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EVALUACIÓN DE TRATAMIENTOS TERCIARIOS PARA LA REUTILIZACIÓN DE AGUA PROVENIENTE DE EFLUENTES INDUSTRIALES

TESIS

QUE PARA OBTENER EL GRADO DE
DOCTOR EN CIENCIAS AMBIENTALES

PRESENTA:

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RESUMEN

La disponibilidad de agua es un problema de nuestra sociedad en regiones de todo el mundo. El uso de este recurso natural provoca un efecto sobre los ecosistemas de donde se extrae y en los ecosistemas donde se utiliza; estos efectos involucran problemas de salud pública, desabasto de agua potable, sobreexplotación de los mantos acuíferos, pérdida de biodiversidad acuática y terrestre, contaminación del aire y suelo, inversión de tecnología y recursos financieros destinados a remediar ríos y lagos.

Las aguas residuales en general pueden ser tratadas eficientemente por plantas de tratamiento biológico o fisicoquímico. Sin embargo, en algunos casos los tratamientos resultan inadecuados para alcanzar la calidad requerida por el uso ulterior del efluente tratado, por lo que se han desarrollado tecnologías avanzadas de tratamiento.

En este trabajo se evaluaron tratamientos terciarios tales como la oxidación con ozono, la electrocoagulación con electrodos de aluminio y la electro-oxidación con electrodos de diamante dopados con boro en aguas residuales industriales de la fabricación del refresco, industria textil y reciclagua para reducir la cantidad de contaminantes e incrementar el volumen de agua residual tratada posibilitando su re-uso y poder hacer frente a la disminución de la disponibilidad actual del agua.

Se empleo ozono para la oxidación de la materia orgánica, dado que tiene un elevado potencial de oxidación (E^o= 2.1 V) capaz de reaccionar con un alto número de moléculas orgánicas e inorgánicas del agua residual tratada ya sea por ataque directo molecular y/o por la descomposición en radicales $HO^{\bullet}$ (E^o= 2.8 V).

Con el proceso de coagulación se eliminó la materia en suspensión del agua residual a través de un proceso físico y químico donde las partículas coloidales, que normalmente tienen carga negativa en la superficie, colisionan con los iones de carga positiva formados por la reacción del coagulante químico con el agua

(policloruro de aluminio – PAC); formando grandes aglomerados que posteriormente sedimentan o pueden ser filtrados.

El proceso de electrocoagulación, cuyo principio es similar al tratamiento físico-químico típico de coagulación, pertenece a los procesos electroquímicos en los que a partir de compuestos procedentes de la disolución de un ánodo, en este caso de aluminio (ánodo de sacrificio), se agrupó la materia coloidal existente en el agua residual, posibilitando su posterior separación, mediante técnicas convencionales.

En el proceso de electro-oxidación, que pertenece a los procesos de oxidación electroquímica mediante electrodos especiales y no sacrificables como los electrodos de diamante dopados con boro (DDB) utilizados, se obtuvieron compuestos capaces de oxidar fuertemente las aguas residuales de los efluentes estudiados.

Los experimentos de oxidación química con ozono acoplado a los procesos de electrocoagulación y electro-oxidación; se realizaron a nivel laboratorio y se consideró el efecto que tienen sobre el agua residual tratada realizando pruebas de DQO, DBO, color, turbiedad, Sólidos totales (ST) y Sólidos Sedimentables Totales (SST).

Dado que los procesos de oxidación avanzada se han desarrollado muy poco en México y en menor cantidad integrados con procesos de electrocoagulación y electro-oxidación para tratar a las aguas residuales industriales, se estableció un nuevo proceso de tratamiento para reducir los contaminantes del agua residual industrial estudiada para su posible reutilización en riego de áreas verdes, sanitarios, en el sistema contra incendios; o bien para fines agrícolas y recarga de acuíferos.

ABSTRACT

The availability of water is a problem in our society in regions around the world. The use of this natural resource has an effect on the ecosystems from which it is extracted and ecosystems where it is used, these effects involve public health problems, lack of supply of drinking water, overexploitation of aquifers, loss of aquatic and terrestrial biodiversity, air and soil pollution, technology investment and financial resources to remediate rivers and lakes.

The wastewater can be treated efficiently by biological or physicochemical treatment plants. However, in some cases the treatments are inadequate to achieve the quality required for further use of the treated effluent, so new treatment technologies have been developed.

In this work terciary treatments were evaluated, such as ozone oxidation, electrocoagulation with aluminum electrodes and the electro-oxidation with boron-doped diamond electrodes in industrial wastewater from the manufacture of soft drinks, textile industry, and Reciclagua to reduce the amount of pollutants and increase the volume of treated wastewater allowing its re-use and facing the current decline in water availability.

Ozone was used for the oxidation of organic matter, since ozone has a high oxidation potential ($E^o = 2.1$ V) capable of reacting with a high number of inorganic and organic molecules of the treated wastewater by either direct molecular attack / o by decomposing into radicals HO • ($E^o = 2.8$ V).

With the coagulation process wastewater suspended matter was removed through a physical and chemical process in which colloidal particles are negatively charged than normal on the surface, ions collide with the positive charge formed by the reaction of chemical coagulant with water (poly aluminum chloride - PAC), forming large agglomerates which then may be sedimented or filtered.

The electrocoagulation process is similar to the typical physicochemical treatment of coagulation, but it is an electrochemical process in which compounds originating from the dissolution of an anode, in this case aluminum (sacrificial anode), agglomerate existing colloidal matter in wastewater, allowing their separation by conventional techniques.

The electro-oxidation process is an electrochemical oxidation process, which uses special electrodes, and not sacrificial electrodes, such as boron-doped diamond (DDB), to obtain strongly oxidizing compounds able to treat wastewater.

Chemical experiments with ozone oxidation coupled to electrocoagulation, electrooxidation and filtration, were conducted at laboratory and evaluated the effect on the treated wastewater measuring COD, BOD, Color, Turbidity, ST and settleable solids.

Since advanced oxidation processes have developed very little in Mexico and even less when coupled to electrocoagulation and electro-oxidation to treat industrial wastewater, this work has the goal of establishing a new treatment process to reduce industrial wastewater pollutants for possible reuse in landscape irrigation, sanitary installations, fire protection systems, agriculture, or aquifer recharge.

CAPÍTULO 1

INTRODUCCIÓN

En los últimos años la contaminación del agua se ha incrementado debido al aumento de las actividades industriales y a la explosión demográfica, llegando a ser un problema muy serio y acentuando la escasez del vital líquido. Por ello, se buscan alternativas tecnológicas adecuadas que sean eficientes y ambientalmente amigables para recuperar su calidad.

Las aguas residuales industriales son tratadas mediante una serie de procesos físicos, químicos y biológicos que tienen como fin eliminar o disminuir la concentración los contaminantes presentes en el efluente; no obstante, debido a la complejidad y variación en sus composiciones estos efluentes son difíciles de tratar con los sistemas biológicos y fisicoquímicos tradicionales.

En el presente trabajo de investigación se evalúa la eficiencia de tratamientos terciarios de aguas residuales industriales aplicados a efluentes de la industria de la fabricación de refresco, textil y Reciclagua con el objetivo de mejorar la calidad del agua residual tratada posibilitando su reutilización. Para lograr este objetivo los tratamientos terciarios acoplados evaluados en este trabajo fueron: oxidación con ozono, electrocoagulación con electrodos de aluminio y electro-oxidación con electrodos de diamante dopados con boro.

En el capítulo 1, se describen la problemática de la contaminación del agua que existe en México y en forma particular en el Estado de México, las características del agua residual de la industria de los efluentes industriales estudiados (fabricación de refresco, textil y Reciclagua) y de los tipos de procesos convencionales existentes para tratarlos, así como de las nuevas tecnologías que incluyen los métodos de oxidación avanzada integrados a los procesos terciarios como son la coagulación, electrocoagulación y electro-oxidación. Además se describen la justificación, hipótesis, objetivos, metodología y las técnicas analíticas empleadas para determinar las eficiencias de reacción que intervienen en los diferentes procesos estudiados propuestos en el protocolo aprobado.

En el capítulo 2, se muestran los resultados obtenidos de la investigación desarrollada de los cuales, el primer artículo fue publicado en la revista indexada: Journal of Environmental Science and Health, Part A, el segundo artículo en: International Journal of Electrochemical Science, el tercer artículo en: Sustainable Environment Research y el cuarto artículo en: Electrochemistry Communications.

En el capítulo 3, se presenta una discusión general de los resultados publicados, destacando los puntos más sobresalientes en cada serie de resultados.

En el capítulo 4, se muestran las conclusiones más contundentes; así mismo las fuentes consultadas.

Finalmente, en la sección de anexos se incluyen las constancias de los trabajos presentados en congresos

Antecedentes

1.1 Contaminación del agua

Las expectativas actuales de consumo, el intenso desarrollo urbano y la creciente industrialización han determinado un uso irracional de los recursos naturales generando, día con día, nuevos problemas ambientales o agravando los ya existentes. Dado su impacto directo en la calidad de vida, el suministro de agua a la población debería ser prioridad de toda actividad humana, pública o privada, pues constituye el elemento básico de subsistencia, de la salud, de la producción de alimentos y de la producción industrial (Ghadouani y Coggins, 2011).

En México la contaminación del agua ha alcanzado elevadas dimensiones que explican el deterioro de la calidad de los cuerpos de agua del país. La poca importancia que se le ha dado a este problema se refleja en el mínimo marco de regulación y su amplio incumplimiento, lo que ha permitido a los agentes contaminadores del agua descargar sus desechos, bajo el supuesto de que la capacidad de asimilación de estos es infinita (Rodríguez y Morales, 2013). Por otro lado, nuestro país se ha desarrollado de manera inversa con la disponibilidad del agua, ya que el 76 % de la población vive donde se localiza tan sólo el 20 % del agua dulce disponible, dando como resultado la sobreexplotación de los acuíferos y el incremento de las cuotas económicas para transferir el agua de una cuenca a otra (CONAGUA. 2013).

En el estado de México, existe la problemática de la sobreexplotación y contaminación de cuerpos de agua natural y mantos freáticos por actividades industriales y agrícolas principalmente. El agua de la Cuenca Lerma enfrenta una grave problemática ambiental local en sobreexplotación y contaminación residual por parte del sector industrial. La industria en esta zona tiene una demanda de agua de 6.1 m^3/s de la cual el 98% es subterránea. Esta zona del Estado de México recibe descargas de agua industrial de empresas de giro químico, metal-mecánico, calzado-curtidora, textil plásticos, farmacéutico, alimentos y automotriz principalmente; además se calcula que el 69% del crecimiento poblacional para el año 2030 ocurrirá en regiones que incluyen al Estado de México, donde la mayoría de sus acuíferos están sobre-explotados (CONAGUA. 2013).

1.2 Agua residual industrial

Las aguas residuales industriales presentan una gran cantidad de contaminantes que tienen una acción muy compleja sobre el medio ambiente, afectando el desarrollo natural de los ecosistemas lo que ha conducido a la implementación de diversos métodos para la remoción de contaminantes presentes (García-Morales *et al.* 2013), sin que se logre, en la mayoría de los casos, una solución adecuada al problema debido a que los contaminantes suelen ser recalcitrantes y no biodegradables, a los altos consumos de reactivos químicos y/o energía necesarios, al cambio de fase del contaminante sin su destrucción completa y a la selectividad por algunos contaminantes, dejando intacta la estructura química de algunos de ellos (Linares-Hernández *et al.* 2010). Estas aguas han sido tradicionalmente tratadas por métodos convencionales. Sin embargo, la efectividad de estos procesos se está viendo seriamente limitada en los últimos años principalmente por restricciones cada vez más estrictas. Estas restricciones son debido al mayor conocimiento del impacto de los contaminantes en el ambiente, la disminución de la disponibilidad de agua, y al aumento de la demanda tanto humana como industrial, lo cual significa mayores caudales de agua residual a tratar (Barrera-Díaz *et al.* 2011).

1.2.1 Agua residual de la industria del refresco

En el proceso de producción de refrescos; los ingredientes se mezclan antes de proceder al proceso de embotellado. Los ingredientes de los refrescos son: el agua obtenida de mantos acuíferos locales, solución de azúcar a una concentración de 60 °Brix (60 g de sacarosa disuelta en 100 g de agua), jarabe concentrado, mezclado con CO_2 o N_2O en la bebida durante el proceso de embotellado (Krones. 2011).

El agua es la principal materia prima para la fabricación de bebidas no alcohólicas, la industria del refresco utiliza 73, 070, 243 m^3 para la elaboración de sus productos de un total de 173, 797, 336 m^3 del agua concesionada a nivel nacional (INEGI. 2011).

De esta cantidad de agua utilizada, 26, 305, 287 m^3 se emplea en el proceso de clarificación de azúcar, enjuague de botellas y en el sistema de limpieza de las líneas y equipo de producción integrado por un enjuague con agua, ácido, sosa, agua caliente y desinfectante en solución.

Las variaciones del proceso de embotellado de refrescos producen producto con los estándares de calidad no requeridos el cual es descargado en el sistema de tratamiento de aguas residuales de la empresa en estudio junto con el agua utilizada en la limpieza de botellas, líneas y equipos de producción.

