, los taninos

hidrolizables pueden causar manifestaciones de toxinas como resultado de la hidrólisis en el rumen del ganado. En general, los taninos condensados pueden mejorar la digestión de nitrógeno en rumiantes de pastoreo. Además, aumentan el crecimiento de lana, producción de leche y cantidad de partos en ovinos y bovinos, así como la reducción de parásitos, mejorando el bienestar animal. Se pueden encontrar en leguminosas como el trébol blanco y rojo para alimentar a los animales de granja. En cantidad muy alta, los nutrientes pueden actuar como una sustancia tóxica y perjudicial, pero en la cantidad requerida son muy beneficiosos para la salud del animal. Por lo tanto, es necesario investigar más para optimizar la dosificación de taninos para diferentes tipos de animales (Shirmohammadli et al., 2018).

1.3.4. Aplicaciones en productos farmacéuticos y medicinales.

Actualmente no se utilizan compuestos puros en los productos farmacéuticos, excepto el ácido tánico y la tannalbina. Pycnogenol, el cual es un extracto patentado de taninos ampliamente utilizado. La mayoría de las aplicaciones medicinales se basan en extractos crudos de plantas ricas en taninos. Pycnogenol es una mezcla específica patentada de procianidinas extraídas de la corteza del pino, *Pinus pinaster Aiton*, se puede tomar para tratar problemas circulatorios, alergias, asma, zumbido en el oídos, presión arterial alta, dolor muscular, dolor, osteoartritis, diabetes, trastorno por déficit de atención con hiperactividad (TDAH), enfermedad del sistema reproductor femenino llamada endometriosis, síntomas de la menopausia, períodos menstruales dolorosos, erección disfunción y una enfermedad ocular llamada retinopatía. También se utiliza para prevenir trastornos del corazón y los vasos sanguíneos; incluyendo apoplejía, enfermedad cardíaca y venas varicosas. Además, Pycnogenol se emplea para retardar el proceso de envejecimiento, mantener la piel sana, mejora la resistencia atlética y mejora la fertilidad masculina (Sieniawska & Baj, 2017).

El ácido tánico presenta propiedades antibacterianas, antienzimáticas, antihistamínicas, antioxidantes, antimutagénicas y antitusivas. Es astringente utilizado en el tratamiento de la diarrea, úlceras, dolor de muelas, heridas, erupciones cutáneas, uñas encarnadas y para detener el sangrado. El ácido tánico no debe usarse de manera continua o en grandes cantidades porque ralentiza la absorción de hierro y posiblemente otros minerales traza. La

ingestión de ácido tánico también puede reducir la eficacia de las enzimas digestivas (Sieniawska & Baj, 2017).

El tanalbin es un complejo de ácido tánico y proteínas. Se emplea en el tratamiento de la diarrea y las infecciones bacterianas y fúngicas mediante la coagulación de proteínas en el intestino y a través de detener la pérdida de agua, así como al unirse a la superficie de la levadura y las bacterias y evitar su colonización, además de adherirse a la membrana de la pared intestinal (Sieniawska & Baj, 2017).

En términos de aplicación tópica, esta capa protectora puede mejorar la velocidad para sanar úlceras, heridas y quemaduras. Además, detiene el sangrado, previene la infección, protege contra irritación química y mecánica, bacteriana y microorganismos. Se sabe que los taninos tienen efectos antiinflamatorios que ayudan a minimizar los síntomas de enfermedades alimentarias como esofagitis, gastritis, enteritis y enfermedad intestinal inflamatoria. Los taninos hidrolizables también han mostrado efectos terapéuticos contra los virus del herpes resistente al aciclovir cuando se aplica en la membrana mucosa de la boca. Además, los taninos han demostrado ser antivirales y con características antiparasitarias (Shirmohammadli et al., 2018).

1.4 Efectos adversos a la salud

La concentración de taninos en los alimentos tiene efectos dañinos en la salud humana, no es aconsejable ingerir una gran cantidad de taninos (ingesta diaria de tanino por debajo del rango de 1.5 a 2.5 g es segura para el consumo), ya que puede estar involucrado en la formación de cáncer al actuar como inductor y promotor si están presentes con otras moléculas cancerígenas (Sharma et al., 2019). El ácido tánico causa necrosis de células hepáticas en humanos, así como en animales de pastoreo. El efecto antinutricional se presenta cuando los taninos forman complejos con minerales como fósforo, calcio y magnesio haciéndolos no disponibles para animales; además, reduce la biodisponibilidad de varias vitaminas (vitamina A y vitamina B12) y son responsables de la inhibición enzimática endógena formando complejos no digeribles. Por otra parte, se relaciona con las migrañas; reduciendo los niveles de serotonina, lo que aumenta su intensidad, esto se debe a la falta de

disponibilidad de almidón, que es limitado por el tanino y es un precursor de la serotonina (Sharma et al., 2019).

1.5 Contaminación por taninos

Los taninos son uno de los compuestos vegetales más abundantes en el reino vegetal y sus múltiples aplicaciones representan un problema ambiental muy serio; estas sustancias están presentes en la mayoría de las aguas superficiales y potables. Como compuestos polifenólicos solubles en agua, se ha demostrado que son tóxicos para los organismos acuáticos, como algas, fitoplancton, peces e invertebrados (Deng et al., 2012).

El tratamiento del agua residual representa uno de los principales problemas ya que de la degradación de los taninos se generan subproductos como las sustancias húmicas (HS) (Tang et al., 2014). Las HS son una clase de compuestos formados durante la humificación, un proceso de transformar materia orgánica biológicamente degradable (principalmente componentes vegetales y microbianos) en fuente de carbono estabilizado. Los HS están presentes en el agua, el suelo y sedimentos, son importantes para sostener el crecimiento de las plantas y controlar el destino de los contaminantes ambientales, son responsables de la estructura y propiedades físico-químicas del suelo, tienen una alta heterogeneidad química, presentan grupos aromáticos, grupos fenólicos y carboxílicos, además son color marrón (Chianese et al., 2020). Por otra parte, el ácido tánico (AT) reacciona con cloro durante el tratamiento de esterilización del agua y producen subproductos de desinfección que causan cáncer y afectan la salud de los seres humanos (Deng et al., 2012). Estos compuestos se metabolizan en el cuerpo humano y luego se excretan y se liberan a través de la orina o las heces al medio ambiente (Mompelat et al., 2009a).

Los taninos al ser compuestos polifenólicos podrían regularse mediante la Norma Oficial Mexicana, NOM-127-SSA1-1994, modificación del 2000, "Salud ambiental, agua para uso y consumo humano, límites permisibles de calidad y tratamientos a que debe someterse el agua para su potabilización" que establece un límite permisible como Fenoles o compuestos fenólicos de 0.3 mg/L. En la norma NOM-001-SEMARNAT-1996 que indica los límites máximos permisibles para descarga de aguas residuales a bienes nacionales, no se encuentra incluido este parámetro.

En cuanto a contaminación del agua, estas sustancias pueden ingresar a las aguas superficiales por la escorrentía de los bio-sólidos esparcidos en tierras agrícolas y también con el riego utilizando fuentes de agua contaminadas. Los contaminantes pueden llegar al agua subterránea mediante lixiviación o filtración (Wang & Wang, 2016), afectando la calidad del agua potable, el ecosistema y la salud humana (Mompelat et al., 2009b).

1.6 Métodos de tratamiento de aguas residuales industriales

Existen varios métodos para el tratamiento del agua residual dependiendo la composición, ya sea que ésta provenga del uso humano, agrícola o industrial, determinará el tipo de tratamiento que se utilizará, entre los principales se encuentran: físico, químico y biológico, o combinación de estos.

El *tratamiento físico* está destinado para eliminar sólidos flotantes y partículas granulares con un diámetro mayor que 0.1 mm, aceites y grasas. Esto se logra mediante el uso de rejillas y pantallas que atrapan y separan objetos sólidos a granel del agua residual. En esta etapa tienen lugar procesos como drenaje, flotación, filtración y sedimentación.

El *tratamiento químico* involucra procesos como: electrocoagulación, coagulación, floculación y ozonización. La electrocoagulación es un proceso simple y eficiente, los electrodos se usan para la producción del agente coagulante que se lleva a cabo *in situ* por electro-oxidación de un ánodo de sacrificio y no es necesario agregar coagulante o floculante químico. La coagulación y floculación: estos métodos son usados para remover sólidos suspendidos y componentes orgánicos, la efectividad depende de la selección del coagulante adecuado (Zajda & Aleksander-Kwaterczak, 2019).

El *tratamiento biológico* involucra el uso de microorganismos (bacterias, hongos, protozoos y algas) para llevar a cabo la eliminación de contaminantes en el agua, aprovechando su actividad metabólica y obtener así un efluente que pueda ser vertido al ambiente. Los procesos de biodegradación se llevan a cabo en reactores biológicos; el diseño y las condiciones de operación, (sistema aerobio o anaerobio, pH, temperatura, oxígeno disuelto en el sistema, cantidad de nutrientes, etc.) buscan mantener en cada momento las condiciones óptimas para el crecimiento microbiano. Considerando estos aspectos, existen múltiples

formas de operar dependiendo de las características del agua y de la carga orgánica a tratar (Oller et al., 2011).

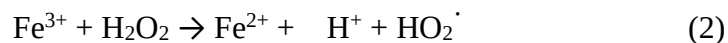
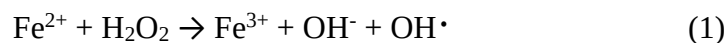
1.6.1 Procesos de Oxidación Avanzada (POA)

La presencia de compuestos orgánicos recalcitrantes como colorantes sintéticos, plaguicidas, productos farmacéuticos, productos de cuidado personal y otros contaminantes no pueden eliminarse fácilmente con las tecnologías existentes (Bello & Raman, 2018b).

Los procesos de oxidación avanzada (POA) se caracterizan por la generación de radicales hidroxilos ($\text{OH}^\bullet$) que son capaces de degradar contaminantes orgánicos. El $\text{OH}^\bullet$ es altamente reactivo con un potencial de oxidación ($E^\circ=2.80 \text{ V}$) y puede reaccionar con el contaminante orgánico, convirtiéndolo en dióxido de carbono, agua y compuestos minerales. Sin embargo, el término POA ahora se usa ampliamente para definir muchos procesos como la oxidación de Fenton, fotocatálisis, ozonización, radiación ultravioleta, cavitación por ultrasonido y oxidación electroquímica (Bello & Raman, 2018a). El tratamiento de las aguas residuales industriales mediante estos procesos se basa en la producción de $\text{OH}^\bullet$ y otros oxidantes, como el cloro, perbromato, persulfato, ozono, peróxido de hidrógeno, percarbonato y otros (Sirés et al., 2014). Asimismo, existen varias especies metálicas, además del hierro (aluminio, cromo, cerio, cobre, cobalto, manganeso y rutenio) capaces de generar radicales hidroxilos ($\text{OH}^\bullet$) a partir de H_2O_2 para la oxidación tipo Fenton de contaminantes orgánicos (Bokare & Choi, 2014).

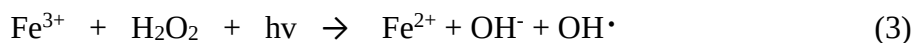
1.6.1.1 Fenton homogéneo

Este proceso consiste en la adición de sales de hierro en presencia de H_2O_2 , en medio ácido, para la formación del radical ($\text{OH}^\bullet$); la combinación de H_2O_2 y sales de hierro se denomina reactivo Fenton (Ec. 1 y 2) (Rubio, Chica y Peñuela 2014).



Además de formarse el radical $\text{OH}^\bullet$, también se genera el radical perhidroxilo ($\text{HO}_2^\bullet$), los cuales inician una reacción de oxidación en cadena para eliminar la materia oxidable. Sin embargo, los radicales ($\text{HO}_2^\bullet$) presentan menor poder de oxidación ($E^\circ=1.70\text{ V}$) que los $\text{OH}^\bullet$. El hierro puede ser añadido en su forma ferrosa (Fe^{2+}) o férrica (Fe^{3+}), siendo esta última conocida como proceso tipo Fenton.

Cuando se combinan las sales de hierro férricas con radiación ultravioleta (UV) o solar, recibe el nombre de proceso foto-Fenton UV y foto-Fenton solar, respectivamente, su eficiencia aumenta significativamente ya que favorece la regeneración del Fe^{2+} y aumenta, al mismo tiempo, el número de radicales ($\text{OH}^\bullet$) generados (Ec. 3) (Rubio et al., 2014).



1.6.1.2 Fenton heterogéneo

En el sistema de Fenton heterogéneo, la producción de radicales ($\text{OH}^\bullet$) a través de la reacción entre Fe(II) y H_2O_2 es el paso más eficiente y esencial para la eliminación de contaminantes. Este método utiliza catalizadores, los cuales incluyen minerales de hierro (magnetita (Fe_3O_4), hematita ($\alpha\text{-Fe}_2\text{O}_3$), pirita (FeS_2), etc.), catalizadores a base de arcilla (hidróxidos dobles en capas (LDHs), catalizadores soportados en arcilla, pilares de arcilla, etc.) y otros catalizadores que contienen hierro nano cero-Valente (nZVI), zeolitas, etc. Las especies Fe(III) están "inmovilizadas" dentro de la estructura de los catalizadores, por lo tanto, pueden retener su estabilidad para descomponer H_2O_2 en ($\text{OH}^\bullet$); evitando la filtración de iones de hierro y la generación de precipitación de hidróxido de hierro.

En consecuencia, estos catalizadores pueden recuperarse fácilmente después de la reacción, quedando en alta actividad después de múltiples usos. La estabilidad de estos catalizadores puede mediar reacciones de Fenton heterogéneas en una amplia gama de valores de pH (incluso a pH neutro) (Zhu et al., 2019).

Existen metales cero-valente (ZVM) como hierro, zinc, níquel, cobre, etc., utilizados para resolver problemas de contaminantes en aguas subterráneas, suelos, aguas superficiales, aguas residuales. El aluminio cero-valente (ZVAI) puede degradar los contaminantes presentes en el agua residual; actúa bien en condiciones ácidas por debajo de pH 4, es un potente agente reductor y adsorbente (Nidheesh et al., 2018).

1.7 Estado del arte

Los POA se han implementado con algunas variantes para la remoción de ácido tánico; en la Tabla 5, se observa que se han obtenido buenos porcentajes de remoción empleando fotoFenton, en comparación con otros procesos reportados. Sin embargo, se reportan resultados en función de los compuestos aromáticos o en presencia de persulfato de potasio utilizando únicamente agua sintética.

Tabla 5. Tecnologías disponibles para la remoción de taninos

Tratamiento	Contaminante	Condiciones de operación	Remoción	Referencia
Bioreactores fúngicos	Tanino de Quebracho (QT) y Tanino Tara (TT)	QT 1 g L ⁻¹ , TT 1 g L ⁻¹ pH: 5.8 QT 180, TT 226 días de operación <i>Aspergillus tubingensis</i> MUT 990.	Quebracho 53%. Tara 90%	Spennati et al., 2019
UV/ K ₂ S ₂ O ₈	Ácido tánico (AT)	AT: 0.17 g L ⁻¹ K ₂ S ₂ O ₈ :14.3 g L ⁻¹ pH: 9 Tiempo: 60 min.	96%	Dbira et al., 2019
foto-Fenton UV/H ₂ O ₂ /Fe ²⁺ Homogéneo	Ácido tánico (AT)	AT: 0.17 g L ⁻¹ , pH: 3 H ₂ O ₂ : 0.99 g L ⁻¹ Fe ²⁺ : 0.01 g L ⁻¹ Tiempo: 120 min.	99%	Dbira et al., 2019
UV//H ₂ O ₂	Ácido tánico (AT)	AT: 82 mg L ⁻¹ H ₂ O ₂ : 6 g L ⁻¹ pH: 9 28 °C	96%	Bensalah et al., 2018
Materiales híbridos sílice sol-gel	Taninos	4 mL Sintan 20 mg de Sílice Temperatura ambiente	90% de adsorción	Benvenuti et al., 2018
Tratamiento	Contaminante	Condiciones de operación	Remoción	Referencia
Resinas magnéticas	Ácido tánico (AT)	AT: 100 mg L ⁻¹ MAEX y MCEX: 0.05g	82% adsorción	Fu et al., 2015

Fotocatálisis	Taninos	50 mL agua residual 18.7 µg GA/mL. Tiempo: 2-8 horas. Compuestos fotoactivos de polímero-cemento	98%	Baltes et al., 2018
Biodegradación por Ozonización y proceso de oxidación Fenton	Taninos	pH:3.5 ±0.1 Fe ²⁺ : 100 mg/L Ozono: 2g/h 30 min. H ₂ O ₂ :2.12g pH:3.5 ±0.1 Reactores 2 L Aireación 1,5-1.6 L/h oxígeno disuelto (OD) de 2 a 2,5 mg / L temperatura ambiente tiempo de operación:30 h	Ozonación 49% Fenton 85%	Kalyanaraman et al., 2015

2. JUSTIFICACIÓN

Industrias a nivel mundial como la curtiduría, viticultura, procesamiento de aceite de oliva, textiles y producción de alimentos descargan un gran volumen de aguas residuales que contienen taninos. La presencia de taninos en las aguas residuales está asociada con problemas de contaminación ambiental y el tratamiento de aguas residuales. Estas aguas residuales son generalmente muy coloridas y difíciles de tratar por métodos comunes como la adsorción (He et al., 2007).