1.2.2 Agua residual de la industria textil

Hay varias formas en las que los colorantes causan problemas en el agua; dependiendo del tiempo de exposición y la concentración de colorante; los colorantes pueden tener efectos agudos y/o crónicos sobre los organismos expuestos; también pueden disminuir la población de peces y algas debido a su alto contenido de nitrógeno y agotar el contenido de oxígeno disuelto en el agua (Trujillo-Reyes *et al.* 2010). La producción anual de colorantes es de alrededor de $7x10^5$ toneladas. La industria textil utiliza cerca de 10,000 diferentes tintes, entre ellos el azul índigo que es importante en el teñido de pantalones de mezclilla (García-Morales *et al.* 2013). Se estima que del 10 al 15% de los colorantes se pierden en el efluente durante el proceso de teñido de telas. Además, algunos colorantes, sus precursores y algunos de subproductos de reacción son cancerígenos, por lo que el tratamiento de sus efluentes es importante para la protección de los cuerpos de agua (Gutiérrez-Segura *et al.* 2009). Debido a que una proporción de los colorantes no son directamente tóxicos para los organismos vivos, pero la fuerte coloración que generan a los medios de descarga puede llegar a suprimir los procesos fotosintéticos, por lo que su presencia debe ser controlada (Trujillo-Reyes *et al.* 2010).

1.2.3 Agua residual de Reciclagua

Reciclagua es una empresa ubicada en el Parque Industrial Lerma, Municipio de Lerma, Estado de México, que trata el agua residual industrial de la cuenca alta de Lerma y Valle de Toluca de un total de 141 empresas que descargan sus efluentes en el río Lerma. La cantidad de agua residual industrial que capta la planta es de 35,000 m^3/día (400L/s) de los cuales el 65% proviene del colector Toluca, 17% del Parque Industrial Lerma y 18% del colector Norte del Valle de Toluca. El agua residual que se descarga al río Lerma y que recibe Reciclagua, tiene un nivel de DBO_5 de 1,495 mg/L. Los tratamientos que aplica son: Tratamiento primario (separación física de materiales sólidos); tratamiento secundario (tratamiento biológico utilizando lodos activados) y tratamiento terciario (cloración) (García-Morales *et al.* 2013).

1.3 Métodos convencionales de tratamiento de aguas residuales industriales

Los contaminantes del agua se clasifican en tres categorías:1) Físicos, 2) Químicos y 3) Biológicos. Los contaminantes químicos comprenden sustancias químicas orgánicas e inorgánicas. El aspecto fundamental resultante de la contaminación por compuestos orgánicos es la disminución de oxígeno como resultante de la utilización del existente en el proceso de degradación biológica de dichos compuestos, esta disminución de oxígeno disuelto lleva a perturbaciones indeseables en el medio y de la biota en ella asentada (Hashem *et al.* 2013). En el caso de la contaminación derivada de la presencia de compuestos inorgánicos su impacto es su posible efecto tóxico, más que la disminución en oxígeno. También hay casos en los cuales los compuestos inorgánicos presentan una demanda de oxígeno, contribuyendo en su decremento. Los sulfitos, nitritos y amonio, por ejemplo, toman oxígeno para transformarse a sulfatos y nitratos. Los iones de metales pesados, tóxicos para los seres humanos, son importantes contaminantes de este grupo, su presencia, aún en pequeñas cantidades puede causar serios problemas.

Alteraciones a las carácterísticas físicas incluyen cambios térmicos (contaminación térmica). En el caso de efluentes de plantas industriales, relativamente calientes después de haber sido utilizadas en los intercambiadores (enfriadores), el color, turbidez (originada por la descarga de efluentes que contienen sólidos en suspensión), espumas, detergentes y/o especies radiactivas.

Los contaminantes biológicos son los responsables de la transmisión de enfermedades en el agua de abastecimiento. Algunas de las enfermedades que se transmiten por contaminación biológica son el cólera y la tifoidea (Ramalho. 2003).

Dependiendo de calidad del agua, de requisitos finales y de aspectos económicos, algunos procesos son más convenientes que otros para el tratamiento de aguas residuales. La tabla 1 presenta una clasificación convencional de los procesos de tratamiento de aguas residual.

Tabla 1. Tipos de tratamiento de aguas residuales (Ramalho. 2003).

Tratamiento	**Proceso**	
Primario	- Cribado - Sedimentación - Flotación	- Separación de aceites - Homogeneización - Neutralización
Secundario	- Lodos activados - Aireación prolongada - Estabilización por contacto - Lagunaje con aeración.	- Estabilización por lagunaje -Filtros biológicos (percoladores) - Discos biológicos - Tratamientos anaerobios
Terciario o avanzado	- Microtamizado - Filtración (lecho de arena, antracita, diatomeas) - Precipitación y coagulación. - Adsorción (carbón activado) - Intercambio iónico	- Ósmosis inversa - Electrodialisis -Cloración - Ozonización - Procesos de reducción de nutrientes

El tratamiento primario se emplea para la eliminación de los sólidos en suspensión y los materiales flotantes, impuesta por los límites; tanto de descarga al medio receptor como para poder llevar los efluentes a un tratamiento secundario. Los procesos de tratamiento primario convencionales están integrados por cribado, sedimentación, flotación, separación de aceites, homogenización y neutralización (Ramalho. 2003)**.**

El tratamiento secundario comprende tratamientos biológicos convencionales. Los objetivos del tratamiento biológico son la reducción de la materia orgánica y la reducción de compuestos inorgánicos. El tratamiento biológico comprende: 1) La conversión de la materia orgánica carbonosa disuelta y en estado coloidal en diferentes gases y tejidos celulares, 2) La formación de lodos biológicos de material celular y de los coloides orgánicos presentes en las aguas residuales, y 3) La subsiguiente remoción de dichos lodos por medio de sedimentación por gravedad (Tejocote-Pérez *et al.* 2010).

En cuanto al tratamiento terciario su objetivo fundamental es la eliminación de constituyentes químicos que no se quitan con los tratamientos biológicos convencionales (Ramalho. 2003)**.**

Las tecnologías convencionales de tratamiento de aguas residuales basadas en la transferencia de la fase simplemente concentran los contaminantes, los cuales tienen que ser eliminados posteriormente. Un proceso innovador para el control de la contaminación en aguas residuales es proporcionado por un proceso integrado, donde se combinan tratamientos biológicos y fisicoquímicos (Durán *et al.* 2009). Un ejemplo típico de un proceso integrado es la combinación de la oxidación química con ozono y el tratamiento de lodos activados, en donde la oxidación química se utiliza para proporcionar la transformación de los contaminantes a otros intermedios más fácilmente biodegradables (Khadhraoui et al. 2009).

1.3.1 Coagulación

En el tratamiento del agua, el objetivo de la coagulación es la eliminación de materia en suspensión. La coagulación es un proceso físico y químico donde las partículas coloidales, que normales tienen carga negativa en la superficie, chocan con los iones de carga positiva formado por la reacción de coagulantes químicos (Katal y Pahlavanzadeh 2011) como el policloruro de aluminio (PAC) con el agua. El proceso de coagulación incluye la promoción de la interacción de partículas para formar grandes aglomerados; lo que constituye un componente esencial en los sistemas de tratamiento de agua integrado con los procesos de sedimentación, filtración, y desinfección para clarificar el agua e inactivar los contaminantes microbiológicos (virus, bacterias, quistes y protozoos patógenos). Aunque la remoción de contaminantes microbiológicos sigue siendo la principal razón para usar el proceso de coagulación, un nuevo objetivo; la remoción de materia orgánica natural (NOM) para reducir la formación de subproductos por desinfección está creciendo en importancia (Zhu *et al.* 2011, Hanay y Hasar 2011). La coagulación normalmente se logra en tres etapas como sigue:

A. Una primera mezcla turbulenta del coagulante con el agua residual. Esto proporciona el contacto entre las partículas que causan la turbidez y el coagulante, con lo que se da la neutralización de cargas.
B. Un período de agitación lenta, lo que permite que los aglomerados (el "floc") crezcan más y así atrapar más materia en suspensión.
C. Un nuevo período de poca o nula agitación para permitir la sedimentación o flotación de los aglomerados (García-Morales *et al.* 2013).

1.3.2 Procesos de oxidación avanzada

Los procesos de oxidación avanzada (POA) han sido considerado como procesos de un gran potencial para aplicarse en los procesos de plantas de agua potable y para tratamiento de aguas residuales (Wang *et al*. 2009). Los procesos de oxidación avanzada implican la generación de radicales que inician la oxidación de compuestos orgánicos. En soluciones acuosas el radical hidroxilo ($OH^{\bullet}$), de elevado potencial de oxidación (E^o=2.8 V) es la especie principal que inicia la mayoría de los POA (García-Morales *et al.* 2013, Khataee *et al*. 2009). Este radical hidroxilo puede ser generado por medios fotoquímicos (inducida por luz solar) o por otras formas de energía, y posee alta efectividad para la oxidación de materia orgánica (Campos *et al.* 2009, Rivas *et al.* 2009). Algunos procesos de oxidación avanzado como el ozono, peróxido de hidrógeno, ozono-radiación UV, fotocatálisis heterogénea, proceso Fenton, proceso Foto-Fenton, recurren además a reductores químicos que permiten realizar transformaciones en contaminantes tóxicos poco susceptibles a la oxidación, como son los iones metálicos o compuestos halogenados (Colindres. 2006). La oxidación química se considera como tecnología completa para la degradación de varios compuestos orgánicos, siendo uno de los pocos procesos que pueden destruir compuestos orgánicos en sitio. Además, la oxidación química puede ser más beneficiosa que otras tecnologías disponibles del tratamiento, que transfieren el problema a otro receptor (aire y/o suelo) (Klamerth *et al.* 2009, Santos et al. 2009)**.**

Los POA logran en diferente medida la destrucción del color, el aumento de la demanda biológica de oxígeno (DBO), la reducción de la demanda química de oxígeno (DQO) y del carbono orgánico total (COT), permiten mineralizar los contaminantes orgánicos, al realizarse reacciones hasta convertirlos en CO_2 y H_2O y reducen o eliminan los problemas de sabor y olor en las aguas residuales (Durán *et al.* 2009).

El ozono es considerado como una interesante alternativa para la desinfección y oxidación de varios contaminantes orgánicos e inorgánicos del agua residual. Además; el ozono se puede utilizar en combinación con otras tecnologías de tratamiento en las complejas mezclas de las aguas residuales (Lovato *et al.* 2009, Khadhraoui *et al.* 2009). El ozono empleado como un pre-tratamiento mejora la biodegradabilidad de las aguas residuales (Khadhraoui *et al.* 2009). La aplicación en un post-tratamiento se usa a menudo como un proceso de desinfección y como un método de tratamiento capaz de degradar las moléculas refractarias las cuales pueden ser más fácilmente degradadas por métodos biológicos (Petala *et al*. 2008). Goel *et al.* 2003 reportaron un incremento en la eficiencia de remoción de sólidos de 25 - 35% a un 50 – 59% llevando a cabo una pre-ozonación de 0.05 g O_3/g a los sólidos suspendidos totales durante la digestión anaerobia; también se reportó un resultado similar cuando el proceso de ozonación fue usado como post-tratamiento al digestor anaerobio.

El ozono puede reaccionar por un mecanismo directo involucrando al ozono molecular o por un mecanismo indirecto con la participación de diferentes productos intermedios altamente reactivos que se derivan de su descomposición (Lovato *et al*. 2009, Rivas *et al*. 2009).

1.3.3 Electrocoagulación

La electrocoagulación es un proceso que aplica los principios de la coagulación-floculación en un reactor electrolítico. Es un recipiente dotado de una fuente de corriente y varios electrodos de aluminio o hierro encargados de aportar los iones desestabilizadores los cuales forman especies coagulantes e hidróxidos metálicos que reemplazan las funciones de los compuestos químicos que se utilizan en el tratamiento convencional, durante el proceso desestabilizan las suspensiones y emulsiones provocando su floculación; de igual manera ocurre una disolución anódica donde se liberan elementos que pueden reaccionar con algunos contaminantes en solución precipitándolos. En los electrodos se generan micro-burbujas de hidrógeno y oxígeno que chocan y se adhieren a los floculos arrastrándolos a la superficie del líquido donde se forma una espuma que puede ser removida mecánicamente. También, las burbujas formadas dentro del reactor ayudan a que el aceite y las grasas floten. La alta carga de cationes generados desestabiliza las partículas coloidales, por la formación de complejos polihidróxidos polivalentes. Estos complejos tienen altas propiedades de adsorción, forman agregados con las partículas contaminantes, de ahí la razón por la cual está siendo utilizada esta técnica, pero dadas estas características también hay que analizar las condiciones de pH, tipo y concentración de contaminante, estabilidad del floculo para optimizar la remoción de sustancias contaminantes presentes en la solución (Campos. 2006)

En el proceso de electrocoagulación con electrodos de aluminio hay generación de coagulantes in situ por la disolución de iones de aluminio de los electrodos. La generación de iones metálicos tienen lugar en el ánodo y en el cátodo hay liberación de burbujas de hidrógeno gaseoso las cuales ayudan a la flotación de las partículas floculadas, las mismas que serán retiradas posteriormente (Linares-Hernández *et al.* 2010). Durante la formación de los hidróxidos metálicos, la generación de los iones está acompañada de la concentración electroforética de partículas alrededor del electrodo, las cuales neutralizan su carga coagulando. La corriente aplicada obliga a los iones OH- a migrar hacia el ánodo, por lo que el pH en la capa límite es más alto que en el resto de la solución, lo que favorece la formación de hidróxidos del metal del electrodo. El hidróxido formado remueve los contaminantes presentes en el agua por complejación o atracción electrostática. Adicionalmente, en la proximidad de los electrodos el aumento de la concentración de los hidróxidos favorece el incremento del valor del pH lo que conlleva la formación de carbonatos que propician junto con los sulfatos la precipitación del calcio y el magnesio, originando así un ablandamiento parcial del agua. Los mecanismos de remoción en electrocoagulación incluyen oxidación, reducción, coagulación, absorción, adsorción, precipitación y flotación. Los iones Al^{3+} son coagulantes muy eficientes para la floculación de partículas, por lo que en EC son frecuentemente utilizados electrodos de aluminio. Los iones de aluminio hidrolizado pueden formar largas cadenas de OH-Al-O-Al-OH las cuales pueden adsorber químicamente una gran cantidad de contaminantes (Piña-Soberanis *et al.* 2011).