En particular los taninos vegetales son difíciles de biodegradar, debido a su naturaleza recalcitrante, toxicidad, tienden a absorber luz y calor y retienen menos oxígeno en sistemas biológicos reduciendo así la eficiencia del tratamiento (Kalyanaraman, et al., 2015).

Estas sustancias representan un importante problema ambiental debido a sus efectos adversos en los ecosistemas y la salud humana (Romero et al., 2020a). Actualmente, los procesos de oxidación avanzada (POA) tienen gran relevancia por su gran capacidad de oxidar contaminantes orgánicos, promoviendo la búsqueda de tecnologías eficientes y sostenibles para eliminar estos compuestos del agua residual.

En razón a lo anterior, el objetivo central de esta investigación fue realizar una revisión que aporte información relevante para identificar el tratamiento más efectivo para polifenoles en agua residual, además de evaluar su ventajas y desventajas.

3. HIPÓTESIS

La revisión crítica de los principales tratamientos y condiciones de operación de polifenoles y derivados presentes en el agua residual permiten identificar el tratamiento más eficiente, asequible y amigable con el ambiente reportado en la literatura.

4. OBJETIVOS

4.1 Objetivo general

Analizar críticamente el estado del arte sobre la remoción de polifenoles y derivados en el agua, para determinar el método más efectivo, las condiciones de operación, ventajas, desventajas y tendencias futuras.

4.2 Objetivos específicos

- a) Investigar, seleccionar y analizar los diferentes métodos para el tratamiento de polifenoles.
- b) Discernir los factores de operación que afectan en cada tratamiento y sus condiciones óptimas.
- c) Valorar las ventajas y desventajas de los POA y adsorción.
- d) Realizar análisis crítico de este estudio, así como de las tendencias futuras para uso en remediación ambiental.

5. METODOLOGÍA

En la Figura 5 se muestra la metodología llevada a cabo en la revisión bibliográfica. A continuación, se explican cada una de las etapas.

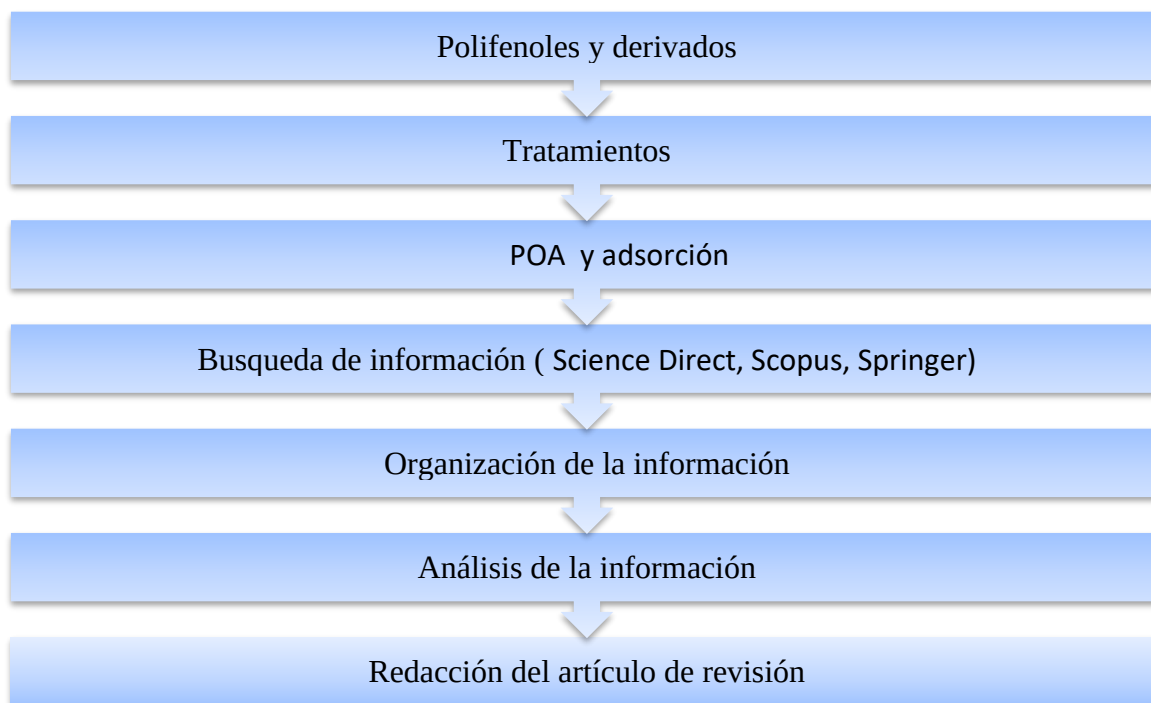


Figura 5. Metodología general

La búsqueda de información se realizó a través de libros, tesis y bases de datos de investigación científica como Science Direct, Scopus, Springer, con el fin de recabar información actual, relevante y pertinente sobre el tratamiento de los polifenoles. Mendeley fue el software utilizado para administrar las referencias y el software Plagiarism Checker X se empleó para verificar el % similitud del artículo de revisión el cual fue del 13 %. En este estudio la mayoría de los artículos seleccionados están relacionados con estudios experimentales sobre la eliminación de polifenoles y derivados utilizando una gama de POA y adsorción. Se seleccionaron otros artículos para proporcionar información complementaria.

El artículo contiene un análisis de tres elementos principales: (a) primero, las características fisicoquímicas, usos, impacto ambiental y efectos en la salud humana; (b) segundo, los

diferentes POA y adsorción para eliminar estos compuestos orgánicos; (c) y tercero, evaluar y comparar las condiciones de operación y eficiencias, así como las futuras tendencias.

6. RESULTADOS

Los resultados del presente estudio se incluyen y discuten en el artículo de revisión, en status enviado a Environmental Science and Pollution Research; Editorial Springer (3.056 Impact Factor, Q1). ISSN Electrónico: 1614-7499; Impreso 0944-1344.

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6.1 Artículo

Removal of persistent and recalcitrant polyphenols and derivates: Critical Review

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ABSTRACT

Polyphenols (PPs) in industrial effluent are one of the main problems in wastewater treatment because of their toxicity and recalcitrant characteristics, which are not easily removed by conventional treatments. A literature survey was conducted using the electronic databases ScienceDirect, Scopus, and Springer. In this study, relevant studies were included and discussed. Physicochemical characteristics, uses, and environmental and human health impacts of PPs were considered to assess and compare operating conditions and efficiencies. In addition, we also reviewed the different Advanced Oxidation Processes (AOP) and adsorption for eliminating PPs. Hybrid AOPs are economically viable techniques because the combined process lowers the operating cost based on energy consumption, which improves •OH availability and treatment efficiency. High effectiveness and low energy consumption make AOPs attractive for wastewater remediation. Adsorption is also an efficient method for eliminating PPs, as we can find ecological and economical adsorbents. The pH of the solution plays an important role in its elimination, where most of the adsorbents work effectively in the pH range of 3.0 to 7.0.

Keywords: Polyphenols; tannins; wastewater; AOPs; adsorption; water treatment

Introduction

PPs are a ubiquitous class of non-volatile secondary plant metabolites that possess unique chemical and physical properties and immense molecular weight (upper value 800 Da) and phenolic substructures able to precipitate the proteins. PPs have attracted the attention of scientists worldwide and can be applied as traditional dye originators in green chemistry, chain breakers, radical scavengers or complexed trace metal ions (Kavitha & Kandasubramanian, 2020).

PPs are composed of a wide range of molecules. They contain at least two phenolic rings attached to one or more hydroxyl groups, although there are also polyphenolic molecules with a single phenolic ring, such as phenolic acids and phenolic alcohols. Phenolic compounds come via two metabolic routes: the Shikimic acid route, where phenylpropanoids are produced, and the acetic acid route, where the primary products are phenols (Belščak-Cvitanović et al., 2018).

Based on the literature review, PPs are classified into five central polyphenolic classes: stilbenes, flavonoids, phenolic acids, tannins, and lignans (Fig 1). All flavonoids share the fundamental structure of diphenyl propane (C6-C3-C6), in which phenolic rings (ring A and ring B) are normally connected by a heterocyclic ring (ring C), which is generally a closed pyran (Singla et al., 2019). Variations in the hydroxylation pattern and oxidation state of the central pyran ring generate diverse flavonoid mixtures, including flavanols, anthocyanidins, anthocyanins, isoflavones, flavones, flavonols, flavanones, and flavanonols. The aromatic ring is the main structure of phenolic acids, tannins, lignans, and stilbenes (Singla et al., 2019).

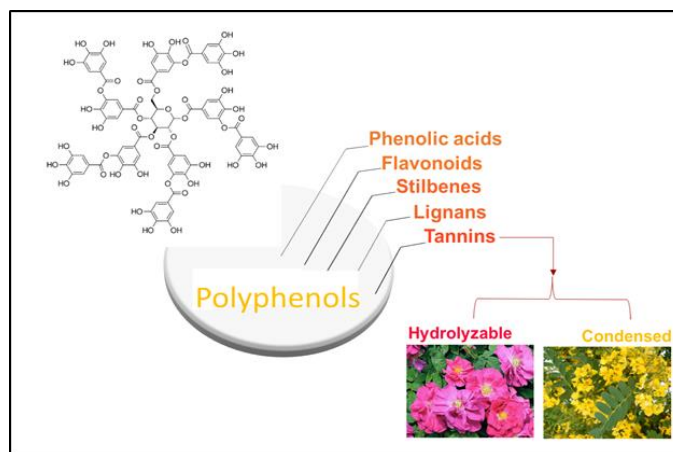


Figure. 1. Classification of polyphenols (own creation)

Tannins are the main PPs owing to their properties and applications in different industries. This review focuses mainly on this kind of polyphenol, which is frequently applied to a complex large biomolecule of polyphenolic nature with adequate hydroxyls and other suitable groups such as carboxyl groups. These form strong complexes with various macromolecules and are the main polyphenolic secondary metabolites. Das et al., (2020) established that they are found in various varieties of plants, present in the stems, buds, bark, wood, leaves, fruit, roots, and seed. Tannins have a molar mass of up to 20000 Da (Khanbabaee & van Ree, 2001).

Tannins are categorized into two groups: hydrolysable (HT) or flavonoid and condensed (CT) tannins (non-hydrolyzable) (Fig 2). Hydrolyzable tannins are sub-classified into gallotannins and ellagitannins; the most popular example is tannic acid (TA), also identified as Chinese tannin or gallotannin (Kalyanaraman et al., 2015). Condensed tannins, also recognized as proanthocyanidins are constituted by the flavans condensation, and HT are decomposable in aqueous solution, such as gallic acid (hexahydroxydiphenic acid) (Kavitha & Kandasubramanian, 2020).

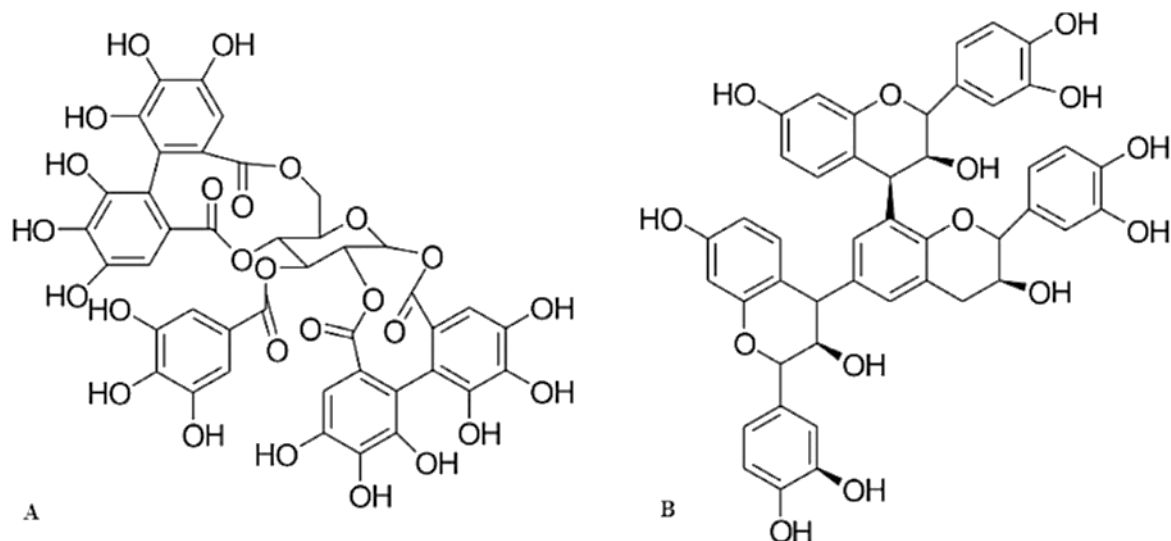


Figure. 2. Structure of (A) hydrolysable and (B) condensed tannins (Sharma et al., 2019).

Properties and toxicity

Tannin possesses various medicinal and calming properties; it presents several pharmacological properties, including anti-toxicity, anticancer, antioxidant, antiallergic, anti-inflammatory, anthelmintic, antimicrobial, antiviral, wound healing, and dysentery curing. As an antioxidant complex, tannin and its derivatives, especially gallic and pyrogallol, prevent lipid oxidation and radical-mediated oxidative DNA damage (Oćwieja et al., 2015). Most condensed tannins and the remaining hydrolysable tannins are for vegetable tanning (Kalyanaraman et al., 2015). Tannins show both reducing and stabilizing properties and are commonly used in silver, gold, and nickel nanoparticle production. Tannins are recalcitrant and persistent; they undergo limited degradation during traditional biological wastewater treatment. This is one of the main problems in this area (Bardi et al., 2017). Tannin degradation produces byproducts such as humic substances, straw-colored, hydrophobic organic acids that are highly persistent (Tang et al., 2014). Both compounds in wastewater contribute to a rise in chemical oxygen demand (COD), and their toxicity generates adverse effects that cause alterations in human health, flora and aquatic fauna (Grandclément et al., 2017).

Ingestion of substantial amounts of tannins may result in unfavorable health effects (Sharma et al., 2019). TA may produce intestinal secretions, damage the intestinal mucosa, reduce

digestive enzymes, and rise the excretion of endogenous proteins. Heavy metals (HMs), which are mostly acute toxic to humans and wildlife even at trace levels, are commonly used in agricultural and industrial applications (Fu et al., 2015).

Copresence of HMs and TA in polluted water has significantly affected humans and the ecosystem because of their combined toxicity, mobility, and carcinogenic characteristics. Tannin and non-tannin components inevitably persist in wastewater. Most of the hard-to-biodegrade complex organic chemicals such as dyes and vegetable tannins present in wastewater are used in post-tanning operations. Post-tanning chemicals in wastewater lead to environmental complications because of their recalcitrant nature and toxicity to microbes (Fu et al., 2015).

Effects on the environment: Adverse health effects

Tannins in food adversely affect human health, and their excess consumption could contribute to cancer by acting as an inducer and promoter in the occurrence of other carcinogens. TA causes necrosis of liver cells in people and in grazing animals. An anti-nutritional effect occurs when complexes are formed between tannins and minerals such as phosphorus, calcium, and magnesium, making them unavailable for animals and reducing the bioavailability of several vitamins (vitamin A and vitamin B12); these indigestible complexes promote the endogenous enzyme inhibition (Sharma et al., 2019).

Water-soluble polyphenolic compounds are toxic to aquatic life, including algae, phytoplankton, fish, and invertebrates (Yan et al., 2020). Furthermore, TA reacts with chlorine during water sterilization and produces disinfection byproducts which may induce cancer and adversely affect human health (Cui et al., 2015).

Tannins have many applications, including in leather tanning, wood adhesives, wood preservatives, dyes, fishing, beverage manufacturing (Sharma et al., 2019), animal feed, medical applications, paper (He et al., 2007), corrosion inhibitors, polyurethane surface coatings, epoxy adhesives and wine industry (Rodríguez-Chueca et al., 2017). Tannins wastewater is frequently dyed; these tannins are extremely difficult to eliminate by ordinary methods such as adsorption and dilution (He et al., 2007) and tend to absorb light, heat, and

maintain a lesser amount of oxygen than unprocessed water in biological systems, reducing the efficiency of treatment (He et al., 2007; Kalyanaraman et al., 2015).

The tanning industry and wood production are among the major causes of tannin contamination (Earl & Semlitsch, 2015). The tanning industry uses vegetable tannins to provide leather-specific properties. Materials derived from tannins come mostly from HT and CT. The polyphenolic structure of tannins is transformed quickly during the tanning process; this hampers effective treatment of effluents (Mwinyihija, 2010).

Effluents from tanneries can achieve COD values ranging 1100–4400 mg/L at pH 3.0–10.0 (Natarajan & Manivasagan, 2018). Additionally, a variety of contaminants in tannery effluents are subject to selective treatments, among which are organic compounds that promote a high content of heavy metals, COD, color, and total suspended solids (Benvenuti et al., 2018; Korpe et al., 2019; Prigione et al., n.d.).

Another highly polluting industry with effluents containing high concentrations of PPs and tannins is the wine industry. This industry contributes to high organic loads and acidic pH values. This and the suspended solids observed in the wine-making process necessitate the adoption of sustainable water management practices by the wineries. These loads lead to high COD (1752 mgO₂/L) TOC (500 mg/L) and total PPs (84 mg gallic acid/L) (Rodriguez-Chueca et al., 2017). Thus, we review the treatment techniques of wastewater contaminated with PPs and derivatives for example tannins.

Polyphenol removal treatments

Advanced Oxidation Processes (AOPs)

As effective approaches for water decontamination, AOPs enable electron transfer to peroxides (e.g., hydrogen peroxide, ozone, and persulfates) by forming strong reactive oxidizing species (ROSs), for example hydroxyl radicals, singlet oxygen, sulfate radicals and superoxide, resulting in efficient degradation (Zhuan & Wang, 2020) or even complete mineralization of toxic organic pollutants into harmless compounds, for instance CO₂ and H₂O (Yin et al., 2020; Giannakis et al., 2020; Arimi et al., 2020). Currently, there are different processes for degrading hydrophobic organic compounds: AOPs, ozonation, sonolysis, UV-

based processes, Fenton, photo-Fenton, photocatalysis, microwave, wet air oxidation, and electrochemical advanced oxidation processes (EAOPs) (Fig. 3) (Arimi et al., 2020).

EAOPs such as electrooxidation (EO) or anodic oxidation (AO) and electro-Fenton (EF) processes have been widely reported and applied for the treatment of recalcitrant and persistent organic pollutants (POPs) from soil and wastewater. These safe, environmentally friendly processes can generate oxidants that can efficiently degrade organic compounds (Ganiyu et al., 2018). They produce in situ hydroxyl radicals ($\bullet\text{OH}$), the second-strongest known oxidizing agent. Production of $\bullet\text{OH}$ in situ allows these processes to be highly capable in removing a wide variety of organic pollutants until complete mineralized as CO_2 . The $\bullet\text{OH}$ react with a wide spectrum of natural organic matter (NOM), both hydrophobic and hydrophilic. Rate constants were measured at $1\text{--}5 \times 10^8 \text{ 1/Ms}$ (Trellu et al., 2016).

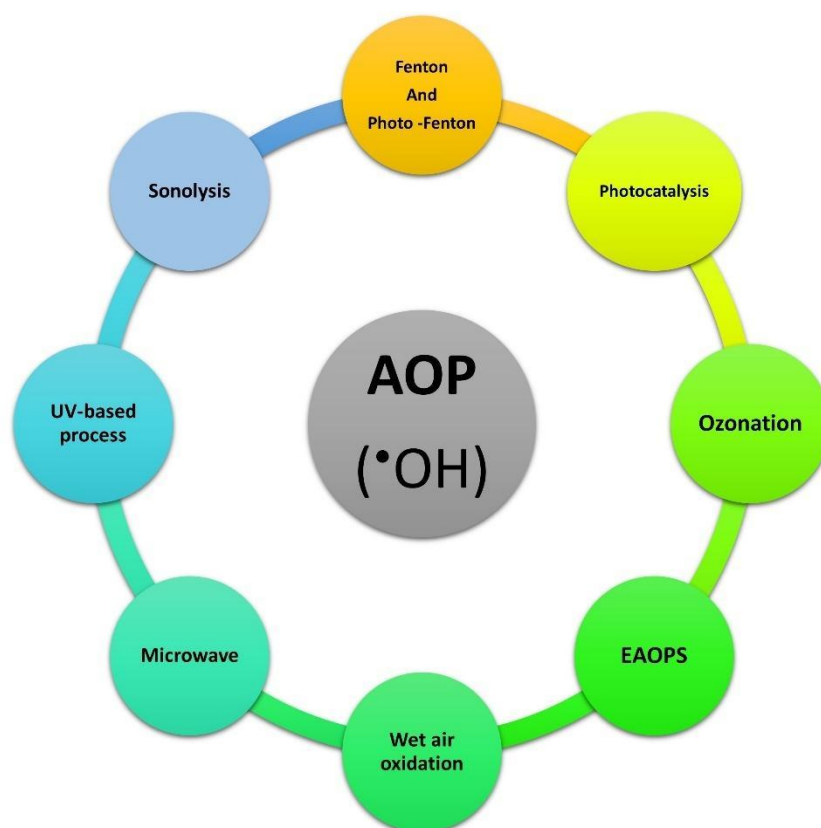


Figure. 3 Classification of AOPs (own creation).

Anodic oxidation (AO)

In AO, the $\bullet\text{OH}$ are formed on the anode surface by the water oxidation, react with organic contaminants (Equation.1). In particular, the boron-doped diamond (BDD) anode because of its high catalytic activity and promotes the generation of large amounts of $\bullet\text{OH}$ to oxidize organic matter (R) (Equation 2 (4.2) and (Fig. 4) (Trellu et al., 2016; Yin et al., 2020).

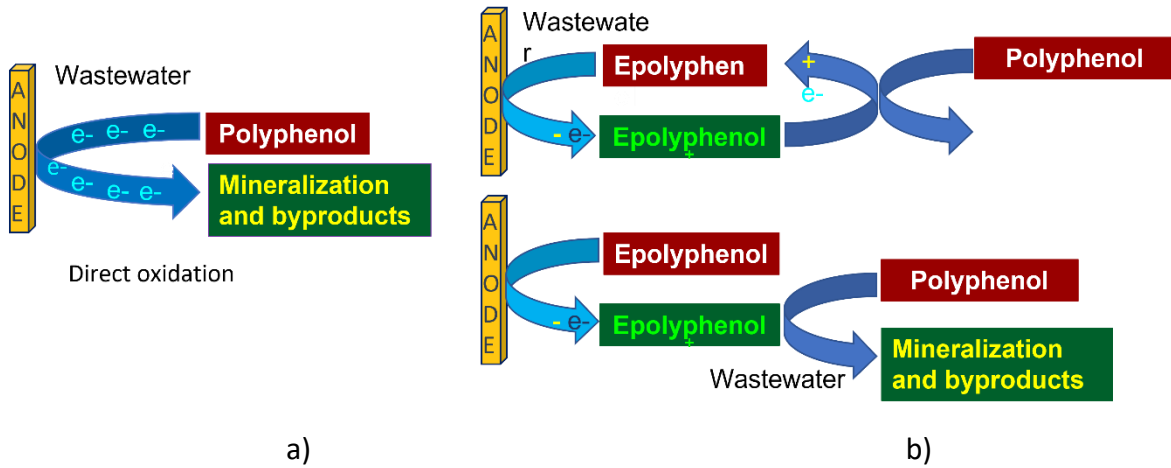
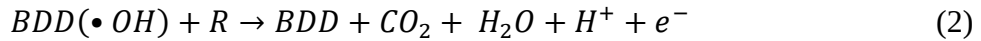
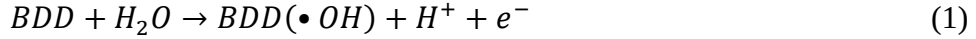


Figure. 4 Mechanisms for the electrochemical oxidation of PPs a) direct and b) indirect (own creation)

Moreira et al. (2015) studied raw winery wastewater with high biodegradability, and biological degradation treatment attained high DOC, BOD_5 , COD, and removal above 97%. However, the wastewater treated biologically consisted of a bio resistant fraction comprising DOC (130 mg L^{-1}), COD ($380 \text{ mg O}_2 \text{ L}^{-1}$) and 8.2 mg L^{-1} caffeic acid, different EAOPs (EF, AO, photoelectro-Fenton (PEF), UVA and solar-PEF (SPE)) were applied to degrade and mineralize recalcitrant pollutants into CO_2 and H_2O . Winery effluent can efficiently degrade by EAOPs at 25°C , pH (2.8), current density (25 mA cm^{-2}), and initial Fe^{2+} concentration (35 mg L^{-1}) for Fenton's reaction-based processes. Oxidizing power of $\text{AO-H}_2\text{O}_2$ 36%, EF 54%, PEF 84%, and SPEF 86% in the DOC removal of treated effluent by biological process increased after a time of 240 minutes (4h). With the weak DOC removal of $\text{AO-H}_2\text{O}_2$ treatment, it showed that BDD has a low capacity to interact with recalcitrant winery

wastewater compounds. Conversely (Trellu et al., 2016) studied the AO of humic substances (HS), which are a part of the organic matter that been decomposed by microorganisms in water and soil. The major extractable component of HS is humic acid (HA) (70 %–80%). These substances contain phenolic groups, quinone structures, aliphatic compounds, nitrogen, and oxygen as bridging units and carboxylic groups located in the aromatic structure. For the AO process, BDD anode and stainless-steel cathode were used, and the % mineralization of the HA solution ($\text{TOC}_0=16.2 \text{ mg L}^{-1}$) reached > 99% after 7 h of AO process and a 1000 mA of current intensity.

When the organic molecules are exposed to electrochemical oxidation, their chemical structure changes through redox reactions—known as direct oxidation; these molecules oxidized at the electrode-solution interface can be degraded, but other molecules, which are even more toxic, can be simultaneously generated; these new molecules cannot be degraded by this process. In indirect oxidation, advanced electrochemical oxidation processes (POEA) based on the electrochemical reactions where highly ROSs are conducted. The oxidizing power of these species causes partial or total mineralization; taking the radical $\text{OH}\cdot$ as an example, the interaction between the electrode and hydroxyl radical is key to increasing the concentration of $\text{OH}\cdot$ and this interaction depends on the type of the electrode. On of the best electrode for treating organic pollutants is the BDD anode, it shows excellent electrochemical stability and chemical inertness in acidic and alkaline media.

This technology is highly efficient, versatile, requires moderate operating conditions, and offers ease of automation. However, the high cost of the electrode and the short useful life are an important limitation. Furthermore, the impact of concentration, electric conductivity, pH, type of pollutant, electrode arrangement, reactor design, and potential density distribution require further study to propose solutions.

Table 2 shows the main disadvantages and advantages of the reported electrochemical technology, including that the AO process generates a low number of by-products and conducts to a rapid mineralization of different organic matter into CO_2 . However, the method requires high-power supply voltage and consumes substantial energy.

Fenton oxidation and Fenton-related processes

Fenton oxidation and Fenton-related processes (e.g., photo-Fenton, electro-Fenton, and photoelectro-Fenton) (Fig. 5) are commonly used to degrade organic pollutants or to increase the biodegradability of pollutants through oxidation (Zhang et al., 2019).

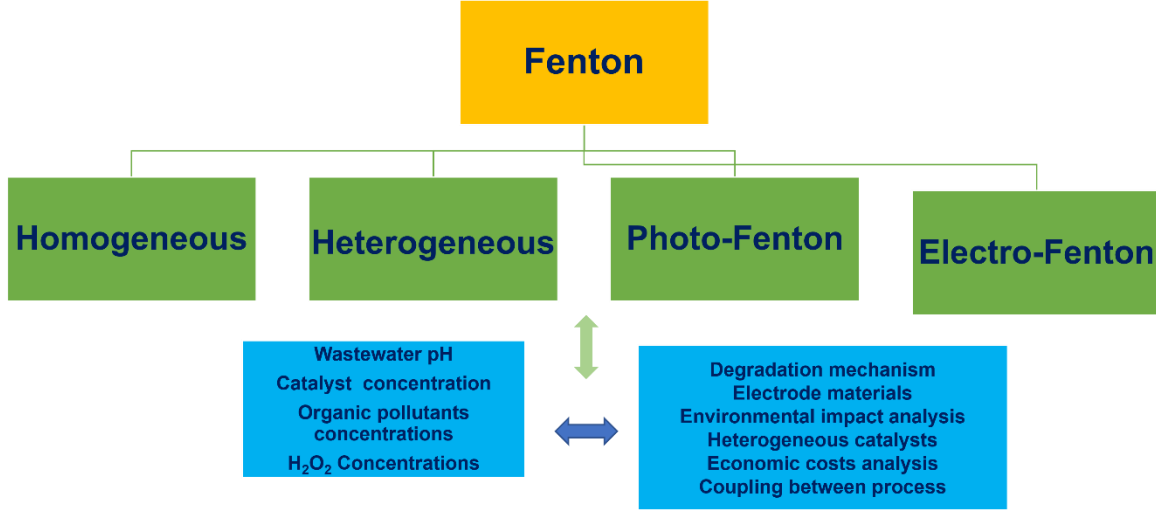
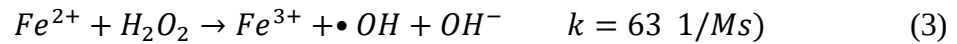


Fig. 5 Fenton processes (own creation)

Fenton reactions can be classified as homogeneous or heterogeneous processes (Duan et al., 2021). The heterogeneous Fenton process could exceed the limitations of homogeneity, formation of Fe-containing sludge, strict pH conditions, and recovery of the catalyst (González et al., 2021). Different kinds of supported and unsupported iron-based catalysts (i.e., clays, alumina, activated carbons, and zeolites) can be reduced to determine their influence on the Fenton or photo-Fenton process (Thomas et al., 2021). H_2O_2 is activated to generate active species at the interface of the solid catalyst (Gou et al., 2021)

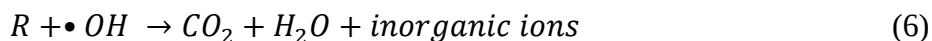


In the photo-Fenton reaction with UV light, enhanced reduction of Fe^{3+} to Fe^{2+} cooperated with the classical Fenton system, where Fe^{2+} with H_2O_2 generates the $\bullet OH$, according to the catalyst used in the process (i.e., free iron ions or iron-based solid catalysts). The photo-Fenton process occurs at $\lambda < 580 \text{ nm}$; therefore, it could be solar-powered (Oller & Malato, 2021).

•OH is produced homogeneously in the EF process from the electrochemically generated Fenton's reagent (mixture of H₂O₂ and Fe²⁺) (Eq. (3)). In the cathode, H₂O₂ is electrogenerated in situ, following Eq. (4) from the two-electron reduction of the dissolved O₂. A catalytic amount of Fe²⁺ is sufficient to increase the rate of the process, owing to the catalytic electro regeneration of ferrous iron at the cathode (Eq. 5) (Yin et al., 2020).



These formed homogeneous/heterogeneous •OH interacts with the organic components until mineralization (Eq. (6)):



Commonly, the main operating variables to evaluate any Fenton process are wastewater or solution pH, catalyst concentration, organic pollutant concentration, amount of H₂O₂, and UV light.

(Boye et al., 2009) studied the effluents of landfills and the leather industry that use too much water (50 to 200 m³/d). These effluents contain organic compounds based on tannins, proteins, lipids, fats and hair, which increase COD and BOD (biological oxygen demand). The main process in this work, H₂O₂-assisted electro precipitation (AEP) with sacrificial Fe anode coupled with Ti(Pt) cathode, combines physico-chemical aspects of the water treatment effluents with EF-based electrochemical oxidation and partial coagulation/precipitation of the remaining compounds. The COD removal was 90% in 8 h for the desalting wastewater and 60–80% in 6 h for the leachate during the AEP treatment. The diffusion cathode and BDD anode applied in EF induce high degradation (75–80%). AO using a BDD anode can remove 99% of COD in an increased treatment time of more than 20 h. AEP treatment, alone or combined with another treatment, can eliminate COD efficiently. AEP-technology is appropriate for industrial applications, especially for recycling tanning effluents and landfill leachate.

Romero et al., (2020) studied no soluble tannins from pine bark under following conditions: pH 3.6, 2.4 mmol/L of H_2O_2 , 150 $\mu\text{mol/L}$ of Fe (III), 800 mg/L of tannins; 98% atrazine and 17.9% TOC were obtained in 30 min and 1 h respectively.