Las reacciones químicas que se llevan a cabo

Anodo:

$$Al_{(s)} \rightarrow Al^{3+}_{(aq)} + 3e^{-} \qquad (1)$$

Catodo:

$3H_2O + 3e^- \rightarrow 3/2H_{2(g)} + 3OH^-_{(aq)}$ (2)

Los iones de Al^{3+} y OH^- generados por las reacciones en los electrodos (1) y (2) reaccionan para formar varias especies monométricas y polimétricas las cuales se transforman finalmente en $Al(OH)_{3(s)}$ de acuerdo a la siguiente compleja cinética de precipitación.

$Al^{3+}_{(aq)} + 3H_2O \rightarrow Al(OH)_{3(s)} + 3H^+_{(aq)}$ (3)

(García-Morales *et al.* 2013)

La electrocoagulación es utilizada en la remoción de contaminantes de muy diversas aguas residuales, tales como las de la industria de galvanoplastia, electro-plateado metálico, fábricas de envasados, industria del papel (desperdicios de molinos de papel), peleterías, molinos de acero, efluentes con contenido de cromo, plomo o mercurio y efluentes con contenido de aceites como los generados por talleres de maquinaria, refinerías, talleres de reparación de autos, transporte, almacenamiento y distribución de aceites, efluentes de la industria alimentaria, lavanderías e industria textil, y finalmente ha sido utilizada en la remoción de los contaminantes del agua para consumo humano y residuales domésticas (Secula et al. 2011)

1.3.4 Electrooxidación

Dentro de los métodos electroquímicos se encuentra la oxidación anódica para la electrogeneración de los radicales OH• producidos por la oxidación del agua en el ánodo empleando como ánodos Pt, PbO_2, TiO_2, SnO_2, y recientemente los electrodos de diamante dopados con boro (DDB) (Tissot *et al.* 2012). Los tratamientos electroquímicos son métodos utilizados para remover tanto contaminantes orgánicos, como inorgánicos de aguas residuales de diferente origen, en estos procesos los contaminantes se destruyen por la oxidación anódica directa (OAD) o indirecta (OAI) del proceso (Michels *et al.* 2010). La OAD empleando DDB se ha aplicado en diferentes tipos de agua residual, por ejemplo en la oxidación electroquímica de un agua residual industrial que contiene cetonas y alcoholes y una alta concentración de compuestos aromáticos logrando la mineralización completa de los contaminantes (Cruz-González et al. 2012), disminución del color índigo en un 80-90% al utilizar DDB, en la remoción de color y DQO de aguas residuales que contienen azul ácido 22 empleando DDB con una eficiencia del 97%, en la degradación de un agua sintética de curtiduría libre de cloruros, en la mineralización completa del ácido 3,4,5-trihidroxibenzoico y de otros compuestos orgánicos refractarios (Linares-Hernández *et al.* 2011)

El fundamento básico de los procesos de electro-oxidación es la oxidación total (mineralización) o parcial (conversión de la materia orgánica a compuestos más sencillo más fácilmente degradables y menos contaminantes) de la materia orgánica utilizando la corriente eléctrica (Ramírez *et al.* 2013). Estos procesos están íntimamente relacionados con procesos anódicos. La oxidación se divide en dos:

A) Directos. En este caso el contaminante es oxidado directamente en la superficie del ánodo mediante la generación de oxígeno activo fisisorbido en la superficie del ánodo (radicales hidroxilo OH· adsorbidos en la superficie del ánodo) u oxígeno activo quimisorbido en la superficie del ánodo (oxígeno en la red del óxido de metal del ánodo). El primero de estos procesos, oxígeno activo fisisorbido produce la combustión completa de los compuestos orgánicos, mientras que el oxígeno activo quimisorbido produce una oxidación parcial de los compuestos orgánicos.

B) Indirectos. La oxidación no ocurre en la superficie del ánodo, en estos caso en el ánodo se generan especies oxidantes como peróxido de hidrógeno, ozono o cloro, proveniente de la oxidación de los cloruros presentes en el agua, que son liberados al agua y son éstos los que realmente oxidan a la materia orgánica presente en el agua (Haidar *et al.* 2013).

En el caso de reacciones directas el principal inconveniente viene dado por la reacción de oxidación de agua para generar oxígeno ya que esta reacción tiene lugar sobre el ánodo, teniendo en cuenta que el agua es el disolvente y está en mayor concentración que el contaminante esta reacción se vería favorecida lo que ralentizaría o evitaría la reacción deseada de oxidación de materia orgánica, disminuyendo la eficiencia de la corriente empleada. Esto se puede evitar parcialmente usando ánodos con materiales con un alto sobrepotencial de oxígeno, los cuales necesitan un mayor potencial eléctrico para exceder la energía de activación para la producción de oxígeno molecular. Los materiales más estudiados han sido Pt (1,3 V potencial de formación de oxígeno), PbO_2 (1,9 V), SnO_2 (1,9 V), IrO_2 (1,6 V) y últimamente electrodos de capas de diamante dopado con boro (BDD) sobre distintos materiales conductores como silicio, niobio o titanio donde dependiendo del espesor de la capa de BDD y la cantidad de boro usado como dopante se alcanzan valores de hasta 2,8 V (Brinzila *et al.* 2012).

1.4 Repurificación y reutilización de efluentes

Existe un amplio rango de opciones para la reutilización del agua. Las formas más comunes de reutilización; son la irrigación agrícola y ornamental.

a) Irrigación agrícola. La irrigación de cultivos es uno de los tipos más antiguos y comunes de reutilización de efluentes. Los cultivos irrigados incluyen árboles, pastos maíz, alfalfa y otros cultivos alimenticios, forrajes y cultivos de fibra. Los cultivos alimenticios también están siendo irrigados con efluentes de tratamientos terciarios desinfectados.

b) Irrigación ornamental. Incluye: Parques, jardines, campos de golf, zonas verdes alrededor de centros comerciales, residencias e industrias.

c) Reutilización industrial. La industria ha hecho uso del agua reciclada principalmente para procesos de enfriamiento, procesamiento del agua para alimentación de calderas, el enfriamiento del agua para torres de enfriamiento e irrigación y mantenimiento de jardines.

d) Recarga del agua subterránea. Ésta provee una pérdida de identidad entre el agua reciclada y el agua subterránea. Esta pérdida de identidad tiene un impacto psicológico positivo cuando se plantea la reutilización. Las restricciones y la poca voluntad de hacer uso del agua reciclada puede ser superada por la recarga del agua subterránea y su subsecuente recuperación. Algunos de los propósitos para la recarga del agua subterránea son:

- Establecimiento de barreras contra la intrusión de aguas marinas
- Provisión para futuros tratamientos y reutilización
- Provisión para almacenamiento subterráneo
- Aumento de acuíferos potables y no potables.
- Control o prevención de asentamientos del suelo.

La recarga de agua subterránea puede estar acompañada tanto de riego superficial como de inyección (Crites y Tchobanoglous. 2000).

Cada uno de los tratamientos propuestos anteriormente van a influir en el tratamiento aumentando la eficiencia de remoción de contaminantes dado que el ozono tiene un elevado potencial de oxidación (E^o= 2.1 V) capaz de reaccionar con un alto número de moléculas orgánicas e inorgánicas del agua residual tratada ya sea por ataque directo molecular y/o por la descomposición en radicales HO• (E^o= 2.8 V) (Lovato *et al.* 2009, Khataee *et al.* 2009). Con el proceso de electrocoagulación se eliminará la materia en suspensión del agua residual a través de un proceso fisicoquímico formando grandes aglomerados que posteriormente se filtrarán (Zhou *et al.* 2008).

Con el proceso de electro-oxidación con electrodos de diamante dopados con boro (DDB) el proceso será capaz de oxidar los contaminantes de las aguas residuales en estudio (Ramírez *et al.* 2013). Debido a la gran cantidad de agua residual generada en el proceso de la elaboración del refresco se consideró importante encontrar el tren de tratamiento adecuado para esta agua posibilitando su re-uso para fines agrícolas y recarga de acuíferos (NOM-001-ECOL-1996).

Los métodos de oxidación avanzada se han desarrollado muy poco en México y en menor cantidad en forma integrada con procesos terciarios para tratar a las aguas residuales industriales, por lo que se pretende establecer un nuevo tren de tratamiento para reducir la carga de materia orgánica en algunos efluentes industriales.

1.5 Justificación

La poca capacidad y eficiencia de las plantas tratadoras de aguas residuales industriales y municipales son un factor importante en el aumento de la contaminación del agua. En el país las plantas del total de aguas residuales municipales tratan únicamente el 35%, en tanto que de las aguas residuales industriales, el porcentaje de tratamiento es sólo del 18%. Por otro lado, el crecimiento de la densidad poblacional contribuye también en el aumento de la contaminación del agua. Se calcula que en el año 2030 el 69% del crecimiento poblacional ocurrirá en el Estado de México en el cual hay déficit en algunos de sus mantos freáticos (46.401765, 43.946817 y 40.493762 millones de metros cúbicos en el valle de Toluca, Texcoco y Cuautitlán respectivamente (CONAGUA. 2013).

Con el fin de hacer frente a la disminución de la disponibilidad del agua, es necesario realizar acciones para reducir su demanda y contaminación como incrementar significativamente los volúmenes de agua residual tratada y su re-uso, considerar nuevas tecnologías, nuevos procesos o modificar los ya existentes (Khadhraoui *et al.* 2009). Entre estas nuevas tecnologías de tratamiento de aguas residuales industriales se pretende utilizar Procesos de Oxidación Avanzada integrados con procesos de electrocoagulación y electro-oxidación; dado que preliminarmente con el proceso de ozonación–coagulación se obtuvieron buenos resultados en el agua residual del proceso de fabricación de refresco disminuyendo considerablemente la DBO, DQO y SST (García-Morales *et al.* 2012).

1.6 Hipótesis

Si se utiliza la capacidad de oxidación del ozono acoplado a los procesos terciarios de coagulación, electrocoagulación y electro-oxidación se removerán en mayor proporción los contaminantes del agua residual tratada en relación con los tratamientos no acoplados posibilitando su reutilización

1.7 Objetivo general

Disminuir los contaminantes del agua residual industrial de los procesos de la fabricación de refrescos, del teñido de la mezclilla y reciclagua por medio de la implementación y desarrollo de un sistema acoplado de oxidación avanzada con procesos terciarios.

1.7.1 Objetivos específicos

1. Caracterizar las propiedades fisicoquímicas del agua residual industrial antes y después de los tratamientos.

2. Determinar las condiciones experimentales óptimas para el tratamiento de agua residual en el proceso de ozonación (pH, concentración de ozono y tiempo de contacto), en el proceso de electrocoagulación y electro-oxidación (densidad de corriente, tiempo de contacto, pH).

3. Evaluar la eficiencia del proceso integrado
   ozono – coagulación - electrocoagulación – electro-oxidación

1.8 Material y métodos

De acuerdo a la calidad del agua del efluente industrial se realizaron pruebas funcionales implementando el proceso ozono – electrocoagulación – electro-oxidación; se realizaron experimentos a diferentes tiempos de exposición con el tren de tratamiento propuesto; así mismo se determinaron los parámetros óptimos de funcionamiento de los procesos en función del porcentaje de remoción de

DQO, DBO, nitrógeno total, fósforo total, color, turbiedad, SST y sólidos sedimentables.

Con el objetivo de disminuir el contenido de contaminantes del agua residual proveniente de la industria de la fabricación del refresco, industria textil y reciclagua se utilizó la metodología que se muestra en las figuras 1, 2 y 3 respectivamente. Al agua residual industrial del proceso de fabricación de refrescos se le aplicó el proceso de oxidación avanzada con ozono y coagulación, A la muestra en estudio de la industria textil se le aplicaron los procesos de oxidación avanzada con ozono y electrocoagulación y finalmente a la muestra de agua residual de reciclagua se le aplicaron los procesos de oxidación avanzada con ozono y electro-oxidación.

Las figuras 1, 2 y 3 muestran las metodologías usadas para cada una de las aguas residuales tratadas por lo que el diagrama es sustituido por estas figuras.