Lofrano et al. (2010) studied the detoxification and degradation of a synthetic tannin (ST) by Fenton (FO) and photo-Fenton (PFC) oxidation processes. The process conditions for FO and PFC were 30 min at pH 3 ± 0.2 , and 40–45 °C. The effect on Fe^{2+} and H_2O_2 concentrations, COD, UV-C light irradiation on oxidation, UV280, UV254 were evaluated. PFC produced COD reduction of more than 80% and 90% for ST in UV280 and UV254 absorbances, respectively.

POAs have attracted attention for their efficiency in eliminating recalcitrant organic substances, such as the Fenton process, which includes different degradation systems implemented in homogeneous or heterogeneous phases such as (Photo-Fenton) (FF) or (Solar-Fenton) (SF), processes involving electricity, such as EF, or combined as the photo electro-Fenton (FEF) process; these are based on $\text{HO}\cdot$ formation through reaction between ferrous ions (Fe_2^+) and hydrogen peroxide (H_2O_2). In the homogeneous Fenton process, the catalysts (ferrous ions) dissolve uniformly in the mixture, favoring production of $\text{HO}\cdot$ from H_2O_2 . However, limitations include generation of sludge, and excessive concentrations of Fe ions are needed to reach the effectiveness of the process.

Heterogeneous Fenton uses catalysts where the Fe species are immobilized and the formation of $\text{HO}\cdot$ occurs by the reaction between H_2O_2 in aqueous solution and the fixed iron species on the surface of the material. The properties of the catalyst should be considered as pore volume, density, surface area, pore size and porosity to achieve a higher catalytic performance; the advantage is that it can mediate reactions over a wide pH scale and avoids filtration of iron species and production of sludge.

Fenton process is commonly used for its different advantages; since it can work at various pH, low interferences, easy operation, fast mineralization, and degradation (50% removal of

tannins and 70% coupled Fenton treatments). However, a cost study is necessary to enhance the process for industrial use (Zhang et al., 2019).

Electrocoagulation (EC)

EC is a method in which chemical coagulants are produced by separating sacrificial anodes (Fe or Al) and on the cathode the production of hydroxyl ions. The liberated metal ions could form various hydroxyl species in water. Hydroxometal species modify suspended, emulsified, or dissolved pollutants or form particles that adsorb pollutants. Moreover, the production of hydrogen bubbles on the cathode surface stimulates the flocculation process and produces larger particles that facilitate the removal of the flocculated pollutants by carrying the particles to the top of the reaction, where they could be removed by flotation (Fig. 6) (Hernández et al., 2017; Mansouri et al., 2011).

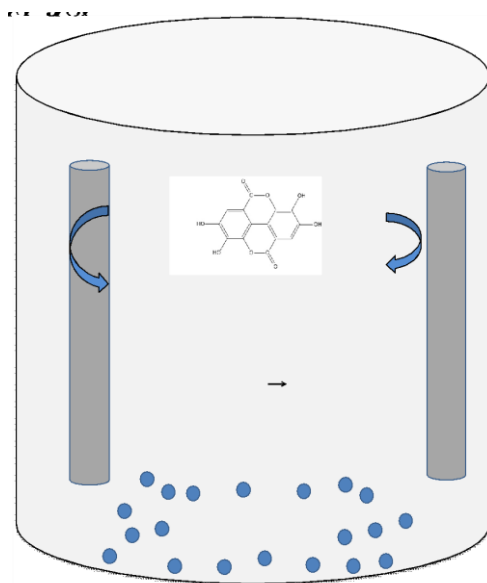


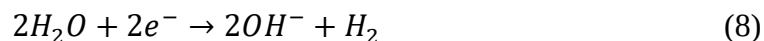
Fig. 6. Electrocoagulation (own creation)

Equations 7–9 show the reactions occurring during the EC (AlJaberi 2019; Dia et al. 2017).

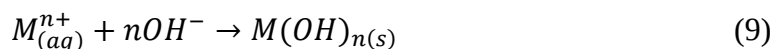
At the anode,



At the cathode,



In the bulk solution,



Electrocoagulation is an effective treatment for removing a wide variety of pollutants from wastewater, including, heavy metals, HS, colorants, and phenols.

This method was used to remove chlorophyll and tannins from the ethanolic extract of the aerial parts of *Anthocleista schweinfurthii* Gilg, using iron electrodes, and the effects of four variables were evaluated: percentage of ethanol (%), current intensity (Amp), concentration of support electrolytes ($g\ L^{-1}$), electrolysis time (min), and their interactions. Chlorophyll reduction (CR), total phenol content (TPC), total tannin content (TTC) were evaluated. Under improved conditions (supporting electrolyte concentration $2.4\ g\ L^{-1}$; ethanol percentage 67%; electrolysis time 75 min and current intensity 0.4 A), CR of 98.23% and TTC of 58.83% were reached while remaining 91.21% of TPC (Tsopjio et al., 2020).

Hassoune et al., (2017) studied EC for vegetable tanning effluents and found it difficult to treat COD. In this research, electrocoagulation with aluminum electrodes in a batch reactor was used to remove polyphenolic compounds from vegetable tannins from solutions. Two types of commercial tannin were used: chestnut (HT), and mimosa (CT). The evaluated parameters were pH, current density, distance between electrodes, ionic strength, electrolysis time and tannin concentration. It was observed that as the current density increased, the elimination percentage of tannins also increased. The optimal value was $47.6\ A/m^2$ for chestnut and $71.4\ A/m^2$ for mimosa at $1,000\ mg/L$. Within these values, 97.4 and 98.8% of tannin PPs can be removed, respectively.

Wagle et al., (2020) studied the behavior of electrocoagulation (EC) using iron as a sacrificial electrode to treat effluent from a paper mill using low current values ($0.6\text{--}1.9\ mA/cm^2$) to remove COD, BOD_5 , color, tannin/lignin and the biodegradability index (BI) was

investigated. The current density that generated the best result was 1.5 mA/cm² in 25 min. Under controlled conditions, removal of tannin/lignin (>70 %) and color (>95 %) and BI increased 0.41 in the relationship BOD₅/COD.

An important factor in electrocoagulation is the current density because of energy consumption and operating costs, contrasted to the electrode wear and treatment time. Studies have indicated that EC uses low current densities to remove bio-refractory organic contaminants and enhance the BI (Wagle et al., 2020). This could be associated with the electrocoagulation process of different effluents, including phenolic compounds, which includes complex formation among ferrous/ferric and phenolic compounds which has an impact on the success of the treatment (Kraljić Roković et al., 2014).

Hydrothermal treatments

Catalytic wet oxidation (CWO) is favorable for the wastewater treatment; it uses high pressures and temperatures, which will allow great efficiency in eliminating organic pollutants (Thayagaraja et al., 2020). It involves creating reactions in the aqueous solution under an oxidizing atmosphere and mild working conditions (125–320 °C and 0.5 MP–20 MPa) (Fig. 7). This alternative has been gaining interest in recent years, and numerous studies have analyzed the impact of hydrothermal treatments on the final distribution of organic acids and/or organic load reduction (Pola et al., 2020; Maree et al., 2020). Biologically refractory compounds are decomposed into simple, easily treated materials, without emitting harmful byproducts such as furans, dioxins, fly ash, HCl, SO₂ and NO_x. The challenge for WO lies in the need for high-temperature and high-pressure operating conditions. Improvement has been made in the development of catalysts to optimize the operating conditions used in this process and reduce the costs. Transition metal catalysts are ideal due to their low cost and can resist poisoning despite their low catalytic activity. There are five stages implicated in CWO: (1) gas-liquid diffusion, (2) adsorption of the reagent, (3) maintaining the reagents contents to allow them to react, (4) desorption of the products from the surface, and (5) diffusion of the products back into the surrounding phase. This method involves formation of free radicals, hydrogen peroxide (H₂O₂) and ROOH. Hydrogen peroxide (ROOH or H₂O₂)

react with metal ions on the surface of the catalyst to generate $\bullet OH$. The reactions of free radicals produce alcohols (ROH), which are oxidized to aldehydes (RCHO), ketones (RCOR), and carboxylic acids (RCOOH). In the occurrence of oxygen, carboxylic acids (ROOH) further break down into short-chain carboxylic acids (R'COOH), water (H₂O) and carbon dioxide (CO₂) (Thayagaraja et al., 2020).

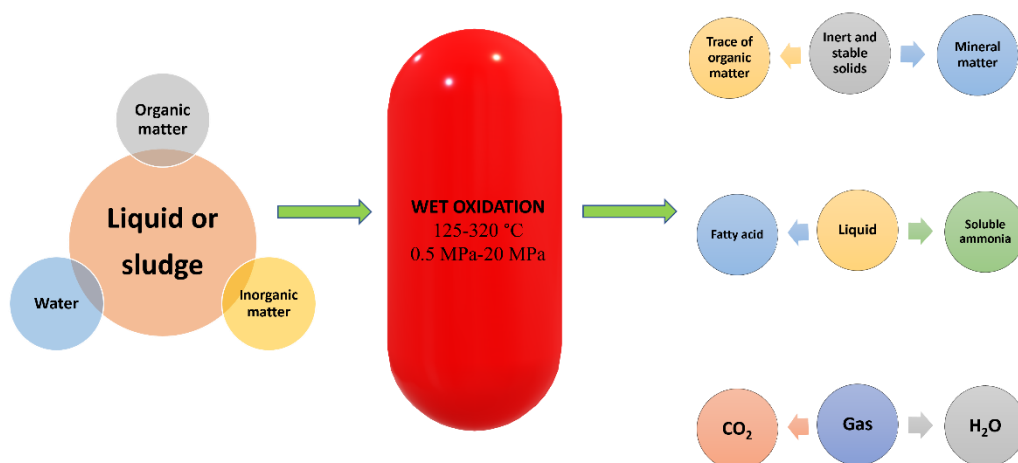


Fig. 7. Wet oxidation (own creation)

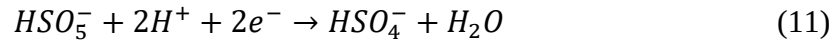
García et al., (2020) studied the oxidation of HA in aqueous solution by CWO; the result was effective mineralization at temperatures (180–220 °C), while the pressure used (65–95 bar) had no effect in this research. However, the variation in pH (4–13) was a critical factor. COD reductions of 70% (180°C), 82% (200°C), and 86% (220°C) were obtained. TOC 70% (180°C), 78% (200°C) and 80% (220°C). Byproducts: Benzoquinones acetic, maleic, lactic and oxalic acid were detected.

The main advantages of CWO are faster degradation and mineralization, high elimination efficiencies of TOC, color, and COD; however, high temperatures (180–220°C), high pressures (65–95 bar) and some refractory species can be formed at alkaline pH.

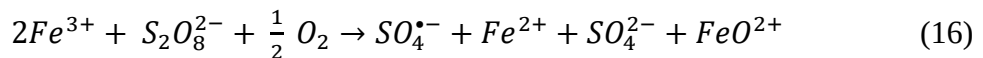
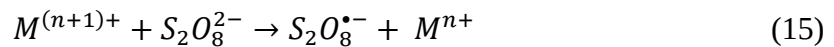
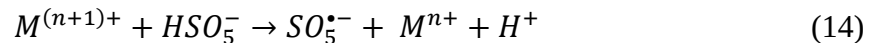
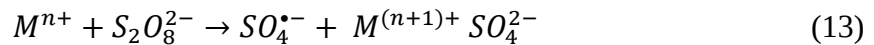
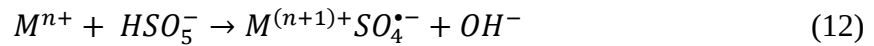
Sulfate radical-based advanced oxidation processes (SR-AOPs)

SR-AOPs are versatile and efficient methods for effluent sanitation. The main advantages over POAs are different methods of activation and production of sulfate and hydroxyl radicals ($SO_4^{\bullet-}$) from peroxydisulfate (PDS, $S_2O_8^{2-}$), or joint sulfate and hydroxyl radical ($\bullet OH$) production from peroxymonosulfate (PMS, HSO_5^-), which have assisted their introduction into numerous remediation and effluent decontamination processes (Giannakis et al., 2020; Li et al., 2019; Yang et al., 2019).

To generate sulfate radicals, a proper oxidant must first be activated. As such, PMS and PDS, two of the greatest oxidants applied in environmental purposes (redox potential: 1.82 V vs. NHE for PMS and 2.01 V vs. NHE (Normal Hydrogen Electrode) for PDS) have been extensively used (Eqs. 10 and 11).



The forms of activation can be heat, UV or visible light, microwave, ultrasound, electrochemical, photocatalytic, alkaline activation, or metallic (Co, Fe, Mn, Cu, Ag, etc.) and non-metallic catalysts that can break the O-O bonds of persulfate ions and produce sulfate radicals (Eqs. 12-20), while higher valance produces $SO_5^{\bullet-}$ and $S_2O_8^{\bullet-}$ with low reactivity (Giannakis et al., 2020).



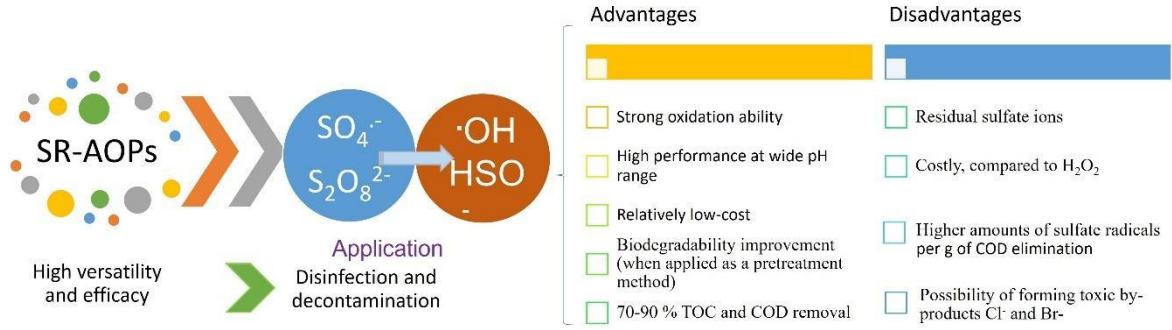
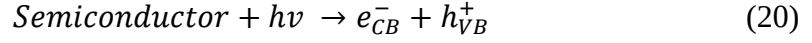
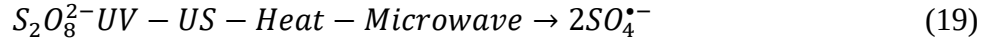
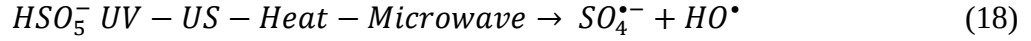


Fig. 8. Sulfate Radical-based AOPs (own creation)

Amor et al., (2018) studied a winery wastewater by applying sulfate radical-based on SR-AOPs. Numerous experiments were performed to evaluate the influence of UV-C radiation, temperature, and some transition metals on the thermal and photolytic/photocatalytic activation of sodium persulfate. COD removal was greater in the UV-C/S₂O₈²⁻ process than in the heat/S₂O₈²⁻ process using an COD₀=600 mg O₂ L⁻¹. After a treatment time of 90 min (at pH=7.0), using 15 mM of S₂O₈²⁻ powered by a UV-C lamp achieved 59% COD elimination, while heat/S₂O₈²⁻ process reached a removal of only 41%. After fusing the thermal activation with transition metals and applying the optimal operational conditions ([S₂O₈²⁻/Cu²⁺] = 1, pH = 7.0, and reaction time of 90 min), 61% of COD reduction was found. Further experiments with longer reaction times and higher concentrations of S₂O₈²⁻ removed 96% of COD and 71% of TOC, respectively.

The best conditions were sodium persulfate dosage of 0.43 mmol/gTS (total solid), Fe²⁺ dosage of 0.58 mmol/gTS and TA dosage of 0.14 mmol/gTS, at which the water content of dewatered mud cake showed (75.89 ± 0.01) % highly close to the expected minimum water content of dewatered mud cake. Some advantages of this method are the high oxidation potential of both SO₄^{•-} and HO[•], the long half-life time of SO₄^{•-}, and it is appropriate over a wide pH range (Xiao et al., 2020b).

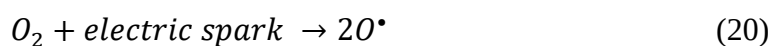
Safe storage of oxidants on a large-scale biodegradability improvement (when used as a pretreatment method) and 70 %–90 % COD and TOC removal.

Some disadvantages are costly, compared to H_2O_2 , and higher amounts of sulfate radicals are necessary per g of COD elimination, compared to H_2O_2 , with the probability of forming toxic byproducts in the presence of Cl^- and Br^- (Giannakis et al., 2021; Gonçalves et al., 2021).