Figura 1. Diagrama de la metodología usado para tratar el agua residual de la industria de fabricación de refresco

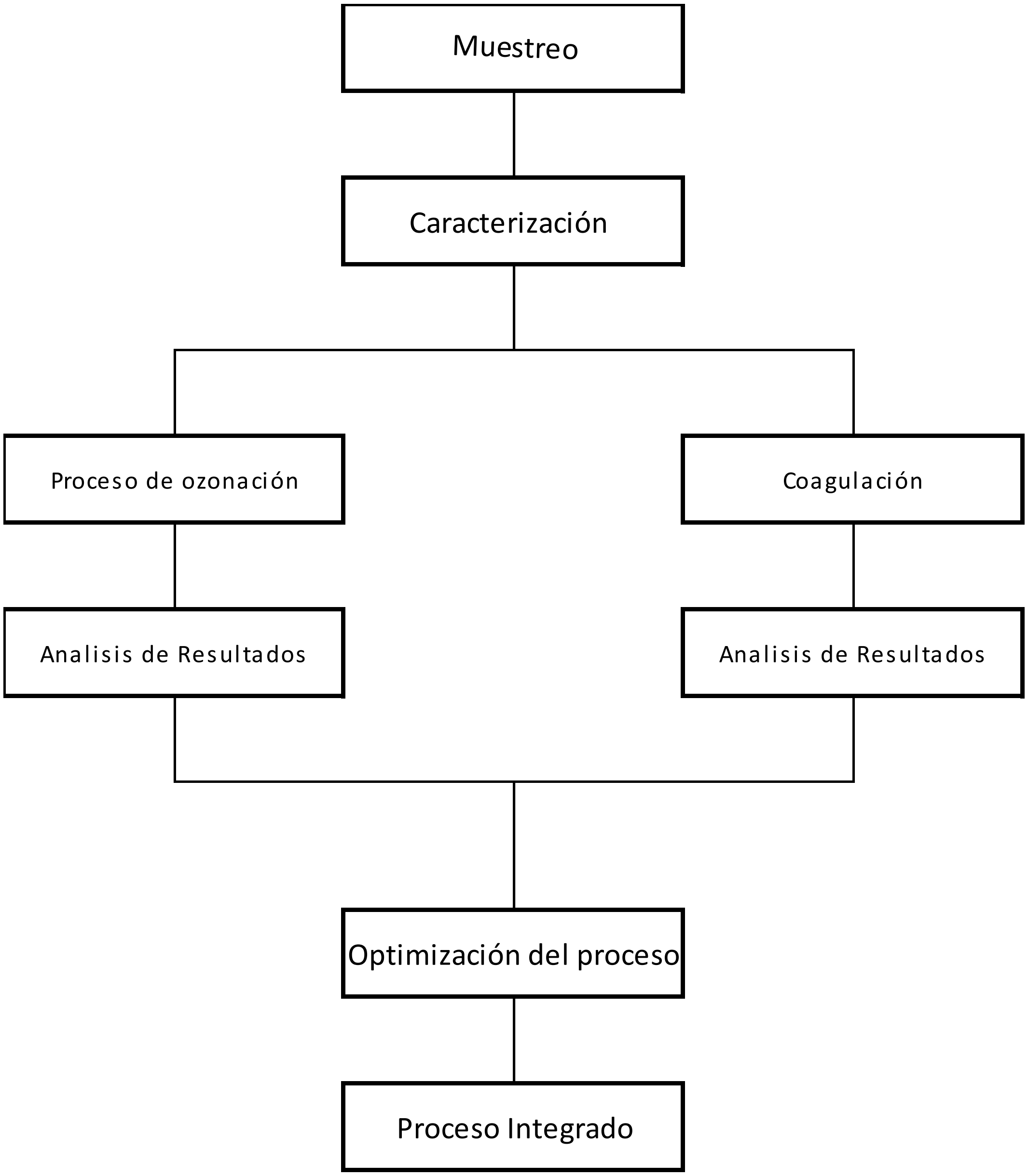


Figura 2. Diagrama de la metodología usado para tratar el agua residual de la industria textil

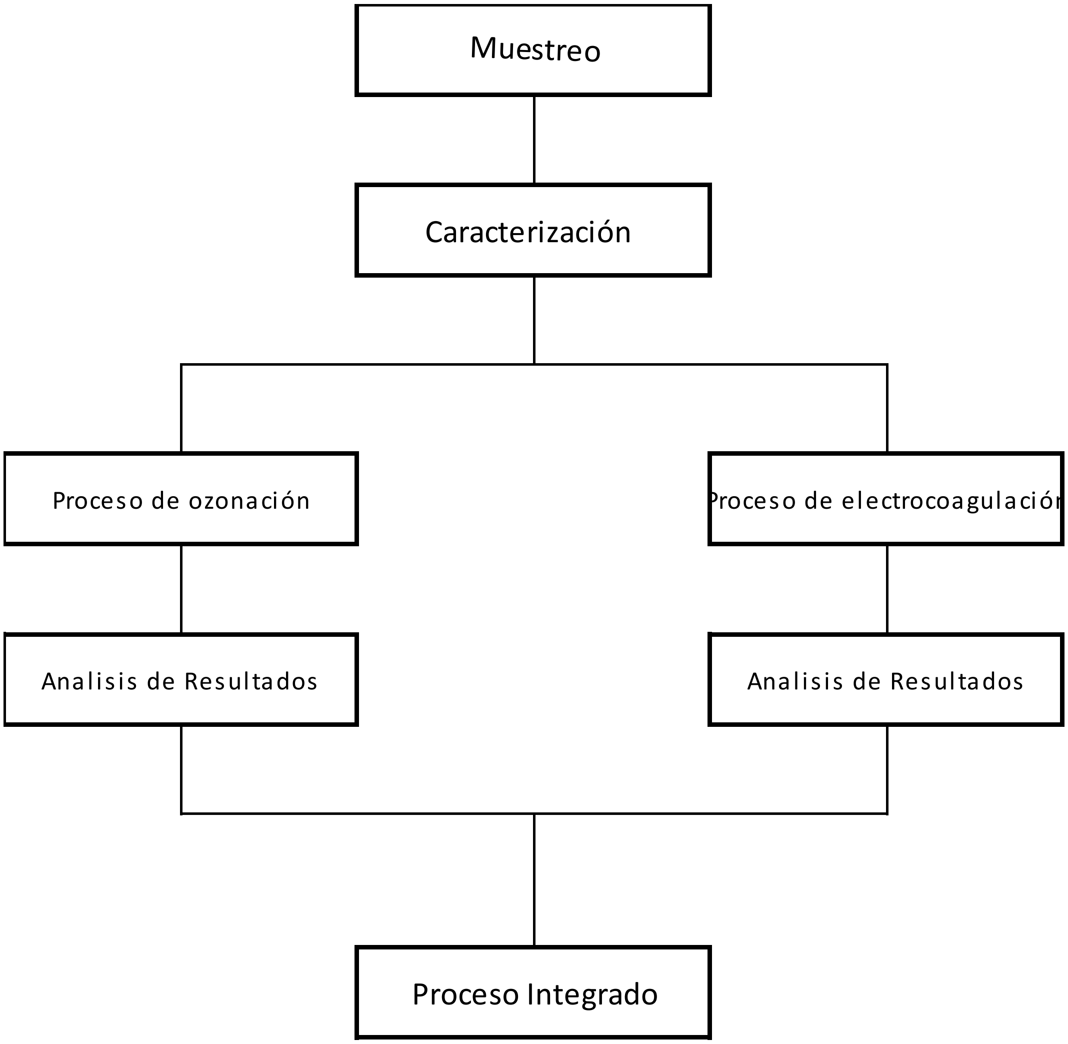
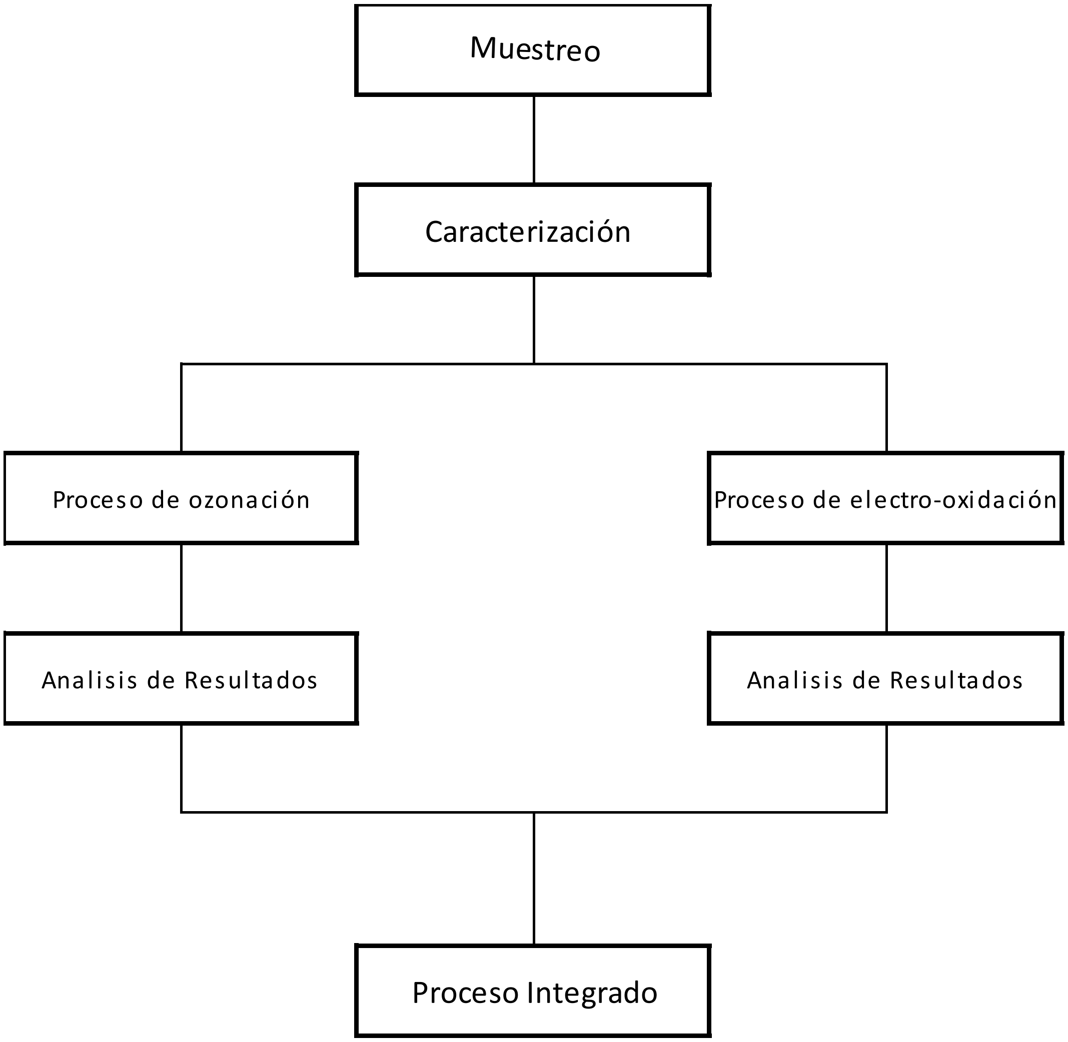


Figura 3. Diagrama de la metodología usado para tratar el agua residual de reciclagua.



1.8.1 Muestreo

El tipo de muestreo fue muestras compuestas (NMX-AA-030-SCFI-2001). Las muestras se tomaron del efluente acorde con métodos normalizados para la examinación de agua y efluentes (APHA/AWWA/WPCF. 1989). Los métodos y normas utilizados para caracterizar el agua residual cruda y tratada en los análisis respectivos de cada muestra se resumen en la tabla 2.

Tabla 2. Resumen de los métodos analíticos empleados

Parámetro	**Método**	**Procedimiento**
DQO	NMX-AA-030-SCFI-2001	Método reflujo cerrado. Método espectrofotométrico
DBO_5	NMX-AA-028-SCFI-2001	Oxígeno que requiere una población microbiana heterogénea para oxidar la materia orgánica de una muestra de agua en un periodo de 5 días
Nitrógeno Total	NMX-AA-026-SCFI-2001	Método Kjeldahl
Fósforo Total	NMX-AA-029-SCFI-2001	Método ácido vanadomolibdofosfórico
Color	Método Normalizado 2120 C	Método espectrofotométrico
Turbidez	Método Normalizado 2130 B	Método Nefelométrico
pH	Método Normalizado 4500-H^+B Potenciométrico	Potenciométrico
Temperatura	NMX-AA-007-SCFI-2000	Físico
SST	NMX-AA-034-SCFI-2001	Gravimétrico
Sólidos Sedimentables	NMX-AA-004-SCFI-2000	Volumétrico
Grasas y Aceites	NMX-AA-005-SCFI-2000	Extracción Solhlet
Coniformes Totales	NOM-112-SSA1-1994	Número más probable

1.8.2 Reactor de ozono

Los experimentos de oxidación avanzada fueron realizados con ozono en un reactor escala laboratorio usando una columna de 60 cm acrílico con 20 cm de diámetro interno. El reactor fue tipo batch utilizando 2.5 L de muestra de agua residual; el reactor tiene una entrada en la parte inferior por donde se inyecta la mezcla gaseosa aire-O_3, esta mezcla asciende pasando a través de un difusor de piedra que distribuye de manera uniforme al ozono en la fase liquida asegurando que las burbujas sean lo más pequeñas posibles para conseguir una mayor transferencia de masa. El reactor también tiene una salida en la parte superior que conduce el exceso de ozono a una trampa de vidrio pirex de 400 mL en la cual se colocó 250 mL de yoduro de potasio 0.1 M para atrapar el ozono residual.

Figura 4. Reactor de ozono.

1.8.3 Producción de ozono

El ozono fue generado a partir de aire utilizando un generador tipo corona de descarga marca Pacific Ozone Technology modelo LAB21 regulando el flujo de aire a 8 SCFH y un porcentaje de generación de ozono en la salida del 90 %, señal enviada al generador de ozono de 3.8 V y presión del reactor 8-12 psi; el equipo provee 5.24 g/h de ozono.

Figura 5. Generador de ozono Pacific Ozone Technology LAB21.

1.8.4 Proceso de electrocoagulación

Laminas rectangulares de aluminio se usaron en el ánodo y en el cátodo en el proceso de electrocoagulación. El área activa de los electrodos es de 343 cm^2 y la relación área volumen es de 0.137 cm^{-1}. Se aplicó una corriente de 0.1 A mediante una fuente de poder obteniendo 0.292 $mAcm^{-2}$ de densidad de corriente, la cual se mantuvo constante durante todo el experimento. La electrocoagulación se desarrollo sin la adición de electrolito soporte.

Figura 6. Electrodos de aluminio.

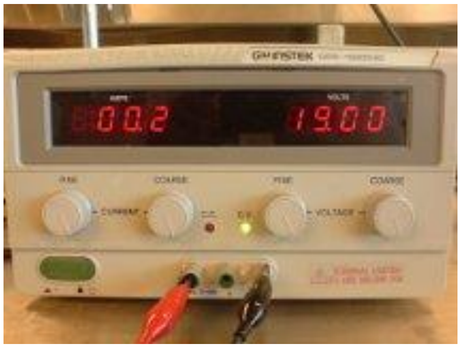


Figura 7. Fuente de poder GW-1820 HD ISTEK GPR.