Ozonation

Decontamination and disinfection of drinking water, deodorization of stench in air, detoxification of dangerous pollutants discharged in the natural environment, and organic syntheses have been universally applied because of the unique nature of ozone (O_3). AOPs and catalytic ozonation are frequently used to decompose hard-to-degrade compounds quickly in water purification plants (Tachibana et al., 2020).

O_3 is an unstable gas; therefore, its generation is generally carried out in situ. The O_3 generation is based on the corona discharge process, which includes the application of a high-voltage emission in a cooled/dried gaseous phase containing oxygen (O_2 or air). The discharge gas reaction is given by Equations 20–21 (Rekhate & Srivastava, 2020a).



O_3 (2.07 V) can destroy organic pollutants make use of two mechanisms: (1) direct electrophilic attack by molecular O_3 and (2) indirect attack by $\bullet OH$ radicals generated through the O_3 decomposition process. Improving the O_3 concentration promoted the degradation rate of some contaminants but had no effect on the degradation of other organic compounds. This may be because O_3 molecules react directly with pollutants according to four categories: (a) The oxidation–reduction reaction, such as the reactions between O_3 and HO_2^- (or $O_2^{\bullet -}$) mostly proceed through the electron transfer process. (b) The ozone reacts with organic contaminants via a cycloaddition reaction by forming a five-member ring ozonide structure. (c) Ozone is an electrophilic agent that can attack the nucleophilic position of the

organic constituents, and the group in the aromatic molecules, such as $-\text{Cl}$, $-\text{NO}_2^-$, and $-\text{OH}^-$ has a significant influence on the reactivity of the aromatic ring with O_3 . (d) O_3 demonstrates nucleophilic properties and nucleophilic reactions occur with molecules, especially when the compound contains carbonyl or double and triple nitrogen carbon bonds.

Benefits of ozonation include sludge reduction and elimination of recalcitrant organic pollutants from wastewater. It was observed that ozonation led to sludge solubilization and reduced overall biomass yield. O_3 mass transfer depends on different factors, which can be hydrodynamic and physicochemical effects. Ozone is mixed with UV light, H_2O_2 , catalysts, photocatalysts, and ultrasound to enhance the production of $\bullet\text{OH}$, which improves the treatment efficiency (Rekhate & Srivastava, 2020a).

Balakrishnan, Kanchinadham, et al., (2020) studied a vegetable tanning process that was conducted by the tanning industry for manufacturing dense leathers employed in shoes, bags, and wallets. Wastewater from the vegetable tanning process (VTW) contains polyphenolic and recalcitrant tannins. The research was centered on ozonation (OZ), Fenton's oxidation (FO), and Fenton's oxidation followed by ozonation (FO+OZ) processes as pretreatment for VTW. The optimized $\text{H}_2\text{O}_2/\text{COD}$ ratio for FO was 1.25, at 30 min of contact time. The maximum removal of tannins observed for each pretreatment were 49.5%, 27%, and 74.6% for FO, OZ, and FO + OZ, respectively.

Ramírez-Ramírez et al. (2016) set up ozonation performance that allows the reduction of tannins included in the residual tannery liquors (RLT) derived from vegetable tanning to reach safe removal. O_3 at an initial pH of 6.3, and advanced oxidation (AO) with ozone at alkaline pH, was applied for aqueous solutions of the lyophilized RLT and quebracho (QS) for 180 min. Generally, the process of AO attained efficiencies of removal between 80 and 100% of total phenols, COD, and color, at the same period in the ozonation these values varied between 50 and 95%.

Conversely, Saroj et al. (2005) studied the mineralization, reduction in color, and reduction of COD of tannin, gallic acid, and lignin by ozonation and a combination of aerobic

biodegradation and ozonation. The ozone application on pure aliquots (stage I) resulted in a decline in COD, TOC, COD/TOC ratio, color and UV absorbance at 280 nm, of the three model compounds examined, with COD reduction of larger than 80% and high elimination (>90%) of UV absorbance (280 nm) and color at an ozone dose of 6 mg O₃/mg initial TOC or higher. Aerobic degradation of tannin, pure gallic acid, and lignin aliquots caused in a COD reduction (36%–38%). Consequent ozonation (stage II experiments) resulted in a decrease in COD, TOC, COD/TOC ratio, and increase in the UV absorbance at 280 nm and color removal. COD and TOC elimination like the phase I experiments were achieved with 30%–40% smaller ozone absorption in stage II research. The biodegradation stage was very efficient (75%) in removing UV absorbance (280 nm). Consequent O₃ application increased the UV absorbance (280 nm) to greater than 90%.

Ji-Min et al. (2008) studied the efficiency and mechanism of the degradation of TA by O₃ and O₃/H₂O₂. These results indicate that adding H₂O₂ does not enhance the ozonation efficiency of tannins. It was remarked that the addition of H₂O₂ reduced the TOC elimination efficiency by 10%. Byproducts of tannins ozonation have been observed to be aldehydes such as acetaldehyde, glyoxal, and methylglyoxal. The ion chromatogram study confirmed that the final tannin products were ketomallonic acid, and oxalic acid, which accounted for TOC 35% in both processes.

Table 2 shows that the main advantage of O₃ is the increase in the BI, direct O₃ achieves 20–30% of COD and tannin removal and low reaction rate, then is common to find coupled treatments (O₃ ozone-biological) or combined with UV light, catalyst and H₂O₂, to enhance the generation of •OH to rise the complete oxidation of organic pollutants.

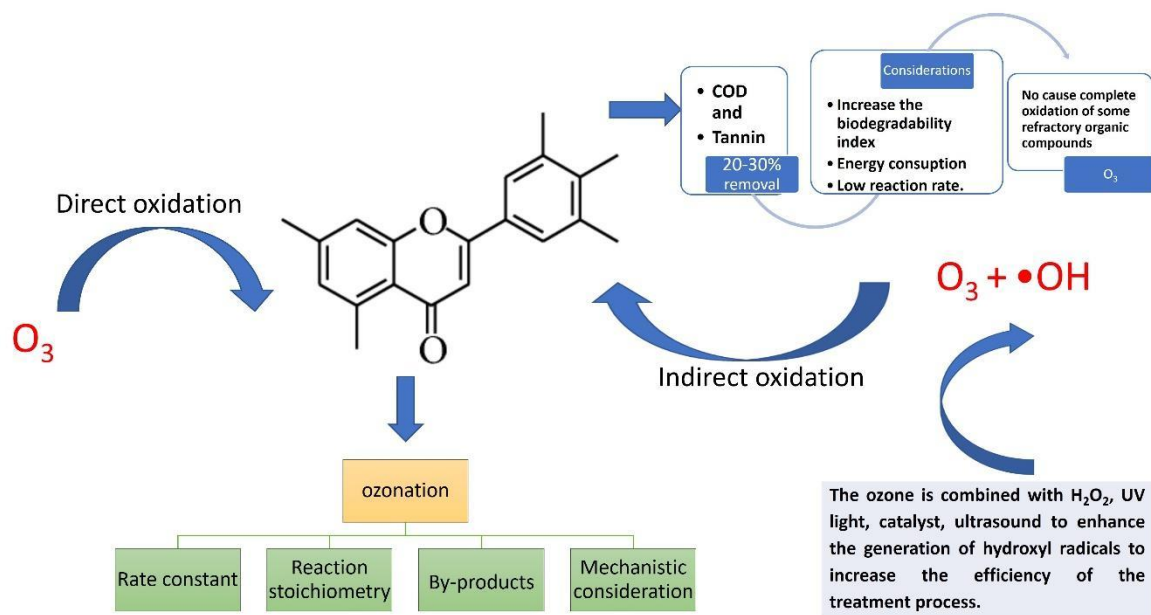


Fig. 9. Ozonation (own creation)

Currently, ozonation is a great technology for treating and recovering wastewater. It is recognized that the pollutant properties present in water determine the level of reactivity with O_3 , but O_3 has several mechanisms to form oxidant species, for example the hydroxyl radical, which can degrade organic compounds. O_3 generation is a costly process, and the very used current technique to obtain O_3 is corona discharge technology. Several factors can improve O_3 production for instance the choice of the electrode and its stability and some researchers have used the BDD electrode and lead dioxide electrodes. Additionally, a suitable support electrolyte such as HCl, H_2SO_4 , and HF should be considered, which favors the production of O_3 .

Ozonation is a nice method for degrading organic molecules; however, more toxic compounds were reported after degradation that O_3 alone is not effective to fully degrade or mineralize them, so coupled methods were developed to improve treatments. For instance, studies have been conducted to improve biodegradation, in which O_3 is applied as a pretreatment and the toxic pollutants present in the water that are partially oxidized could eventually perform as a substrate for microorganisms in a consequent biological treatment.

Table 1. AOPs for tannins and derivates removal or degradation

Treatment	Pollutant	Operational conditions	Results	References
Electrocoagulation	Tannic acid	Electrodes: iron Current: 1-10 mA/cm ² pH=1-13 Galvanostatic Electrolysis 1.1 M Na ₂ SO ₄ + 0.01 M NaCl C ₀ =50 mg/L Tanic acid	COD removals 72% (pH 2), 78% (pH 5), 82% (pH 7) 83% (pH 11)	(Mansouri et al., 2011)
Anodic Oxidation (AO)	Humic Acids	BDD anode Stainless steel cathode TOC ₀ = 16.2 mg/L t=7 h Current: 1000 mA 0.05 M Na ₂ SO ₄	TOC > 99%	(Trellu et al., 2016)
Electro- Fenton (EF)		EF-Pt process (300, 600 and 1000mA), 0.1 mM Fe ²⁺ t= 0.7 h and 9 h t=0.7 and 5 h	TOC _{ads} was diminished 85-22% of the TOC ₀ TOC _{sol} increased 8-40% of the TOC ₀	
Ozonation	Tannins	pH 3.5 (adjusted with formic acid) Bubble column of bench scale glass reactor of diameter 70 mm and height 1200 mm. 100 g/h of ozone. 30 min	20% COD 49% total phenol BOD ₅ /COD ratio increased to 0.298	(Kalyanaraman et al., 2015)
Fenton		FeSO ₄ and H ₂ O ₂ (30%) were used at the pH of 3.5 H ₂ O ₂ /COD ratios (w/w), ranging from 0.25 to 1.5. Fe ²⁺ dose was remained at 100 mg/L	51% COD and 85% phenol BOD ₅ /COD ratio from 0.196 to 0.443.	

Fenton	Re-complexation of polyphenol-Cr complex and their products	300 mL tannin-Cr solution pH 3.5 stirring at 60 rpm tannin dosage 250-750 mg/L, H ₂ O ₂ dosage (11-44 mmol/L) and mole ratio of Fe ²⁺ /H ₂ O ₂ (1:2-1:6) TOC 87.85 mg/L 189.56 mg/L and 254.94 mg/L, [Cr]= 63.48mg/L	TOC 81.63% and Cr 63.71%, at H ₂ O ₂ dosage of 22 mmol/L	(Ma et al., 2020)
Fenton	Insoluble tannins from pine bark	pH of 3.6, 2.4 mmol/L of H ₂ O ₂ 150 µmol/L of Fe(III) 800 mg/L of tannins, 30 min	98% atrazine (30 min), 99.69 (2h) TOC 17.9% (1h)	(Romero et al., 2020)
Electrochemical-driven carbocatalysis	Simultaneous HA and Cr(VI) removal	BDD anode Pt cathode 100 mg/L HAC and 20 mg/L Cr(VI) 0.05 M Na ₂ SO ₄ pH=3 0.4 g carbon-based particles. 100 mA, 25°C	TOC > 90% and Cr(VI) > 90%.	(Yin et al., 2020)
Bifunctional photoelectrochemical	Humic acid degradation and hydrogen production	TiO ₂ -1 wt% Au@TiO ₂ /Al ₂ O ₃ /Cu ₂ O multi-layered p-type photoelectrodes 1h of treatment time -6.32 mA/cm ² at 0 V vs. Reversible Hydrogen Electrode (RHE)	87% humic acids	(Peerakiathkajohn et al., 2021)
Coagulation/floculation (CF) -Electrooxidation	Vinasse, from alcohol distillation processes	CF process with a FeCl ₃ =10-20 g/L pH of 8.4, 20 min 120 rpm /30 rpm pH 8.4 Ti/RuPb(40%)Ox electrode was	COD (84%), color and turbidity (~99%). COD 95% 100% for color and turbidity.	(Zayas et al., 2007)

The subsequent EO step		used as the anode and a Ti/PtPd(10%)Ox electrode as the cathode. 65 mL, 5V, pH=3-9 20 min		
Wet oxidation	Humic acids	Temperature effect 180-220°C Pressure effect 65-95 bar pH effect pH 4-13 480 min	COD reduction 70 % (180°C) 82 % (200°C) 86 % (220°C) TOC 70 % (180°C) 78 % (200°C) 80 % (220°C) By-products: Benzoquinones Lactic, acetic, oxalic, and maleic, formic, malic and pyruvic acids. COD 49 % (65 bar) 51 % (80 bar) 54 % (95 bar) pH of 4 (88%COD and 82%TOC) was the highest mineralization pH 8 (72 % COD and 78% TOC) pH 13 (60 % COD and 55% TOC)	(García et al., 2020)
Wet oxidation	Kraft Black From paper mills	Semi-batch reactor of 1L 150 rpm 1800 mL/min 210 min 70 bar	50% of organic carbon was mineralized. 90% color COD 50%, 67% and 72% at 170, 190 and 210 °C (at 70 bar) and 62%, 67% and 73% at 55, 70 and 85 bar (at 190 °C).	(Pola et al., 2020)

Sulphate radical based-advanced oxidation processes (SR-AOP) Thermally (heat/S₂O₈²⁻) vs. UVassisted persulphate activation (UV-C/S₂O₈²⁻) Thermal activation with transition metals	Winery wastewater	COD₀= 600 mg O₂ /L. t=90 min pH = 7.0 15 mM of S₂O₈²⁻ UV-C lamp [S₂O₈²⁻] /Cu²⁺= 1, pH = 7.0, t=90 min 25 mM [S₂O₈²⁻] at pH 7.0, 240 min of treatment	Heat/S₂O₈²⁻ process attained a removal of 41%. (UV-C/S₂O₈²⁻) 59% of COD 61% of COD 96% and 71% of COD and TOC	(Amor et al., 2018)
Fe ²⁺ /persulfate/tannic acid process to enhance dewaterability	Tannic acid	SPS dosage of 0.43 mmol/gTS (total solid), Fe²⁺ dosage of 0.58 mmol/gTS and TA dosage of 0.14 mmol/gTS	Dewatered sludge cake showed (75.89 ± 0.01) %	(Xiao et al., 2020a)
Oxidation - Filtration Catalytic study of CuFe₂O₄ / Tailored ceramic membrane (CM) (Via peroxymonosulfate Activation)	Humic acid (HA)	CuFeCM 20 mg/L HA volume= 200 mL 70 rpm Filtered with 0.22 mm acetate-fiber syringe filters	Specifically, CuFeCM and CM removed ~49.4% and ~24.5% of the HA	(Zhao et al., 2020)
Fenton (F) Ozonation (O₃) F+O	Vegetable tanning process	-----COD 25 450 mg/L BOD 4050 mg/L BOD/COD= 0.15 Tannins 19750 mg/L In Fenton's oxidation, the H₂O₂/COD (w/w) was 1.25 and Fe²⁺ dose of 1000 mg/L, pH 3.5, 30 min Ozonation time 30 min, 3g/h ozone, pH 3.5	Fenton: 49.5 % Tannins, BOD/COD = 0.42 Ozonation: 27 % tannins BOD/COD = 0.36	(Balakrishna n, Bala, et al., 2020)

			F+O = 74.6 % Tannins	
UV/H ₂ O ₂ process	Tannic acid (TA)	TOC= 82 mg/L pH 9 H ₂ O ₂ =6 g/L 28°C 7.9 kWh/g TOC	Absorbance at 276 nm (> 96%) TOC 94% K=3.5x10 ⁻³ and 2x10 ⁻³ min ⁻¹ a) Formation of aromatic intermediates: gallic acid and pyrogallol b) transformation of aromatics into aliphatic carboxylic acids such as oxalic and maleic acids by aromatic rings opening c) mineralization of aliphatic carboxylic acids to carbon dioxide and water.	(Bensalah & Bedoui, 2018)
Vacuum-ultraviolet (VUV) photo-initiated oxidation	Phenolic homologues removal in humic acid solution phenol, <i>o</i> -dihydroxybenzene (ODB), <i>m</i> -dihydroxybenzene (MDB), <i>p</i> -dihydroxybenzene (PDB), paranitrophenol (PNP) and <i>o</i> -chlorophenol (OCP).	COD=2.39 mg/L DOC= 5.96 mg/L pH= 6.80 T=23°C A 14 W low pressure mercury lamp (GCL300T5VH/4, Light-Tech, America) emitting radiation both at 254 nm and 185 nm	76.85 % Phenol 77.81 % ODB 71.91 % PDB 79.15 % PNP 55.69 % OCP in the MDB solution 79.73 % Phenol 82.80 % ODB 95.36 % PDB 80.38 % PNP 92.64 % OCB In the benzoic acid (BA) solution Byproducts Catechol, hydroquinone, <i>o</i> -benzoquinone, <i>p</i> -benzoquinone, biphenyl, muconic acid, maleic acid, fumaric acid, carbonic acid, other organic acids, NO ₃ ⁻ and Cl ⁻	(Ting-ting et al., 2019)