1.8.5 Proceso de electro-oxidación

El proceso de electro-oxidación se llevó a cabo en un reactor cilíndrico. El reactor contiene un par de electrodos de DDB, cada electrodo mide 20.0 cm de largo y 2.5 cm de ancho obteniendo un área de 50 cm^2. Se trataron 0.7 L de agua residual en cada corrida en forma batch. Se aplicó una corriente directa con una fuente de poder correspondiendo a 0.5 1.0 y 1.5 A correspondiendo a 10, 20 y 30 mA/cm^2 de densidad de corriente.

Figura 8. Electrodos de diamante dopados con boro.

CAPÍTULO 2

RESULTADOS

2.1 Artículo 1 (Publicado)

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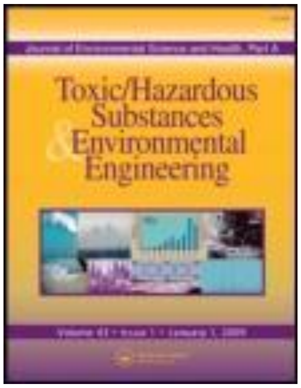

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Treatment of soft drink process wastewater by ozonation, ozonation-H_2O_2 and ozonation-coagulation processes

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In this research, we studied the treatment of wastewater from the soft drink process using oxidation with ozone. A scheme composed of sequential ozonation-peroxide, ozonation-coagulation and coagulation-ozonation treatments to reduce the organic matter from the soft drink process was also used. The samples were taken from the conventional activated sludge treatment of the soft drink process, and the experiments using chemical oxidation with ozone were performed in a laboratory using a reactor through a porous plate glass diffuser with air as a feedstock for the generation of ozone. Once the sample was ozonated, the treatments were evaluated by considering the contact time, leading to greater efficiency in removing colour, turbidity and chemical oxygen demand (COD). The effect of ozonation and coagulant coupled with treatment efficiency was assessed under optimal conditions, and substantial colour and turbidity removal were found (90.52% and 93.33%, respectively). This was accompanied by a 16.78% reduction in COD (initial COD was 3410 mg/L). The absorbance spectra of the oxidised products were compared using UV-VIS spectroscopy to indicate the level of oxidation of the wastewater. We also determined the kinetics of decolouration and the removal of turbidity with the best treatment. The same treatment was applied to the sample taken from the final effluent of the activated sludge system, and a COD removal efficiency of 100% during the first minute of the reaction with ozone was achieved. As a general conclusion, we believe that the coagulant polyaluminum chloride - ozone (PAC- ozone) treatment of wastewater from the manufacturing of soft drinks is the most efficient for removing turbidity and colour and represents an advantageous option to remove these contaminants because their removal was performed in minutes compared to the duration of traditional physical, chemical and biological processes that require hours or days.

Keywords: Ozone, advanced oxidation processes, ozone-PAC, wastewater soft drink treatment.

Introduction

In the soft drink production process, the ingredients are mixed before filling. The ingredients for soft drinks are water obtained from the local water utility, sugar solution (60°Brix) and concentrated syrup; they are blended with CO_2 or N_2O during the mixing process. The CIP (clean in place) system also plays an important role in the process by ensuring that the line operates in complete microbiological safety. Batch water, caustics, acids, hot water, disinfectant solution and fresh water are used in the cleaning procedure in line production.[1]

The production of an effluent that meets the required standards requires a combination of biological treatment and advanced chemical wastewater treatments.[2, 3] For the biological treatment, the activated sludge process is considered to be the most cost-effective way to remove organic materials from wastewater. Ozone is currently a standard oxidising agent for the advanced treatment of wastewa-ter, and the integrated activated sludge ozone system has been successfully applied in the treatment of a number of wastewaters.[4]

Advanced oxidation processes (AOPs) optimise the application of ozone, and the concentrations of hydroxyl radicals (E^0 = 2.80 V) that are produced by O_3-decomposition in aqueous solutions produce a significant increase in the decomposition rate of pollutants.[5, 6] The primary field of ozone application is the water industry, although ozone has been increasingly applied to solve gaseous and liquid problems in other industries and in medical therapies. In water treatment, ozone can be used in various steps of the treatment process to enhance biological processes and micro-flocculation, remove iron and manganese, degrade pesticides and other micro-pollutants,[7] remove colour,[3–7–10] remove pharmaceutical compounds during drinking and wastewater treatments,[11] oxidise trace organic impurities in ultra-pure water,[12] treat wine vinasses and disinfect potable water.[13,14]

The high reactivity of ozone makes it appropriates for achieving certain objectives when applied either alone or

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in combination with other processes. These objectives relate to either the need to achieve higher quality standards prior to the final discharge or to meet standards for effluent recycling.

The addition of H_2O_2 is known to increase the rate of ozone oxidation by allowing an enhancement in the quantum yield of the formation of the hydroxyl radical OH•. It has been shown that the conjugate base of hydrogen peroxide at millimolar concentrations can initiate the decomposition of ozone into more reactive hydroxyl radicals. H_2O_2 reacts with O_3 according to Reactions 1 and 2:[15]

$$H_2O_2 + H_2O \rightarrow HO_2^- + H_3O^+ \qquad (1)$$

$$HO_2^- + O_3 \rightarrow OH^o + O_2^- + O_2 \qquad (2)$$

H_2O_2 produces HO^-_2 under basic conditions. HO^-_2 induced from H_2O_2 reacts with O_3 and produces some free radicals.[16] Consequently, in this work, the O_3 process using the H_2O_2 solution was used.

In water treatment, the purpose of coagulation is to remove suspended matter from water to bring about clarification. Coagulation is a chemical and physical process in which colloidal particles that normally carry a negative surface charge react with positively charged ions formed by the reaction of coagulant chemicals with water. The neutralisation of the surface charge on the particles results in their cohesion and agglomeration into larger particles, which appear as spongy gelatinous masses that are frequently referred to as “floc.” Floc has a very high surface area that can absorb or entrap bacteria, protozoa and other turbidity caused by particles that settle rapidly.[17–19]

Although many previous studies have reported on the treatment of wastewater by ozonation, there are no reports using ozonation-H_2O_2 or ozonation-coagulation for the treatment of wastewater from soft drinks process. Therefore the purpose of this paper was to compare the efficiency of these methods for the treatment of wastewater from the soft drink process to remove organic contaminants.

Materials and methods

Sampling

The samples were taken from the conventional activated sludge treatment of the soft drink process and studied in the homogenisation tank of the on-site biological treatment plant according to the standard methods for conventional characterisation APHA/AWWA/WPCF. The oxidation processes were monitored by determining the chemical oxygen demand (COD), the fading of colour, turbidity and pH. These parameters were analysed according to the standard methods described in NMX-AA-030-SCFI-2001-DQO for COD measurements.[20] The colour and turbidity were measured directly by spectrophotometry at 465 and 860 nm, respectively, using the equipment HACH DR/4000U. The pH was measured using a conductronic pH 15 Digital pH-mV-°C-Meter.

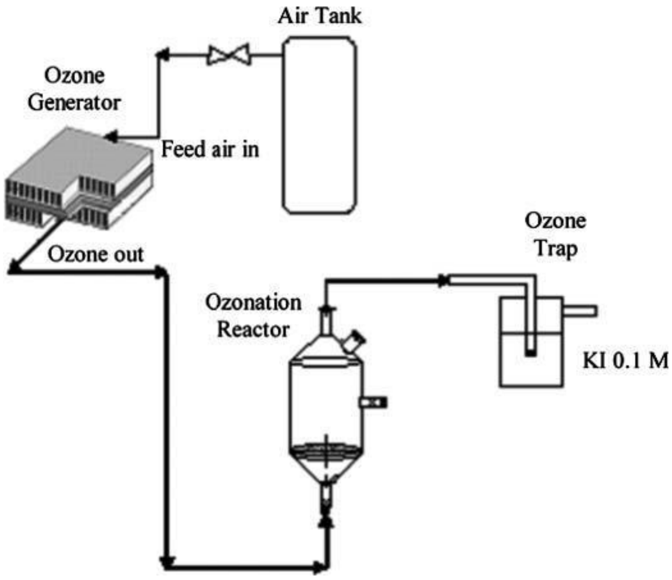

Fig. 1. Ozonation system.

Ozonation process

The chemical oxidation experiments with ozone were performed in the influent of the on-site biological treatment plant. The experiments were performed using a sample of 1 L. Ozone gas was supplied at the bottom of the reactor through a porous plate glass diffuser for 60 minutes. Samples were taken every 10 minutes, and the ozone input was adjusted to 5.2 g of O_3 h^{-1} throughout the experiments. The excess ozone gas was passed through an ozone trap containing a 0.1 M KI solution, and preliminary ozonation experiments were performed following the above mentioned procedure to determine the optimum ozone contact time.

The ozonation system consists of four components (Fig. 1).

i. The feed air system - dry air (20.95% O_2) was flowed at rate of 10 SCFH and 6 psi.

ii. The ozone generator - ozone was generated when diatomic oxygen was exposed to an electrical field typically generated by corona discharge reactor cells. Oxygen was flowed through a high-voltage electric field produced between conductive and dielectric surfaces, and the ozone was generated on-site using Pacific Ozone Technology model LAB21.

iii. The ozonation reactor consisted of the gas phase containing ozone and the fluid phase, to which the ozone must be adequately transferred for chemical reaction. Ozone was introduced in the liquid phase of the ozonation reactor, forming small bubbles and thereby increasing the reaction zone area located in the gas/liquid interface to its maximum. The process of dissolving the ozone gas into solution was achieved by bubbling ozone gas through a column of water via diffusion by a porous plate glass diffuser.

iv. The off-gas treatment system - excess ozone gas that did not dissolve into the diffuser reactor was flowed from the top of the tank into the ozone trap.

Ozonation-H_2O_2 process

The concentration of H_2O_2 in the wastewater was 0.05 mol/L before the ozone entered the reactor. The original concentration of hydrogen peroxide used during the experiment was 30% w/w and was supplied by Merck. The mean pH value of wastewater-H_2O_2 in this work was 5.12, and an insignificant change in the pH was observed throughout the experiment.

Ozonation-coagulant-ozonation processes

A sample of 1 L of wastewater was ozonated for 10 minutes under the same conditions as those described above for the ozonation process. After treatment, the sample obtained from the ozonation process was placed in a jar-test apparatus equipped with six beakers of 1 L capacity. In a typical coagulation run, the appropriate dosage of coagulant (polyaluminum chloride; PAC) in the range of 0.01–0.08 mg / L was added directly to 1 L of wastewater while stirring for 2 min at 250 rpm to destabilise the suspension. This was followed by slow stirring for 10 min at 35 rpm to facilitate floc agglomeration. The sample was then left to rest for 45 minutes, and as soon as separation was achieved, the colour and turbidity parameters were determined in the supernatant.

The supernatant obtained from the coagulant process was ozonated again. The ozonation process lasted for 60 minutes, and samples were taken every 10 minutes under the same conditions as described above in the ozonation process to monitor the removal of COD, discolouration, turbidity and pH.

Coagulant, ozonation processes

A sample of 1 L of wastewater was coagulated with a dosage of 0.03 mg/L coagulant (PAC) under the same conditions as those described here for the coagulant process. After treatment, the supernatant was ozonated. The ozonation process lasted for 60 minutes, and samples were taken every 10 minutes under the same conditions as described here for the ozonation process to monitor the removal of COD, discolouration, turbidity and pH.

Table 1. Initial physicochemical parameters from treated wastewater.

Parameter	*Value*	*Units*
COD	3410	mg/L
Colour	1035	Pt-Co
Turbidity	190	FAU
pH	4.89	
TDS	1309	mg/L
Conductivity	2620	μS/cm
Alkalinity “P”	0	mg $CaCO_3$/L
Alkalinity “M”	157.6	mg $CaCO_3$/L
Total Hardness	175.4	mg $CaCO_3$/L
Calcium Hardness	43	mg $CaCO_3$/L
Chlorides	1218	mg Cl^-/L

Results and discussion

Wastewater characterisation

Table 1 presents the initial physicochemical parameters of wastewater from the soft drink production process. The wastewater presented contamination with organic and inorganic matter that is reflected in the values of the analysed parameters. This pollution was caused by the ingredients used in the process, such as solutions used in the cleaning procedure during line production and backwash water (produced in the backwash - the sanitation or regeneration of sand, carbon, ion exchange columns of softeners or dealkalysers filtered from the treatment system for the water treatment process) together with the impurities in the process for clarifying sugar and caustic and acid solutions used in the regeneration procedure in the ion exchange columns. Due to the high levels of pollution of the wastewater in the soft drink preparation process, we believed it was important to use a tertiary treatment of advanced oxidation with ozone.

COD removal by ozonation process

The COD removal efficiency is defined by Equation 3:

$$E = \frac{C_i - C_0}{C_i} \times 100 \qquad (3)$$

where E is the COD removal efficiency (%), C_i is the COD concentration in the waste water (mg/L), and C_0 is the COD concentration after the ozonation process.