O ₃ /UV-A-Vis	Phenolic compounds	An experimental design methodology based on Doehlert matrixes: effect of pH (between 3 and 12), ozone dosage (0.2 -1.0 g/h) and initial concentration of the pollutants (1-6 mg/L each) xenon lamp (Heraeus TXE 150), 220 w, radiation < 300nm	Bioassys detoxification (from 100% to less than 30% after 1min of treatment with initial pollutant concentration of 6 mg/L, pH=9 and ozone dosage of 0.8 g/h)	(García-ballesteros et al., 2019)
Photochemical treatment (Sulfate radical)	Tyrosol, in olive mill wastewater	UV lamp 254 nm pH 6.8) UV irradiation at 0, 40, 80, 160, 320 and 640 mJ/cm ² .	Maximum TOC reduction of ~35% was obtained by UV/Persulfate at 640 mJ/cm ² .	(Kilic et al., 2018)
Adsorption and photocatalytic degradation	Humic acid	Dosage of reduced graphene oxide (rGO-TiO ₂) = 1.2 g/L T= 303 K Light intensity 4.37W/m ² pH 7	88.7 % humic acid	(Zhou et al., 2019)
Ultrasound Cavitation (US) combined with AOP	Tannery wastewater	Ultrasound cavitation 22 KHz 130W 250 mL. 0.122 W/mL 1 h, pH 2-6	US: 58% TOC, 1h, pH 3 US +H ₂ O ₂ (2220ppm): 72% TOC	(Korpe et al., 2019a)

Table 2. Advantages and disadvantages of different AOP

Process	Advantages	Disadvantages
AOPs		
Wet oxidation	Faster humic degradation Higher decolorization Mineralization and organic acids were carried out at acid and neutral pH 90% color, 70% COD, 70% TOC	High temperatures (180–220 °C) High pressures (65 bar–95 bar) Some refractory compounds are founded at alkaline pH
UV/H ₂ O ₂ Vacuum-ultraviolet	Higher mineralization Organic acids are produced -90% COD, TOC	Aromatic intermediaries are formed High electrical consumption for UV light
Ozonation	O ₃ , causes non-selective oxidation reactions O ₃ is used with UV light, H ₂ O ₂ , ultrasound, catalyst, to enhance the generation of hydroxyl radicals to enhance the effectiveness of the treatment. O ₃ has been proved to be successful in purifying a wide range of industrial discharges containing pharmaceutical products, recalcitrant pollutants, dyes pesticides, tannins and humic acids and phenols. 20-30% COD and tannins Enhance the biodegradability index	O ₃ alone does not produce complete oxidation of some refractory compounds and the reaction rate is low. Electrical consumption Effective systems for the detection and destruction of O ₃ are required for the safety of workers in several processing plants as exposure to O ₃ could cause irritation to the nose, eyes, and throat. High O ₃ levels (up to 95 mg/L) can have fatal effects on people (García-ballesteros et al., 2019; Rekhate & Srivastava, 2020a)
Sulfate radical (SR)	$SO_4^{\bullet-}$ and $HO^{\bullet}$ benefit because of the high oxidation potential of both Exploits the long half-life time of $SO_4^{\bullet-}$ Appropriate in wide variety of pH	Residual sulfate ions (effluents may need further treatment for sulfate removal) Costly, compared to H ₂ O ₂ Higher amounts of sulfate radicals are necessary per g of COD elimination, compared to H ₂ O ₂

	Safe storage of oxidants on a big scale Biodegradability improvement (when applied as a pretreatment method) COD and TOC removal: 70–90 %	Toxic byproducts could be formed in the existence of Cl^- and Br^- (Giannakis et al., 2020; Gonçalves et al., 2019)
Electrochemical treatments	In neutral and alkaline pH, dissolved metals are rapidly transformed into insoluble hydroxo-metal species that show a critical role in removing tannins from water by coagulation. Supporting electrolyte promotes the electrochemical corrosion of sacrificial anode. In the existence of sulfate ions, the formation and breakdown of metal hydroxide/oxide film depends on electrode potential. Adding 0.1 M Na_2SO_4 or 0.01 M NaCl leads to the breakdown of the passive film Solar energy, wind energy and biomass energy can further compensate for power consumption 70–80% COD removal by EC 90% TOC by EO	The main disadvantages for electrochemical technology are high-energy supply voltage and high energy consumption. The presence of Cl^- in water accelerates dissolution of Fe by pitting corrosion while phosphate ions reduce the corrosion of Fe by formation of a thick passive layer of iron hydroxide/phosphate on iron surface (Mansouri et al., 2011).
Fenton	Fenton optimization processes reduce operational costs and environmental risks Wide application variety Easy operation Fast mineralization and degradation 50% removal of tannins and 70% coupled Fenton treatments	Economic costs are the limiting factors for the large-scale development and application Full economic costs evaluation can give a powerful cost support for the industrialization of the optimization processes (Zhang et al., 2019).

Adsorption

Adsorption improves the content of a specific compound on the interface of the two phases. These compounds are transferred from one phase to another and subsequently adhere to the superficies of the sorbent. It accounts for a complex phenomenon and is determined mainly for the surface chemical or the properties of the sorbent, sorbate, and system conditions among these two phases (Patel, 2019). Modifying a common, low-cost adsorbent material is common practice to enhance the adsorption capability and improve the adsorption ratio. Adsorption processes are highly efficient for eliminating dissolved organic matter from water/wastewater under simple operational conditions (Singh & Kushwaha, 2014). Investigation on the elimination of PPs from solutions using various adsorbent materials was reviewed. According to this review, adsorption methods can be proposed, including ion-exchange resins, polymers, nanocomposites, minerals, resins, and polysaccharide-based adsorbents (Fig. 10).



Fig. 10. Adsorbents for polyphenol removal (own creation)

Polymers

Adsorbents for polyphenol removal Polymers Poly(acrylamide) is a high molecular weight hydrophilic synthetic polymer that groups $-NH_2$ on its side chain and can form hydrogen bonds with any other polymers. Polyacrylamide has previously been demonstrated to be a useful material in the purification of water as a flocculant for the agglutination of heavy metals to form coordination bonds, and cationic polyacrylamide has too been applied for antimicrobial applications. It has also been extensively applied for wastewater treatment (Rajeswari et al., 2020). Cross-linked polyacrylamide hydrogel beads were made and utilized to eliminate TA from solutions (imitating drinks) or alcohol-aqueous solutions (imitating alcoholic drinks), although most of the low molecular weight PPs, such as epigallocatechin gallate and catechin, are beneficial for health. Adsorption capacities and elimination percentages were positively associated with the molecular weights of the PPs, and only hydrogen bonding was designed to execute the adsorption. Adsorbed PPs were completely desorbed with hot water from the adsorbent. This could be ascribed to the deterioration or damage of hydrogen bonds (Cao et al., 2020).

Vavouraki (2020) conducted adsorption research of polyphenols from olive grinder wastewater (OW) applying a cross-linked styrene-divinilbumin polymer (FPX 66) as sorbent. As a result, it obtained a reduction of 68% of polyphenols, in the first hour. At pH of the OW effluent below 7.5 the removal of polyphenols with FPX 66 was 77% and for pH above 9.0 it decreased by 40%. For batch studies, the kinetic data were fitted to the pseudo second order model and the isotherms were adjusted to the Langmuir and Freundlich models. Regeneration studies indicated that at low pH value it is effective for the recuperation of phenolic compounds, which implies that the main regeneration mechanism could be chemisorption (Vavouraki, 2020).

Polyaniline, a well-known conductive polymer, possesses large amounts of amine and imine groups that can interact with heavy metals and organic pollutants, making them suitable for

the adsorption of water contaminants (Kim et al., 2016; Sun et al., 2017). Sun et al. studied polyaniline formulated through chemical oxidation to eliminate TA by adsorption from an aqueous solution. Among the analyzed coexisting anions, PO_4^{3-} significantly inhibited TA adsorption due to improved repulsive interactions. The mechanism that controls the adsorption of TA on PANI in compliance with different operational conditions was estimated by applying a combination of electrostatic interactions, hydrogen bonds, p-p interactions, and van der Waals interactions (Sun et al., 2017).

Biopolymers

Biopolymer chitosan, a natural biopolymer cation and cheap material, has been widely used as an excellent adsorbent for heavy metal cations and neutral or positively charged organic species as reactive dyes, because the amino ($-\text{NH}_2$) and hydroxyl ($-\text{OH}$) groups of the biopolymer chain can act like coordination and reaction sites (Agarwal et al., 2018). Coal fly ash is a solid waste generated in large quantities worldwide; therefore, it is important to develop techniques for productive reuse. Synthesized zeolites have been extensively researched for water treatment as a measure to use coal fly ash. Agarwal et al. (2018) compared TA adsorption efficacies with fly ash, NaOH-modified fly ash, and chitosan-modified NaOH (chitosan compound/NaOH/fly ash) modified fly ash. Chitosan/NaOH/fly ash possesses a higher adsorption efficiency for TA than fly ash and NaOH-modified fly ash. TA adsorption decreased slightly with increasing NaCl-adjusted ionic strength. The values of ΔG , ΔS , and ΔH indicate spontaneous and exothermic processes (Fig. 11).

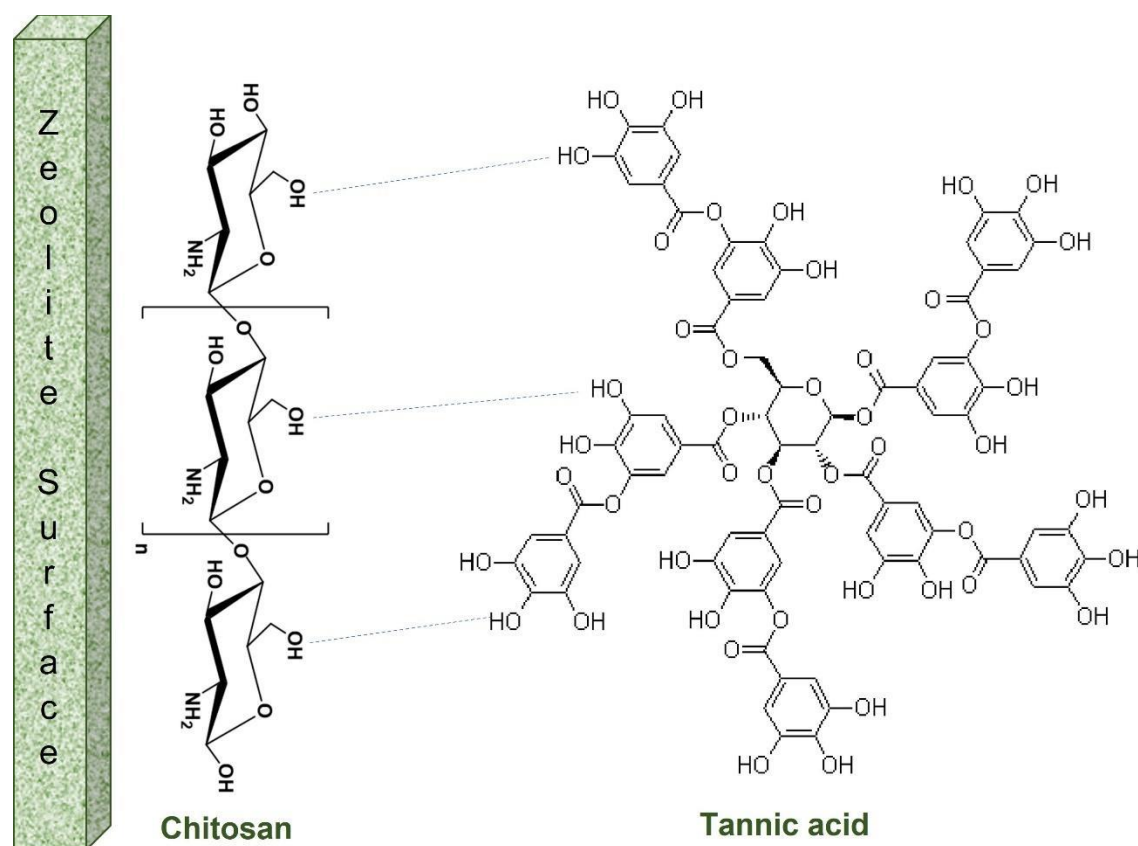


Fig. 11. Schematic representation of chitosan-modified surface with hydrogen bonded tannic acid (Modified from Agarwal et al., 2018).

An efficient adsorbent was developed using the molecular imprinting method in a sol-gel matrix (hybrid sol-gel silica adsorbent). The Absorption capacity of the organic-inorganic hybrid adsorbent material has been researched on tannin composites, i.e. phenolic substances that are difficult to remove in industrial effluent. The (3-aminopropyl) triethoxysilane functionalized adsorbent was an efficient adsorbent material for the tannin complexes analyzed, with around 90% elimination in solutions (Benvenuti et al., 2018).

Nanocomposites

Graphene Nanoplatelets (GNP) are being used as carbon for adsorption experiments and are more stable than single-layer graphene (Chen et al., 2017). Zr-based metal organic structures and graphene nanoplatelets nanocomposites utilizing an acid-promoting method have been utilized for adsorption of two distinct PPs: hydroxytyrosol and oleuropein. The adsorption kinetics and isotherms were researched at various pH of the solution. The results showed

good fit of the adsorption of hydroxytyrosol in Zr-based metal organic structures and the adsorption of oleuropein in graphene nanoplatelets nanocomposites to the Langmuir and Sips isotherms. Accordingly, the prepared nanomaterials could be contemplated as potential adsorbents for the adsorption and removal of the PPs from water (Şahin et al., 2019).

Activated carbon

Singh and Kushwaha (2014) studied and optimized the parameters of adsorbent dose, pH, temperature, initial concentration of TA, and contact time with commercial activated carbon. They studied three isotherms, namely the Langmuir, Temkin, and Redlich–Peterson isotherms (R-P) and found that the Langmuir and R-P isotherms generally fit the experimental equilibrium adsorption data. Taking into account the price of commercial activated carbon, tannic-acid-loaded activated carbon regeneration studies have been conducted using thermal desorption methods and solvents (Singh & Kushwaha, 2014). Jung et al. carried out pyrolysis to produce an efficient biocarbon, with its physicochemical properties enhanced by chemical activation, resulting in an adsorbent appropriate for the removal of organic matter, including hydrophobic and hydrophilic substances, as TAs and humic acids. Additionally, we evaluated adsorption affinities of various combinations of TAs and humic acids in organic matter solutions, and observed a higher adsorption affinity for TAs in the activated biochar (Jung et al., 2015). Contreras-Contreras et al. evaluated the elimination of PPs from sugarcane vinasses with activated carbon as a complementary treatment subsequently biochemical processes with three Upflow Anaerobic Sludge Blanket (UASB), which operate isothermally, because biochemical treatment alone was insufficient to remove phenolic compounds present in the vinasses (Fig. 12) (Contreras-Contreras et al., 2020)



Fig. 12. PPs removal using activated carbon after biochemical treatment Upflow Anaerobic Sludge Blanket (UASB) Reactors (own creation).

Minerals

Bentonite is a natural clay mineral found in many places worldwide. Any volcanic clay that contains montmorillonite is called bentonite. The adsorption features of bentonite can be enhanced by modifying its surface (Anirudhan & Ramachandran, 2006). Organoclays have been researched for a large variety of environmental applications, like the adsorption of phenol compounds with hexadecyltrimethylammonium bromide modified bentonite. Organo-bentonites were prepared with hexadecyl trimethylammonium bromide and benzyl triethylammonium chloride. Surfactants of two different types of cation exchange capacities (50% and 100%) of bentonite were used. The adsorption efficiency of the organo-bentonites was less than activated charcoal. Improved adsorption efficiencies were observed for organo-bentonites formulated with greater quantities of cationic surfactants (Marsal et al., 2009). Bentonite clay modified with cationic surfactant hexadecyltrimethylammonium chloride was studied using a discontinuous system. The data obtained from the adsorption isotherms at different temperatures were adjusted to the Langmuir model. Thermodynamic parameters were calculated to predict the theoretical behavior of the adsorption of tannins in organic clays, being observed to be of exothermic nature and reduced with an increase of the ionic force. With the above, it is shown that organic clays remove tannin from aqueous solutions (Anirudhan & Ramachandran, 2006).