A preliminary study was conducted to determine the ozonation conditions of the process and to optimise COD, colour and turbidity removal. For this purpose, the ozone flow-rate was fixed at 5.2 g of O_3 h^{-1}, and ozone feeding times of 0, 10, 20, 30, 40, 50 and 60 min were applied. The COD reduction efficiency was 6.99% when the ozone feeding time was 10 min. The removal of COD was constant up to 20 min. From 20 to 30 min, the removal of COD

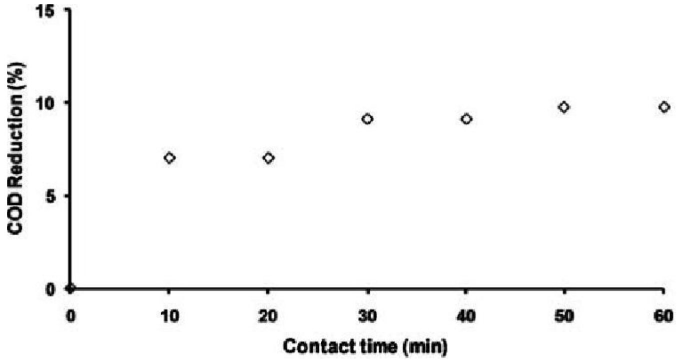

Fig. 2. Graphic COD reduction percentage versus ozonation process time.

(9.79% of COD removed). At 20, 30, 40, 50 and 60 min contact time, which are not likely to be feasible in practice, there was a 9.79% COD removal, as shown in Figure 2.

The COD values resulting from these small, newly formed molecules can be further reduced by a biological process.[15] Dogruel et al.[9] reported an efficiency of 9% COD removal in 10 min of ozonation using solutions from the textile industry. This result agrees with our results.

Discolouration ozonation process

The removal of colour increased considerably as the duration of the ozonation increased from 10, 20, 30, 40, 50 and 60 min, with values of 28.87%, 41.86%, 49.69%, 55.46%, 60.41% and 62.06%, respectively, and the percentage of colour removal was similar for the 50 and 60 min dura-tions, as shown in Figure 3. Hassan et al.[8] and Papic et al.[21] reported an efficiency of 90% and 85%, respectively, using the same technique for textile wastewater. The composition of the wastewater may affect the efficiency of the process (alkalinity, hardness, chlorides, pH, conductivity, TDS); therefore, it is important to consider the compo-nents of the wastewater.[15]

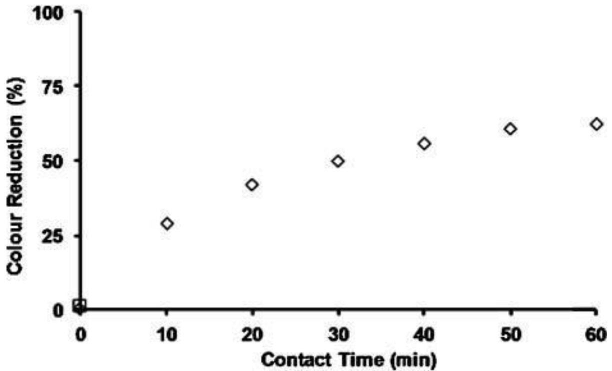

Fig. 3. Graphic colour reduction percentage versus ozonation process time.

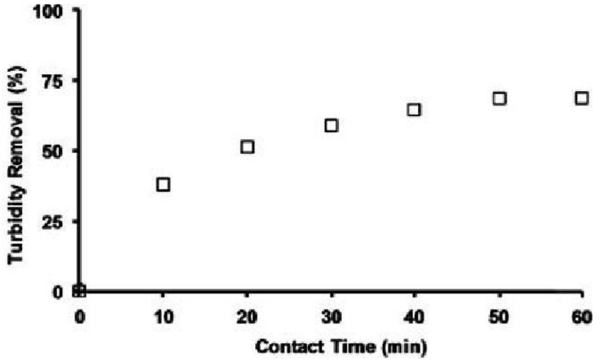

Fig. 4. Graphic turbidity reduction percentage versus ozonation process time.

Turbidity removal ozonation process

Figure 4 shows the turbidity reduction in the samples; most of this reduction was achieved in 50 min. The turbidity of the samples was reduced by 68.89% through ozonation. The turbidity was the same from 50 to 60 minutes of ozonation. However, the turbidity removal increased as the contact time increased to 37.78%, 51.11%, 58.89% and 64.44% for 10, 20, 30 and 40 minutes, respectively.

The changes of the properties of the organics, such as a decrease in molecular size and ionisation, could be the reason for the reduction in the turbidity from the wastewater after the ozonation process.[22]

Evolution of pH during the ozonation process

The pH was monitored during the ozonation process as a function of contact time with the wastewater and is shown in Figure 5. The pH value slightly decreased during the ozonation process from 4.89 to 4.82 after 10 min. Subsequently, the pH values were similar up until 60 minutes. Kong et al.[23] reported the effect of pH on ozone decomposition in aqueous solution using deionised water

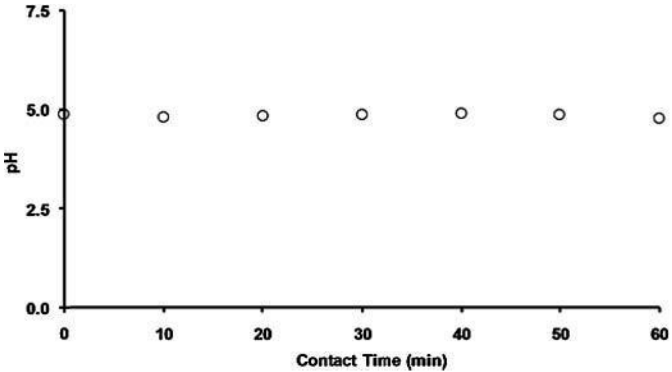

Fig. 5. Graphic evolution of pH versus ozonation process time.

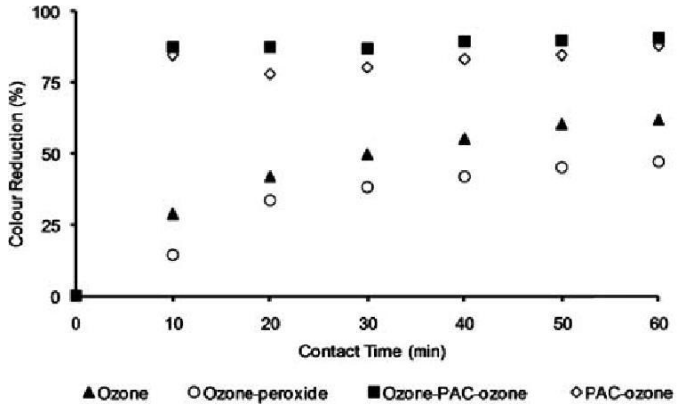

Fig. 6. Graphic colour reduction percentage for ozone, ozone-peroxide, ozone-coagulant-ozone and coagulant-ozone treat-ments.

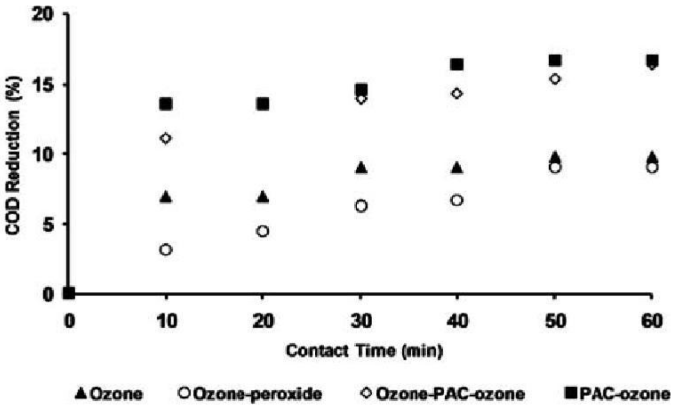

Fig. 8. Graphic COD reduction percentage for ozone, ozone-peroxide, ozone-coagulant-ozone and coagulant-ozone treat-ments.

at different pH values. Their experimental conditions were different and depended on the pH of the solutions.

Comparison of the results of the wastewater in the treatments: Ozone, ozone-peroxide, ozone-coagulant-ozone and coagulant-ozone

The results show that the wastewater treatment process combined with ozone-coagulant provides the best efficiency for removing colour and turbidity, as shown in Figures 6 and 7, respectively, and that the coagulation-ozone treat-ment showed very similar results. On the other hand, the treatment with the lowest removal efficiency of turbidity and colour corresponded to the process of ozone-peroxide. The process with ozone (alone) was not very efficient and could be substantially improved by a combination with PAC.

The presented results revealed that the discolouration process using the O_3/H_2O_2 process was less efficient than O_3 alone. This phenomenon can be explained by considering the scavenging effect of hydrogen peroxide on hydroxyl radicals. It is worth noting that hydrogen peroxide can re-act with $OH^\bullet$, thereby decreasing the concentration of free hydroxyl radicals and leading to less reactive species, as shown in Equation 4:

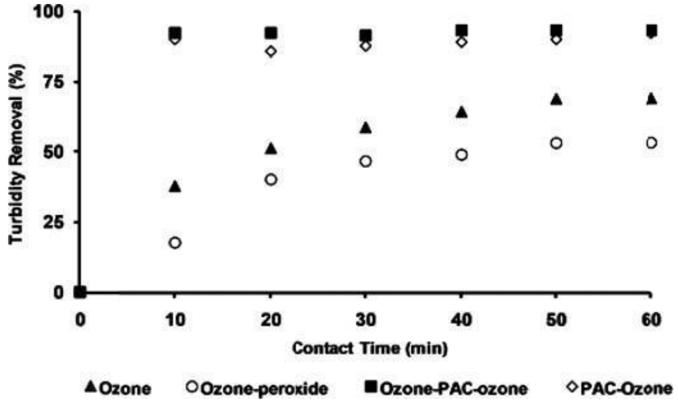

Fig. 7. Graphic turbidity removal percentage for ozone, ozone-peroxide, ozone-coagulant-ozone and coagulant-ozone treat-ments.

$$H_2O_2 + OH^\bullet \rightarrow OOH^\bullet + H_2O \tag{4}$$

Another possible explanation could be a different early reaction pathway depending on H_2O_2 concentration that leads to more resistant intermediate products and further oxidation using the O_3/H_2O_2 process.[15]

With respect to COD removal, the best treatment was the combined PAC-ozone process in the first 10 minutes of the reaction. After 20 minutes of reaction time, the efficiency was the same as the ozone-PAC and ozone-APC-ozone treatments. The removal efficiency was reversed from 30 to 60 minutes, and PAC-ozone-ozone was the best process, as shown in Figure 8.

The treatment with the lowest removal efficiency for the removal of COD was the combined ozone–peroxide process. The treatment with ozone was not good, but its ef-ficiency was increased in combination with PAC. There was no significant change in the pH values of the wastewater during the experiment for any of the four treatments, the pH values remained close to the initial value (pH = 4.89 ± .2).

Kinetics of the discolouration and turbidity removal of wastewater treated with PAC-ozone

The kinetics of the ozonation process play an important role in assessing the efficiency and feasibility of treating contaminated wastewater. The reaction takes place at the gas–liquid interface in ozone applications where semi-batch reactions with ozone bubbling from the bottom of

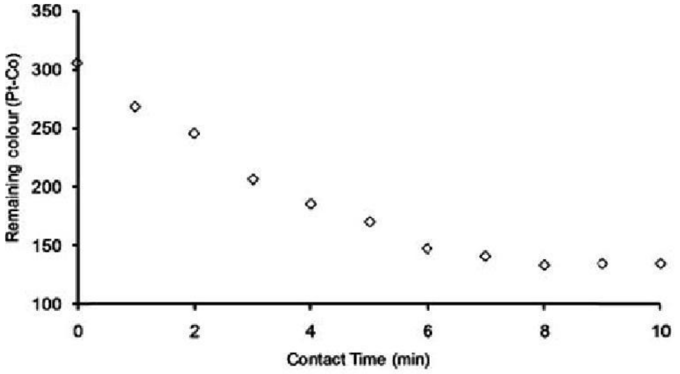

Fig. 9. Graphic remaining colour as a function of contact time in the coagulant-ozonation process.

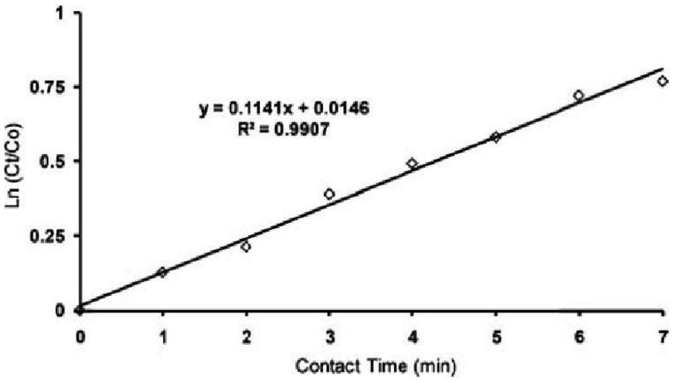

Fig. 11. Graphic discolouration kinetics of the wastewater in the coagulant-ozonation process.

the reactor are used. In this study, the kinetics of wastewater ozonation were evaluated by plotting $Ln(C_t/C_0)$ values versus reaction time following Equation 5:[15]

$$Ln(C_t/C_0) = -k_d t \qquad (5)$$

where C_t and C_0 are the concentrations of colour or turbidity at any reaction time (t) during the ozonation and the initial concentration of colour or turbidity, respectively. k_d stands for the first-order reaction rate constant. Figures 9 and 10 illustrate the disappearance of the concentration of the colour and turbidity versus time, respectively, which was fast in the first 6 min of ozonation. Afterward, the disappearance rate of COD was slower.

Using data obtained from Equation 2, Figures 11 and 12 show that the curve was well-fitted to the first-order kinetics for discolouration and turbidity removal, respectively, and the square of the relative correlative coefficient (R^2) of the experimental results was 0.9907 for the discoloura-tion kinetic and 0.9902 for the turbidity removal kinetic. The slope of the linear curve represents the first-order rate constants, which were approximately 0.1141 min^{-1} 0.1128 min^{-1} respectively.

UV–Vis spectra of the wastewater in the PAC-ozone process

Figure 13 shows the UV–vis spectra of the raw wastewater and the treated wastewater (alone and with PAC) for different contact times with the ozone. The spectrum for the wastewater (x) presents a band with an absorption maximum absorbance at 290 nm and also a basic absorbance, which is associated with the contaminants in this matrix (3410 mg/L COD) and the turbidity of the sample (190 FAU). In the case of treated water with 10 minutes of contact with ozone (♦), there was a decrease in the absorption band at 290 nm; this behaviour was due to the oxidation of organic contaminants. The wastewater treated with PAC-ozone (•) showed the highest efficiency in removing colour, turbidity and COD (130 Pt-Co, 19 FAU and 2945 mg/L, respectively) together with a decrease in the band of 290 nm. The spectra of wastewater by ozonation causes

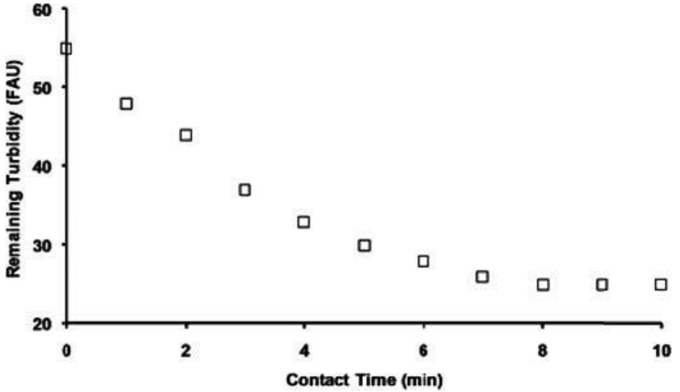

Fig. 10. Graphic remaining turbidity as a function of contact time in the coagulant-ozonation process.

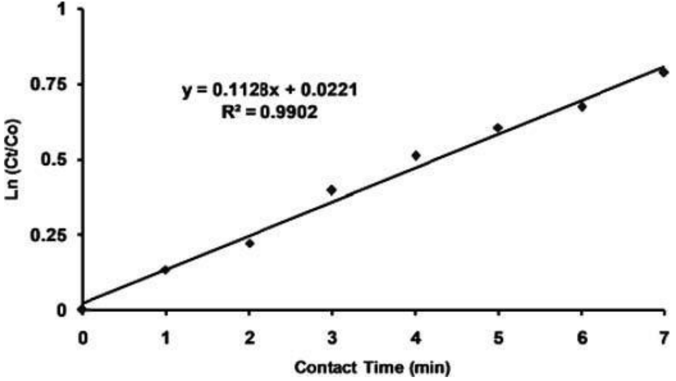

Fig. 12. Graphic turbidity removal kinetics of the wastewater in the coagulant-ozonation process.

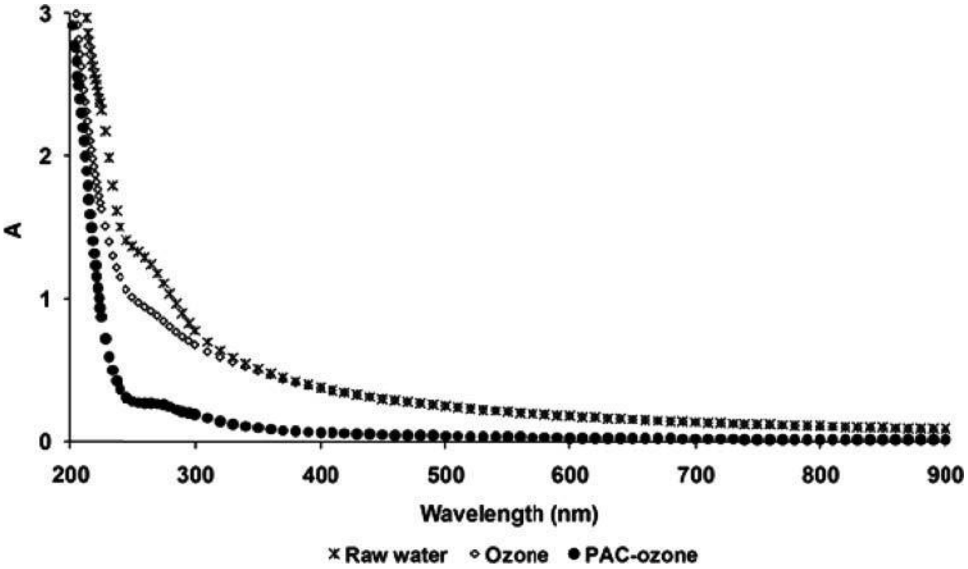

Fig. 13. Graphic UV–Vis spectra of the wastewater in the ozone and PAC-ozone processes at different contact times.

continuous decreases in the intensities of the UV and visible band without the appearance of new absorption bands in the UV–vis region. The decrease in the intensity of the spectrum indicates the oxidation of wastewater by ozone. It is worth noting that ozone reacts in a conjugate system with the wastewater either through direct or indirect oxidation.[15].

PAC-ozone treatment applied to the effluent of activated sludge process

Table 2 presents the initial physicochemical parameters of the effluent of the activated sludge system of a soft drink production process. Subsequently, the wastewater sample was treated with PAC-ozone under the same conditions as the previous sample for 10 minutes and obtained 100% COD removal during the first minute of reaction, as shown in Figure 14. It maintained this value for the following 9 minutes of ozonation.

Table 2. Initial physicochemical parameters of the effluent of activated sludge system from treated wastewater.

Parameter	*Value*	*Units*
COD	40	mg/L
Colour	38	Pt-Co
Turbidity	4	FAU
pH	7.86	
TDS	1940	mg/L
Conductivity	3870	μS/cm
Alkalinity “P”	0	mg $CaCO_3$/L
Alkalinity “M”	1003.8	mg $CaCO_3$/L
Total Hardness	135.8	mg $CaCO_3$/L
Calcium Hardness	49.2	mg $CaCO_3$/L
Chlorides	1412	mg Cl^-/L

The colour was slowly decreasing from 1 to 5 minutes with increasing reaction time, obtaining a value of 8 Pt-Co in the 5 minutes of reaction. From 6 to 10 minutes, it remained constant with a value of 5 Pt-Co, as shown in Figure 15. For the removal of turbidity, there were two time intervals in which the value was constant. The first interval was 1 to 4 minutes, with a constant value of 2 FAU, and the second interval was 5 to 10 minutes, with a value of 1 for FAU turbidity, as shown in Figure 16.

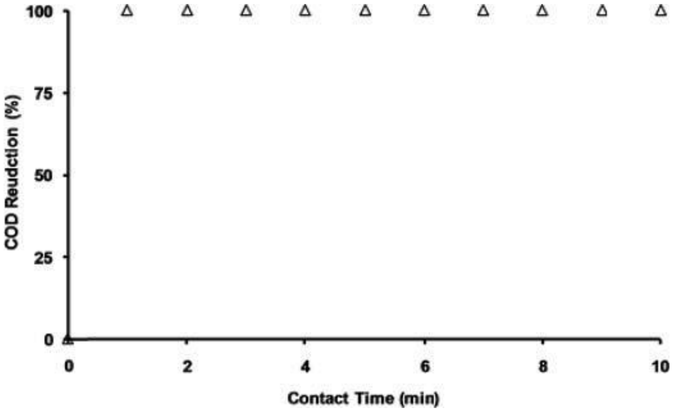

Fig. 14. Graphic COD reduction percentage in the effluent of activated sludge process for the coagulant-ozonation treatment.

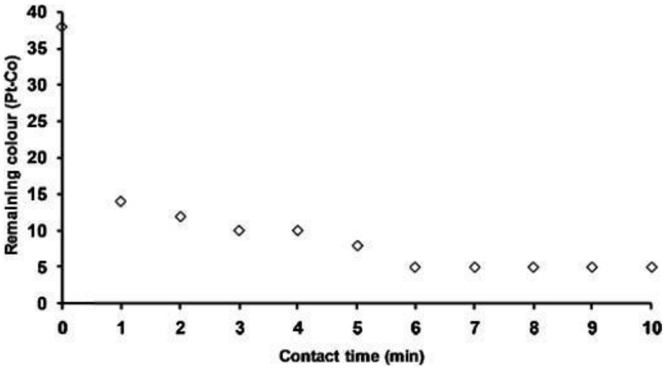

Fig. 15. Graphic remaining colour as a function of contact time in the effluent of activated sludge process for the coagulant-ozonation treatment.

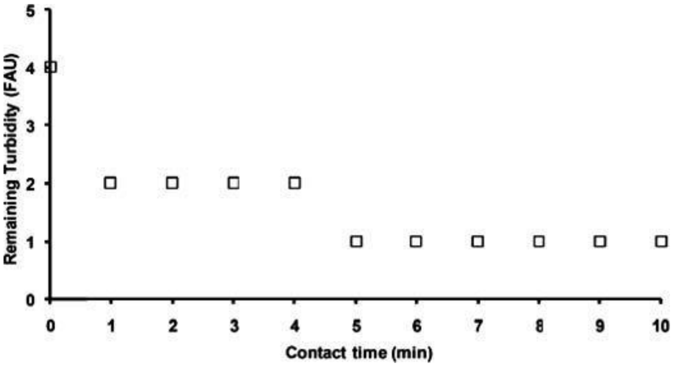

Fig. 16. Graphic remaining turbidity as a function of contact time in the effluent of activated sludge process for the coagulant-ozonation treatment.

Conclusions

Given the physicochemical characteristics of the treated wastewater from the soft drink process, the chlorides, carbonates, bicarbonates, hardness and TDS could compete with the hydroxyl radicals by decreasing the efficiency of COD removal in the treatments with ozone, peroxide, ozone and ozone-PAC. The combined PAC-ozone treatment was the best process for the removal of COD, decolouration and removal of turbidity, whereas the ozone-peroxide treat-ment was the least efficient. Using the coagulant (PAC), the treatment efficiency of ozonation to remove COD in-creased relatively little considering that we believed that the major portion of COD in this wastewater was soluble COD.

The pH was maintained without significant change dur-ing the processes of ozonation in all of the treatments. The reaction kinetics for the removal of colour and tur-bidity in the PAC-ozone were first-order, and the corre-lation coefficients (R^2) of the experimental results were 0.9907 and 0.9902, respectively. The decrease in the inten-sity of the spectrum between the raw wastewater and the treated wastewater indicates the oxidation of wastewater by ozone. The PAC-ozone treatment proved to be much more efficient when it was applied to the final effluent of the activated sludge system, obtaining an efficiency of 100% for the removal of COD during the first minute of the reaction.

Acknowledgments

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2.2 Artículo 2 (Publicado)

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Integrated Advanced Oxidation Process (Ozonation) and Electrocoagulation Treatments for Dye Removal in Denim Effluents

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The present research aims to study the removal of indigo carmine dye used in industrial denim dyeing processes. For this purpose, integrated advanced oxidation process comprising ozone and electrocoagulation techniques were used. After ozone was applied 64% color removal, 78% turbidity removal and 3% COD reduction was observed. With the electrocoagulation treatment a 22%, 21% and 9% of color removal, turbidity removal and COD reduction were achieved, respectively. However; using the integrated process, 65% color removal, 76% turbidity removal and 37% COD reduction could be attained. The synergistics associated to coupling both processes yielded increased removal of color, COD and turbidity efficiencies as compared with the results obtained with the single treatments. The decrease in the intensity of the Uv-vis spectrum between the raw wastewater and the treated wastewater indicated that oxidation and organic's removal took place in the integrated process. This result is consistent with the cyclic voltammograms obtained.

Keywords: dye removal, denim effluents, electrocoagulation, ozone, process coupling.

1. INTRODUCTION

The wastewaters from textile industries are intensely colored, bearing quite frequently a complex and variable nature [1, 2]. It is estimated that more than 100,000 synthetic dyes are available in the world with over 7×10^5 tons of dyestuff produced annually [3]. Dye-containing effluents can obstruct light penetration in lakes, rivers or lagoons, thus inhibiting the biological processes based on photosynthesis. Moreover, these effluents can contain toxic chemicals, carcinogenic, mutagenic, or teratogenic to various microbiological or animal species [4, 5]. Conventional treatments of dye effluents include biological oxidation and adsorption [6]. Although less expensive than other approaches, the biological treatment is in effective for decoloration because the dyes are toxic [3],[6]. Adsorption onto activated carbon transfers most of the contaminant from the wastewater to the solid phase. This method therefore requires further disposal of the sludge [6]. An alternative approach to addressing the problem of color and toxicity in textile dyeing effluents, has involved the development of effluent treatment methods such as ozonation, advanced oxidation processes and electrochemical methods [5, 6].

Ozonation is particularly attractive for wastewater treatment because ozone, is soluble in water and can decompose quickly to form several free radicals including $OH^\bullet$ (hydroxyl), $HO_3^\bullet$, $HO_4^\bullet$ and O_2^- (superoxide). Such free radicals are readily available to react instantly with any organic compounds present in water, like the dyes [7, 8]

Further, the electrochemical techniques have been found particularly interesting for textile wastewater remediation due to advantages like: high efficiency, ease of operation and environmental compatibility since there is no need of adding chemicals [5, 9, 10]; this process involves the *in situ* generation of coagulants by electrolytic oxidation of an appropriate sacrificial anode upon application of a direct current [4, 11].

Given the advantages of ozonation and electrocoagulation for wastewater treatment, in the present research both processes are integrated in a batch reactor to increase the efficiency of wastewater color removal from dyeing denim compared with the treatments alone.

2. MATERIAL AND METHODS

The samples for this study were collected at the exit of denim's dyeing process, preserved and analyzed according to the standard methods for conventional characterization APHA/AWWA/WEF. The ozone, electrocoagulation and integrated processes were monitored through determining removal of color, turbidity, chemical oxygen demand (COD) and pH variation. Spectrophotometry at 465 and 860 nm, respectively, served to determine color and turbidity by means of an HACH 110 DR/4000U equipment. The chemical oxygen demand was analyzed according to closed reflux; colorimetric method. A Waterproof OAKTON pH/CON 300 Series, was used for pH measurement at different stages of the various treatments.