Resins

The ion exchange process was utilized to treat water in fixed-bed columns filled with ion exchange resins, ranging from 0.3 to 1.2 mm in diameter. However, the large-scale application of fixed-bed columns for water treatment has some unavoidable deficiencies, such as high capital costs and limited flow. The strongly basic anion exchange magnetic resin, slightly acidic cation exchange resin, and their combination processes were used to remove at the same time heavy metals such as Ni (II), Cu (II) and TA. The integration method based on strong basic magnetic anion exchange resin and slightly acidic cation exchange fully mixed in the same reactor can at the same time eliminate Ni (II), Cu (II), and TA with elevated efficacies. The synergistic elimination of TA and Cu (II) by magnetic resins is done through the TA-Cu complexation bridge formation mechanism, which was demonstrated by fluorescence spectra. Furthermore, hydrogen bonding and ion exchange are attributed to TA adsorption (Fu et al., 2015).

Polysaccharide-based adsorbents

Konjac glucomannan is a low-cost neutral polysaccharide that originates from the tubers of *Amorphophallus konjac* (Xu et al., 2009). Liu et al., (2010) analyzed the adsorption of tannins by deacetylated konjac glucomannan regarding the impact of the adsorbent dose, initial pH, temperature, contact time, and initial concentration of tannins. The adsorption process was greatly determined on temperature and pH and followed pseudo-second-order kinetics. Improving the adsorption temperature would result in a decreased adsorption capacity, indicating that tannin adsorption on deacetylated konjac glucomannan is exothermic in nature. The adsorption mechanism verified the interaction between deacetylated konjac glucomannan and tannin across hydrogen bonds (Liu et al., 2010).

Membrane processes

Membrane processes are increasingly used in various industrial applications and in wastewater treatment (Conidi et al., 2011; Huang et al., 2011; Mousa, 2007). Compared to other concentration and separation systems, the most important benefit of membrane processes is that concentration and separation are achieved in most situations without a

change in state and utilizing chemicals or thermal energy; therefore, membrane technology is environmentally friendly (Romero-Dondiz et al., 2015).

Romero-Dondiz et al. (2015) evaluated the operation of various commercial polymer ultrafiltration membranes, fouling, operating conditions, and selectivity of the ultrafiltration process to treat a depleted synthetic vegetable tannin liquor from the leather industry. The consequences of the transmembrane pressure on the permeate flow, the flow decrease were analyzed, the resistance to fouling and the rate of fouling of the membranes and indicated a retention of tannins of 83% and a recovery of the water flow after cleaning the membrane with water of 41% to 45%. The significance of this study sets precedents for the removal of tannins by UF polymeric membranes, and it also represents a preliminary study for future research.

Adsorption is considered a green technology, effective in the treatment of recalcitrant substances in wastewater, it is a slow process of physical separation, whose challenge lies in regenerating the adsorbent used, but it has a notable advantage, there are many materials that you can use as adsorbents, some with the ability to naturally adsorb and desorb other substances, they are inexpensive and can be modified to improve their performance.

Modification methods are an interesting topic since other materials can be adapted and hybrid materials form. On the other hand, carbon-based materials are the most used as activated carbon due to its large surface area and porosity, it is used to eliminate soluble non-biodegradable organic pollutants in wastewater and drinking water.

Factors that must be considered because they affect removal by adsorption are polarity, solubility, size of the molecule (limits diffusion and access to pores), branching of the molecule, functional groups, and pH.

Table 3. Comparison of adsorbents for polyphenol removal

Adsorbent	Tipo de polyphenol	Conditions	Model	Efficiency	Reference
magnetic resins	tannic acid	0.05 g of adsorbent 100 mL, 100 mg/L	-	88.4%,	Fu et al., 2015

Polyaniline	tannic acid	1 h and 4 h for 20 mg/L and 100 mg /L, pH 8 to 11	pseudo- second-order model, Langmuir model	230, 223 and 1023 mg/g	Sun et al., 2017
cross-linked polyacrylamide beads	tannic acid, epigallocatechin gallate, catechin and gallic acid,	0.1 g of the adsorbent in 25 mL of individual adsorbate 25 °C for 24 h.		tannic acid 90.1% (161 mg/g), EGCG 16.1% 38.8, Catechin 0.84 % (2.1 mg/g)	Cao et al., 2020
Zr-based metal organic frameworks and graphene nanoplatelets nanocomposites	oleuropein and hydroxytyrosol	60 and 180 min pH 4, 7, 10	Langmuir, Freundlich, Sips isotherm	274.76 mg oleuropein / g GNP/UiO-66 nanocomposite at pH 4, and 142.07 mg of hydroxytyrosol /g UiO-66 nanoparticles at pH 10.	Sahin et al., 2019
commercial activated carbon	tannic acid	T = 301 K, t=7h Co = 100 mg/l, adsorbent dosage (mad) = 20 g/l pH = 2, 3	Langmuir, Temkin, and Redlich and Peterson	67.5, pH 2 and 66.02 % pH 3	Singh et al., 2013
Coagulation- adsorption Pinus taeda activated biochar	humic acids and tannic acids	Co = 2.5 to 10 mg/L pH = 7	pseudo second-order rate, Freundlich isotherm	9.3 - 44.99 % humic acids 8.2 – 29.3 % tannic acids	Jung et al., 2015
Organo- bentonites	PPs from the mimosa extract	Co = 0.03– 0.30 g/L	Freundlich		Marsal et al., 2009
Cationic surfactant- modified bentonite clay	tannic acid	t = 6 h, Co = 10 and 25 µmol/L tannin, pH 2 to 8	Langmuir and Freundlich		Anirudhan and Ramachandran et al., 2006
Chitosan / NaOH / fly ash composites	tannic acid	pH = 5.5 to 7	pseudo- second-order kinetic, Langmuir, Freundlich, Dubinin - Redushkevich, Redlich- Peterson	243.90 mg g ⁻¹	Agarwal et al., 2018

Magnetic strongly basic anion exchange resin (MAEX) and weakly acidic cation exchange resin (MCEX)	tannic acid	25, 50 mg/L tannic acid			Fu et al., 2015
Cross-linked styrene–divinylbenzene polymer	phenols	4 g/L phenolic compounds t = 12 h (125 rpm) T = 25°C initial pH = 5 adsorbent dosage = 5, 10, 12.5, 15, 17.5, 20 %	Pseudo second-order kinetics Langmuir and Freundlich isotherm	77% pH below 7.5	(Vavouraki, 2020)
Deacetylated konjac glucomannan	hydrolysable tannin (mean relative molecular mass of tannin: 1701.23)	pH = 2 to 6	pseudo second order kinetics, Langmuir and Freundlich isotherms	90%, 1331.58 $\mu\text{mol g}^{-1}$, 50 °C	Liu et al., 2010
Hybrid sol–gel silica	tannic acid	C ₀ = 25 and 50 ppm		90%	Benvenuti et al., 2018
Activated Carbon After Biochemical Treatment	PPs in the vinasses, gallic acid equivalent	3600 mg of gallic acid	Langmuir model	70.2%. 1428.6 mg/g	Contreras-Contreras et al., 2020

The adsorption process depends significantly on pH, ionic competence, regeneration, and the final arrangement of the material loaded with PPs. Table 4 summarizes the advantages and disadvantages of some adsorbents used for the removal of PPs.

Table 4. Advantages and disadvantages of adsorbents for PPs removal.

Adsorbent	Advantages	Disadvantages
Activated carbon	Locally available adsorbent materials. High efficiency. Cost effective Is relatively inexpensive when it comes from by-products, low operating, and maintenance costs	High production cost and difficulty in regeneration, leading to an increase in treatment costs

Polyaniline	Continuous flow adsorption studies suggested good flexibility and adaptability of the Polyaniline adsorbent under distinct flow rates and influent TA concentrations. Could be utilized as a flexible and adaptable adsorbent for remediation of tannic acid contaminated wastewater, especially in alkaline media	PO_4^{3-} significantly inhibited TA adsorption
Biochar	Higher adsorption attraction of TA on activated biochar was observed due for its superior chemisorption tendencies and size-exclusion effects compared with that of HA	Hydrophobic interactions between adsorbent and adsorbate were deficient
Polyacrylamide hydrogel	High adsorption selectivity, high adsorption capacity, spherical morphology, which is beneficial for column method, low cost, and green and ecological-friendly regeneration process.	
Konjac glucomannan polysaccharide	The advantages of KGM applied as an adsorbent to adsorb tannins from wastewater stay in its biodegradability, abundance, and the relative simply chemical modification.	Cannot be applied directly as an adsorbent to adsorb tannins from aqueous solution, because of its elevated solubility in aqueous solution (Liu et al., 2010).

Suggestions and future trends

AOPs

AOPs have been shown to be efficient in treating a broad variety of industrial discharges, pesticides, pharmaceutical products, and recalcitrant organics such as tannins and humic acids. Future studies need to focus on the detection of reaction intermediates assisted by

chromatographic techniques such as HPLC and GC, advancement of rate expressions, and identification of scale-up parameters.

Occasionally, intermediate/transformation products are even more toxic than the original compounds. Toxicity tests should be employed to evaluate the toxicity of these compounds. Future research should emphasize the cost efficiency of the AOP and should explore the actual amount of energy expended in the case of ozone, electrochemical treatment, and UV applications. It is necessary to carry out pilot plant-scale experiments with real industrial wastewater to identify scale-up parameters (Rekhate & Srivastava, 2020).

Sulfate radicals (SR): The efficiency of SR-AOPs presents a unique niche opportunity for their application. These processes have high applicability because of the elevated quantities of contaminants that can be degraded. However, the problems of inefficient reactor designs, with key issues in mass transfer limitations and catalyst recovery capabilities, are still an impediment to their wide dissemination. This is understandable to a particular extent, since the SR-AOPs span less than 20 years and more competitive solutions (e.g., ozone) have a significantly longer trajectory, which allowed its successive improvement.

Electrochemical treatment is an interface process. From a kinetic viewpoint, the mass transfer efficiency can be improved by optimizing the reactor design. Remarkably, the efficiency of the interfacial process depends on the advancement of novel electrode materials or electrode catalytic materials. Total cost-effectiveness of existing electrochemical processes for pollutant treatment can be improved by building electrochemical processes from the perspective of increasing effectiveness, stabilizing contaminants, and getting energy/material (Deng et al., 2020).

Fenton optimization processes must concentrate on degradation kinetics of organic contaminants, identification of reaction intermediates and evolution of rate expressions based on the degradation mechanism.

Iron content, low leaching rate, high stability, high catalytic activity, and minimal preparation costs are the principal factors to be considered to develop heterogeneous catalysts. Development of heterogeneous catalysts is necessary to enhance the efficacy of organic wastewater treatment and reduce treatment costs. Additionally, the exploration of catalysts

containing other metals has gradually become a trend in the advancement of heterogeneous catalysts. Detailed information on economic costs, such as energy consumption costs, reactor investment costs, chemical costs, and so on must be correctly offered in future work. To avoid unexpected consequences resulting from the advancement of large-scale Fenton systems in optimizing systems, it is necessary to evaluate their environmental effectiveness. The use of Fenton to optimize the processes with other methods will be a trend in organic wastewater treatment. The latest combination processes show efficient wastewater treatment owing to synergistic effects through processes (Zhang et al., 2019).

Membrane technology

Studies that investigate the use of membrane technology in the leather industry have reported major fouling problems due to the elevated concentration of organic matter in the effluents. Due to severe fouling of membranes, nanofiltration achieves limited TA removal and is very expensive (Gallego-Molina et al., 2013; Mendoza-Roca et al., 2010). Therefore, some authors have suggested the recovery of permeate flow through the implementation of cleaning methods (Mendoza-Roca et al., 2010; Romero-Dondiz et al., 2015).

Among the advantages of membrane processes is that they are environmentally benign and afford the recuperation of tannins. The elimination of tannins from the wastewater effluents of membrane processes could be an effective treatment stage in water purification plants that process these effluents (Romero-Dondiz et al., 2015).

Adsorption

Adsorption has been applied to remove PPs from both water and plants, although most previous studies have been performed using synthetic water; very few have been conducted using real wastewater. Hence, additional studies require to be performed using real water. Techniques to regenerate these adsorbents have been developed using solvents and thermal desorption methods; these are the most efficient thermal method for activated carbon, and the adsorbed TA and epigallocatechin gallate from the polyacrylamide beads can be completely desorbed by treatment with hot water at 95 °C (Cao et al., 2020). Alternatively, several studies have described regeneration of adsorbents using alkaline solutions. It is highly

unlikely that a single technique will sufficiently remove compounds such as PPs, and it is anticipated that the combination of economically viable techniques will resolve this problem.

Superior adsorption capacities and physicochemical properties of biochar by-product are recommended as an adsorbent, as activated carbon is a very effective adsorbent, and this adsorbent material is relatively inexpensive. In addition to the exceptional adsorption capacity, the use of alum combined with coagulation produced a synergistic effect with appropriate organic matter compositions. Thus, studies have shown the effectiveness of hybrid technologies for achieving superior water purification in the treatment scheme (Contreras-Contreras et al., 2020; Jung et al., 2015). Other research should consist of experiments at the pilot plant level to evaluate the use of adsorbents directly in a plant for the adsorption of PPs (Contreras-Contreras et al., 2020). Since very few studies have presented results with real water, additional study is needed to evaluate adsorption efficiency of adsorbents using real wastewater and other organic pollutants. A cost-benefit calculation is also required before making a final decision to incorporate these technologies.

Conclusions

Tannins and humic acid can be efficiently removed by AOPs such as wet oxidation, UV/H₂O₂, electrochemical, sulfate radical, Fenton, etc., and hybrid methods.

A higher temperature promotes faster humic acid removal, decolorization, and mineralization for wet oxidation. Conversely, the pressure effect was negligible during the wet oxidation of humic acid and PPs in the range tested (65–95 bar).

According to different studies, tannin degradation by the UV/H₂O₂ system involves some steps, including a) the formation of aromatic intermediates such as pyrogallol and gallic acid, b) transformation of aromatics into aliphatic carboxylic acids such as maleic and oxalic acids by aromatic ring opening, and c) mineralization of aliphatic carboxylic acids to carbon dioxide and water. It can be concluded that UV/H₂O₂ is a very effective method capable of concurrently removing and mineralizing tannins and humic acids.

SR-AOPs: Recent advances in precursor activation mechanisms, complex catalytic materials, and the use of sophisticated or expensive activator technologies present a unique opportunity for tannins, humic acids, and all kinds of organic compound treatment. However, the development of highly active catalysts for organic elimination, materials with exceptional light absorption and photocatalytic capacity, or the induction of non-radical pathways, coupling with expensive processes such as microwave or ultrasound, and processes that otherwise seem inapplicable at major scale.

The electrochemical process exhibits potential for pre-treatment or advanced treatment in practical engineering applications. Therefore, it is necessary to further research the construction of a continuous running reactor. This is crucial to developing high-performance electrochemical equipment. Considering the response relationship between the treatment cost and the treatment effect, some electrochemical AOPs (electro-Fenton, photoelectro-Fenton process, electro-catalytic ozonation, and electrochemical-persulfate oxidation processes) were combined to further improve the mineralization rate of pollutants and shorten reaction time. The commonalities among these technologies lie in their dependence on pH and the difficulty of removing ammonium-N.

Fenton: The heterogeneous Fenton method can surmount the disadvantages of the conventional Fenton method, which is limited to a thin working pH scale and produces a great amount of iron sludge. The key to the heterogeneous Fenton method is the advancement of heterogeneous catalysts and their recycling. The photo-Fenton process can surmount the disadvantages of the traditional Fenton process, which produces a large quantity of iron sludge. The maximum elimination of organic pollutants by Fenton optimization processes can be achieved at the optimum pH range, optimal catalyst, and H_2O_2 concentration. Most Fenton optimization processes can obtain high degradation efficiencies with low concentrations of organic pollutants.

Hybrid methods are economically viable for treatment of a large range of industrial effluents. The combined process decreases the operational cost based on energy consumption, enhances $OH^\bullet$ availability, and enhances treatment efficiency. The high effectiveness and minimal energy consumption make the AOP process an attractive process for wastewater remediation.

Adsorption appears to be an attractive method for the elimination of PPs from water. It is eco-friendly and simple. The pH of the solution plays a very significant role in polyphenol removal, where most of the adsorbents work effectively in the pH range of 3.0–7.0. Various adsorbents under different categories, such as biopolymers, nanomaterials, minerals, and other adsorbents, have been reviewed. The results indicate that polyaniline and polyacrylamide hydrogel beads could be utilized as flexible and adaptable adsorbents for the remediation of TA-contaminated wastewater, especially in alkaline media where the ionic strength and TA concentration fluctuate in influent water.

Availability of data and materials All data generated or analyzed during this study are included in this article.

Author contribution All authors contributed to the study conception and design. The literature search and data analysis were performed by Ivonne Linares-Hernández, Elia Alejandra Teutli-Sequeira and Eduardo Rico-Santiago. The first draft of the manuscript was written by Verónica Martínez-Miranda and Guadalupe Vázquez-Mejía. All authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

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7. DISCUSIÓN GENERAL

El análisis crítico del estado del arte sobre las tecnologías de tratamiento para polifenoles y sus derivados ha permitido establecer qué tipos de tratamiento podrían ser los más efectivos y rentables tanto a nivel operacional como a nivel de coste. Además, permite a otros investigadores extraer conocimiento a través de los resultados obtenidos en cada estudio y sirve como base para una propuesta de tratamiento que minimice las limitaciones de la tecnología elegida en la eliminación de estos contaminantes del agua residual, siendo la tecnología híbrida la que puede presentar mayores rendimientos.

Los tratamientos de oxidación vía radical hidroxilo como los POA han demostrado una alta eficiencia de eliminación de contaminantes orgánicos recalcitrantes, aunque tiene un elemento importante a considerar, que es la generación de subproductos no deseables como ejemplo los cloratos en la oxidación anódica, por lo que es necesario más estudios para buscar las condiciones operativas adecuadas para limitar la formación de especies tóxicas no deseadas.

La adsorción a base de carbón activado (CA) es la tecnología más adecuada para el tratamiento de contaminantes orgánicos, aunque el factor más limitante son los altos costos de las condiciones operativas resultantes como la regeneración o reemplazo de CA, sin embargo, la literatura revisada muestra que se están utilizando adsorbentes como sílice sol-gel híbrido y glucomanano konjac ya que presentan una gran capacidad para absorber contaminantes orgánicos con eficiencia del 90 % de retención de polifenoles. El desarrollo de procesos que integre la adsorción con POA puede mejorar la eficiencia de remoción usando un solo tratamiento.

8. CONCLUSIONES

Los taninos y el ácido húmico se pueden eliminar de manera eficiente mediante POA como oxidación húmeda, UV / H_2O_2 , electroquímica, radicales sulfatos, Fenton, etc., y métodos híbridos.

Para la oxidación húmeda, una temperatura más alta promueve una eliminación, decoloración y mineralización más rápida del ácido húmico. Por otro lado, el efecto de la presión es insignificante durante la oxidación húmeda de ácido húmico y polifenoles en el rango probado (65 - 95 bar).

Según diferentes trabajos, la degradación de taninos por el sistema UV/ H_2O_2 implica varios pasos que incluyen: a) formación de intermedios aromáticos como el ácido gálico y pirogallol, b) transformación de aromáticos en ácidos carboxílicos alifáticos como los ácidos oxálico y maleico mediante la apertura de anillos aromáticos y mineralización de ácidos carboxílicos alifáticos a dióxido de carbono y agua. Se puede concluir que el proceso UV/ H_2O_2 es eficiente para remover y mineralizar simultáneamente taninos y ácidos húmicos.

SR-AOP: los avances recientes en los mecanismos de activación de precursores vía radical sulfato, promueve la síntesis de materiales catalíticos complejos y el uso de tecnologías de activadores sofisticados o costosas que presentan una oportunidad única para el tratamiento de taninos, ácidos húmicos y todo tipo de compuestos orgánicos. Sin embargo, el acoplamiento con procesos costosos como microondas o ultrasonido, parecen inaplicables a gran escala.

El proceso electroquímico tiene potencial para pretratamiento o tratamiento avanzado en aplicaciones prácticas de ingeniería. Por lo tanto, es necesario seguir investigando sobre la construcción de un reactor de funcionamiento continuo, que también es crucial para el desarrollo de equipos electroquímicos de alto rendimiento. Teniendo en cuenta la relación entre el costo del tratamiento y la eficiencia, se combinaron algunos POA electroquímicos (proceso electro-Fenton, foto electro-Fenton, ozonización electrocatalítica y oxidación electroquímica-persulfato) para mejorar aún más la tasa de mineralización de contaminantes

y acortar el tiempo de reacción. Los puntos en común entre estas tecnologías radican en su dependencia del pH y la dificultad de eliminar el amonio.

El proceso de Fenton heterogéneo puede superar las desventajas del proceso de Fenton convencional, que se limita al estrecho rango de pH de trabajo y produce una gran cantidad de lodo de hierro. La clave del proceso Fenton heterogéneo es el desarrollo y la reutilización de catalizadores heterogéneos. La máxima eliminación de contaminantes orgánicos mediante los procesos de optimización de Fenton se puede lograr en el rango de pH óptimo, el catalizador óptimo y la concentración de H_2O_2 para obtener una alta eficiencia de degradación de contaminantes orgánicos.

Los métodos híbridos son técnicas económicamente viables para el tratamiento de una amplia gama de efluentes industriales, incluyendo taninos y ácidos húmicos. El proceso combinado de uso disminuye el costo operativo basado en el consumo de energía, mejora la disponibilidad de $OH^\bullet$ y mejora la eficiencia del tratamiento. La alta efectividad y el bajo consumo de energía hacen del POA un proceso atractivo para la remediación de aguas residuales.

La adsorción parece ser un método atractivo para eliminar los polifenoles del agua. El pH de la solución juega un papel muy importante para la eliminación de polifenoles, donde en la mayoría de los adsorbentes funcionan eficazmente en un rango de pH de 3,0 a 7,0. Se han revisado varios adsorbentes, como biopolímeros, nanomateriales y minerales. Los resultados indican que las perlas de hidrogel de polianilina y poliacrilamida podrían emplearse como un adsorbente flexible y adaptable para la remediación de aguas residuales contaminadas con ácido tánico, especialmente en medios alcalinos donde la fuerza iónica y la concentración de ácido tánico fluctúan en el agua afluente.

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10. ANEXO

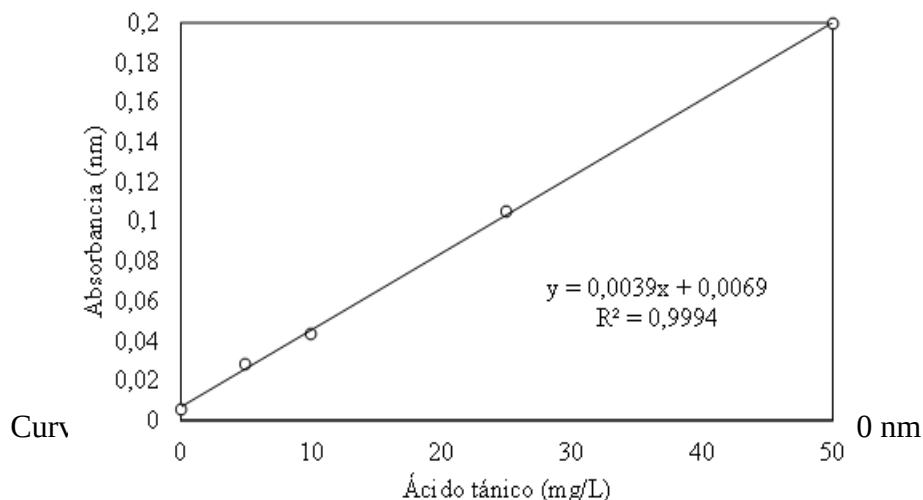
La información contenida en este anexo son las actividades realizadas en el proyecto que llevó por nombre **“Remoción de taninos en agua residual proveniente de una industria de fragancias y sabores mediante foto-Fenton heterogéneo”** y que derivado de la emergencia sanitaria y cambios en la infraestructura del laboratorio del instituto quedó suspendido; por estas razones se decidió realizar una revisión crítica de los tratamientos de polifenoles y derivados aprovechando la investigación que se hizo del proyecto original.

Tratamiento foto-Fenton heterogéneo.

Para determinar el efecto de los iones Fe, Al y del H_2O_2 en la degradación de ácido tánico, se efectuaron los experimentos en un colector parabólico compuesto (CPC), el colector consta de cuatro concentradores formados por reflectores cubiertos con papel de aluminio que cumplen la función de reflejar la luz solar hacia los tubos de borosilicato, con un grado de inclinación aproximado de 20° orientación Norte-Sur. El reactor se colocó en una plataforma fija en las instalaciones del Instituto Interamericano de Tecnología y Ciencias del Agua.

Pruebas preliminares

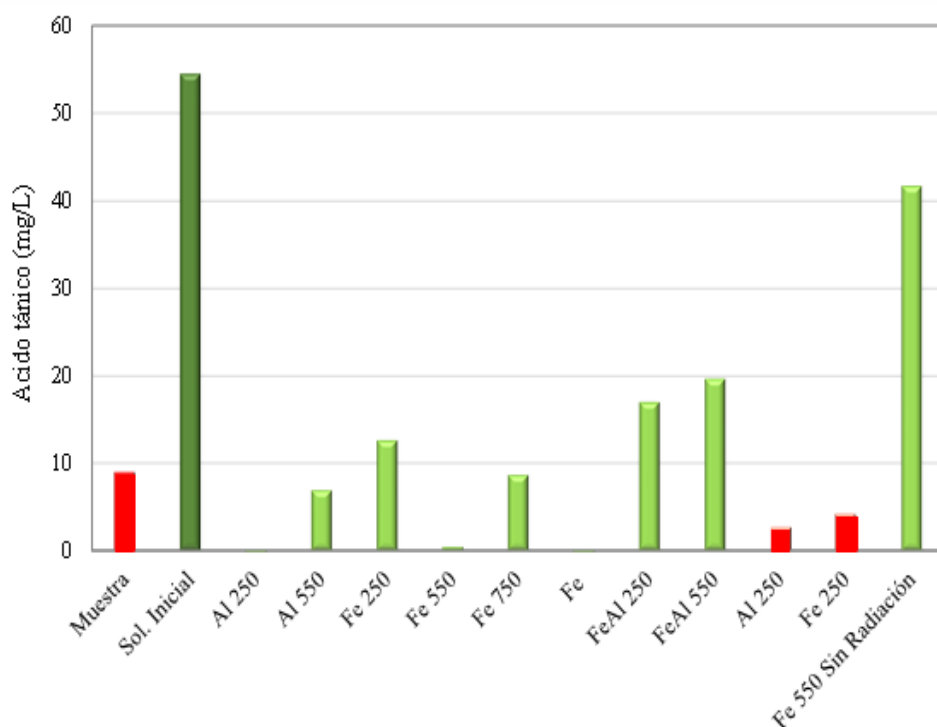
Se realizó la curva de calibración de ácido tánico en un rango de concentración de 0 a 50 mg/L a partir del método tungsteno-molíbdeno-fosfórico. En la Figura 6 se presenta la curva de calibración con un coeficiente de determinación de $R^2 = 0.9994$, con esta curva se obtuvieron las concentraciones de las muestras a analizar.



Proceso de adsorción y foto-Fenton heterogéneo

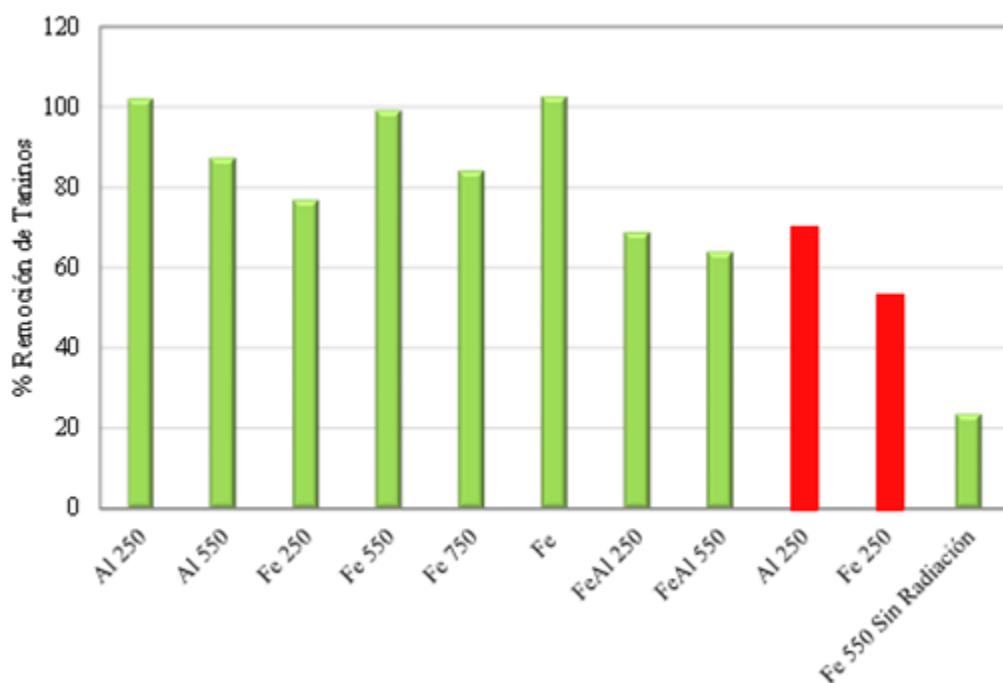
Se realizaron pruebas de adsorción con cada uno de los materiales zeolíticos modificados (Al 250, Al 550, Fe 250, Fe 550, Fe 750, Fe, FeAl 250, FeAl 550) a diferentes temperaturas, con lo que se demostró que los materiales no degradaron ácido tánico por este método. Al adicionar peróxido de hidrógeno, en presencia de luz solar se verificó que el método que se llevó a cabo es el foto-Fenton heterogéneo utilizando una concentración inicial de 250 mg/L de ácido tánico y se obtuvieron resultados favorables degradación hasta el 100 % de ácido tánico.

En la Figura 7 se observan los resultados obtenidos después del tratamiento foto-Fenton heterogéneo de soluciones de ácido tánico y muestras de agua residual de la industria fragancias y saborizantes utilizando zeolita modificada con Fe y Al a diferentes temperaturas como catalizador. La concentración inicial de ácido tánico en la muestra fue de 9 mg/L y en solución fue de 54 mg/L.



Comparación de zeolita modificada como catalizador en la degradación de ácido tánico con solución acuosa (verde) y agua residual (rojo) mediante foto-Fenton heterogéneo

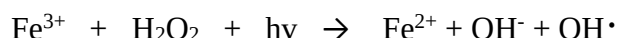
En la figura 8 se observa el porcentaje de degradación de ácido tánico mediante foto-Fenton heterogéneo utilizando zeolita modificada electroquímicamente con Fe y Al a diferentes temperaturas. Las condiciones utilizadas fueron de pH 6, temperatura ambiente, 0.1 g de zeolita modificada y H_2O_2 0.1 mg/L en un volumen total de 10 mL. Los mejores resultados obtenidos fueron con Fe, Al 250 y Fe 550. Los resultados que se muestran en color verde se obtuvieron con una solución de ácido tánico, los de color rojo utilizando una muestra de agua residual proveniente del proceso para la elaboración de fragancias y saborizantes usando solo dos materiales modificados Al 250 y Fe 250. El porcentaje de degradación de ácido tánico para cada material es el siguiente: Al 250 (100%), Al 550 (87%), Fe 250 (76%), Fe 550 (99%), Fe 750 (84%), Fe (100%) y FeAl 250 (68%), FeAl 550 (63%), Al 250 (70%), Fe 250 (52%) y Fe 550 sin radiación (23%).



Porcentaje de degradación de ácido tánico en solución acuosa (verde) y agua residual (rojo) mediante foto-Fenton heterogéneo.

Por otra parte, se llevó a cabo una prueba con la zeolita modificada con Fe a 550 °C en ausencia y presencia de radiación solar, alcanzando un incremento del 76% en la degradación del ácido tánico en presencia de radiación solar, por lo tanto, el efecto de radiación solar en el proceso es significativo.

Reacción foto-Fenton-solar



Reacción fotólisis



Conclusiones preliminares

De acuerdo con las pruebas realizadas con los diferentes materiales modificados electroquímicamente y mismas condiciones, se puede concluir que los materiales con mejores resultados fueron Fe 550, Al 250 y Fe, ya que se degradó el 100% de ácido tánico en solución acuosa, por lo tanto; estos materiales tienen el potencial para lograr un tratamiento efectivo de ácido tánico mediante el proceso de foto-Fenton heterogéneo.

Con base en los resultados obtenidos de los materiales Al 250 y Fe 250 en las pruebas hechas con agua residual industrial, se puede afirmar que no son opciones para remover el ácido tánico, considerando la concentración inicial de 9 mg/L.

Existe la probabilidad de obtener mejores resultados para degradar el ácido tánico en agua residual industrial porque aún se puede experimentar con los materiales Al 550, Fe 550, Fe 750, Fe, FeAl 250, FeAl 550.