A comparison between the UV-VIS spectroscopy absorbance spectra of the oxidized products was realized using a Perkin Elmer Lambda 25 UV/VIS Spectrometer, USA.

Cyclic voltammetry of crude and treated wastewater were performed using a standard three-electrode cell. The waveforms were generated by an Epsilon^{TM} Electrochemistry Basi Cell Stand C-3 Potentiostat; using a round carbon paste electrode (CPE) as working electrode, prepared from a 1:1 mix of 99.99% pure single-crystal graphite (Alfa Aesar) and nujol oil (Aldrich). The paste was transferred into a PVC tube and compacted to eliminate trapped air then a copper conductor was back-inserted before the paste set. The surface of the electrode was renewed through light polishing after each potential scan. The scan rate was 100 mVs^{-1} with an Ag/AgCl reference electrode and a glassy carbon counter electrode.

2.1 Ozonation process

Ozone was generated using a laboratory-scale ozone generator (LAB 21 ozone generator) capable of generating ozone continuously at a 5.2 g of O_3 h^{-1} rate, using air (20.95% O_2) as feed gas flowing at 10 Standard Cubic Feet per Hour (SCFH) rate and 6 psi of pressure. The generator used the corona discharge to produce ozone by passing dry air through a very strong electric field, which splits diatomic oxygen molecule (O_2) into two highly excited oxygen atoms (O^-) that due to their inherent instability combine readily with other oxygen molecules to form ozone [1].

The chemical oxidation experiments with ozone were performed in a laboratory-scale reactor comprising a 60 cm long acrylic column of 20 cm inner diameter (ID) fitted with a stone diffuser at the bottom to aid uniform distribution and good mixing of the ozone gas and the effluent. The reactor was run in a batch mode at 2.5 L effluent per batch: first, the ozone was supplied through the diffuser stone at the reactor's bottom, for 120 minutes. Samples were taken every 10 minutes; the sample pH was monitored during the treatment. The excess ozone flowed from the top of the reactor into the ozone trap containing a 0.1 M KI solution.

2.2 Electrocoagulation process

The electrocoagulation was carried out in the same laboratory scale reactor described previously for the ozone process; two rectangular commercial aluminum plates served as anode and cathode. The anodic and cathodic active surface area were 343 cm^2 immersed in wastewater with 0.1372 cm^{-1} of SA/V ratio. A DC power source supplied the system with 0.1 A, corresponding to a 0.2915 mA cm^{-2} current density that was kept for 1 minute every 10 minutes intervals during the experiment; the sample pH was monitored during the treatment. The electrocoagulation was performed without additional electrolyte. The electrodes were connected to a digital DC power supply (G^W ISTEK GPR-1820 HD, 0-18 V; 0-20 A, China). 25 mL of sample were taken every 10 minutes during the 2 h of electrocoagulation process. The samples were allowed to settle for 1 h, and then analyzed.

2.3 Ozone-electrocoagulation process

The ozone and electrocoagulation treatments were coupled into a combined ozone-electrocoagulation process and carried out simultaneously using the conditions described previously for each of the treatments alone. The samples also were taken every 10 minutes during 2 h and allowed to settle for 1 h before being analyzed.

3. RESULTS AND DISCUSSION

Table 1 shows the initial physicochemical parameters of wastewater from the dyeing denim process. The color value obtained is harmful to aquatic life obstructing light penetration in the water, inhibiting thus the photosynthesis-based biological processes [5]. On the other hand, substances such as indigo carmine dye forms chelates with metal ions, which results in high hardness. The high value of electric conductivity indicates an excessive mineralization that causes high solids levels and turbidity in wastewater; therefore filtration, flocculation or other processes should be used for remove them. The value of Biochemical Oxygen Demand (BOD_5) limits their discharge into water bodies due to harmful effects on living systems. The COD value shows high pollution due to organic and inorganic matter susceptible to be oxidized that favors the presence of color in this wastewater. The pH is similar to the natural waters value (7.2 to 7.8).

Table 1. Initial physicochemical parameters from treated wastewater

Parameter	*Value*	*Units*
BOD_5	1174	mg/L
COD	2308	mg/L
Color	630	Pt-Co
Turbidity	110	FAU
pH	7.23	
TS	3460	mg/L
Conductivity electric	1510	µS/cm
Chlorides	306	mg/L
Total Hardness	508	mg $CaCO_3$/L
Alkalinity (HCO_3^-)	224	mg /L

3.1 Color removal efficiency

The color, COD and turbidity removal efficiency (%) at the different processes were calculated using the equation 1:

$$E = \frac{C_0 - C_i}{C_0} X100 \qquad (1)$$

Where E is the dye, COD or turbidity removal efficiency (%), C_0 is the initial value of the color of dye (Pt-Co), COD (mg/L) or turbidity (FAU) in the wastewater, and C_i is the color value of dye (Pt-Co), COD (mg/L) or turbidity (FAU) at time t after the different processes.

The treatment with the best efficiency for the removal of color at 120 min of reaction was the integrated process of ozone-electrocoagulation, which increased to 64.27% of color removal. A similar result, 63.63% of discoloration was obtained in the ozone process, as shown in figure 2. Further, the treatment with the lowest color removal efficiency corresponded to the electrocoagulation process, with 21.73%.

With the combined ozone-electrocoagulation process, the color removal increased gradually as the reaction time increased. Following the same tendency, values of color removal smaller than the prior process were obtained with the ozone process. Finally; color removal did not increase significantly from 10 to 120 minutes of reaction in the electrocoagulation process.

For the ozone process, the color reduction could be attributed to the ozone reaction with the unsaturated bonds of the indigo carmine, leading to the splitting of bonds and the dissociation of the rings, according to the Criegee mechanism [12]. In the electrocoagulation process, the Al^{3+} and OH^{-} ions generated at the electrode surfaces react in the wastewater to form aluminum hydroxide [13]; the amorphous and gelatinous aluminum hydroxide that displayed various shapes and sizes (flocs) [9] destabilize and aggregate the suspended particles or precipitate and adsorb dissolved contaminants [14, 15]. Given the physicochemical characteristics of the treated wastewater; the hardness, chlorides, alkalinity, conductivity and TS could compete with the hydroxyl radicals by decreasing the efficiency of color removal in this treatment [13, 16]. The synergic effect associated to the integration of both processes (ozone and electrocoagulation) resulted in an increased color removal efficiency in the ozone-electrocoagulation process.

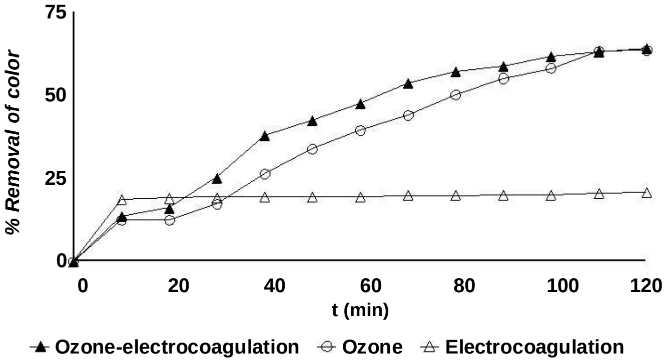

Figure 2. Color removal efficiency in the wastewater treated with different processes

3.2 COD removal efficiency

After 120 min of reaction; with 36.85% of COD reduction, the ozone-electrocoagulation process showed the higher efficiency on the values obtained by electrocoagulation and ozone processes; as shown in figure 3. Most COD removal in this process was obtained after the first 10 min of reaction (30.75%); from 10 to 120 min there was not a significant increase (6.1%). For the electrocoagulation and ozone processes, the efficiencies were the lowest achieved; 8.50% and 2.63% of COD removal at 120 min of reaction; respectively.

In the ozone process the chemical oxidation was accomplished by a hydroxyl radical reaction mechanism (indirect oxidation) under alkaline conditions [12, 17]. The oxidation activity of the hydroxyl radical might be limited by the presence of scavengers (hardness, chlorides, alkalinity, conductivity, TS) [12, 13, 16]; these ions terminate the chain reactions and inhibit ozone decay to hydroxyl radicals; which causes incomplete degradation of the organic loading of a sample [12].

The oxidation activity of hydroxyl radicals is limited by the presence of scavengers, which causes incomplete degradation of the organic loading of a sample. High alkalinity indicates the presence of carbonate and bicarbonate ions, which terminate the chain reactions and inhibit ozone decay to hydroxyl radicals, hence promoting ozonation through direct pathway-mechanism. Some researchers reported that during ozonation several substances were converted to other more hydrophilic and polar compounds. As a result, the removal of the produced substances by prolonged ozonation or by other techniques becomes even more difficult [12].

On the other hand, the electrocoagulation removes anions and organic compounds due to aluminum hydroxide formed that precipitates and adsorbs dissolved contaminants [9, 15]; due to contaminants in this matrix, the oxidation activity of hydroxyl radicals might be limited [12], thus decreasing the efficiency of COD removal [12, 13, 16]. Once again, the synergistic coupling of both processes increased the COD percent removal of the ozone-electrocoagulation process.

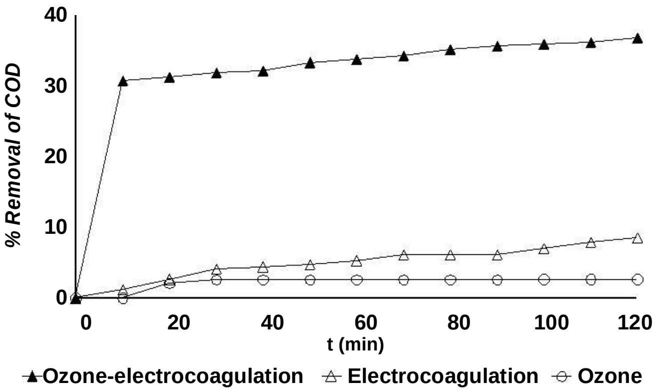

Figure 3. COD removal efficiency in the wastewater treated by means of three different processes

3.3 Turbidity removal efficiency

With slightly higher efficiencies, turbidity removal follows the same pattern as that of color removal in the different treatments after 120 reaction minutes. Again, the integrated process ozone-electrocoagulation and ozone treatment had obtained the highest efficiency values of 75.30% and 77.77%, respectively, as well as the electrocoagulation process showed that showed the lowest efficiency with 20.71% of turbidity reduction, as shown in figure 4.

The changes of the properties of the organics, such as a decrease in molecular size, could be the reason for the reduction in the turbidity from the wastewater after the ozone and ozone-electrocoagulation processes [18]. Electrocoagulation also removes turbidity [9] but the presence of scavengers in the wastewater caused low efficiency in its removal [12, 13, 16].

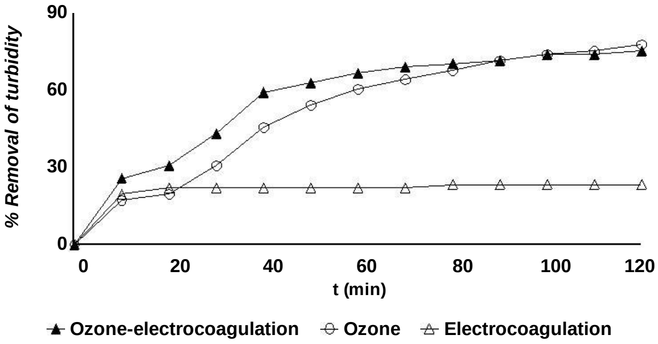

Figure 4. Turbidity removal efficiency in the wastewater treated by means of different processes

3.4 Evolution of pH in the different processes

There was no significant increase in pH values during the reactions for any of the three processes carried out; the pH values remained close to the initial value (7.23 pH) after 10 reaction minutes (8.34, 8.51 and 8.20 for ozone-electrocoagulation, ozone and electrocoagulation processes; respectively). Subsequently, the pH values were similar up until 120 minutes of reaction as shown in figure 5. The increase of wastewater pH during the processes is mainly attributed to the increase of hydroxide ions (HO^{-}) concentration [4].

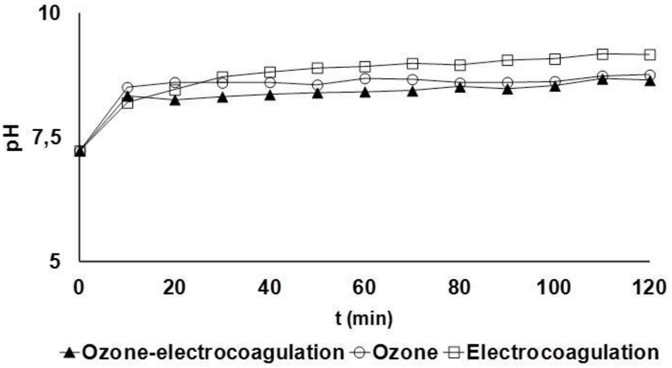

Figure 5. Evolution of pH in the wastewater treated by means of different processes

3.5 Kinetics of discoloration and turbidity removal of wastewater treated in ozone-electrocoagulation process

In this study, the kinetics of wastewater treated were evaluated by plotting $\frac{1}{[C]_t} - \frac{1}{[C]_0}$ values versus reaction time following equation 2

$$\frac{1}{[C]_t} - \frac{1}{[C]_0} = k_d\, t \qquad (2)$$

Where C_t and C_0 are the concentrations of color or turbidity at any reaction time (t) during the ozone-electrocoagulation process and the initial concentration of color or turbidity, respectively. k_d stands for the second-order reaction rate constant.

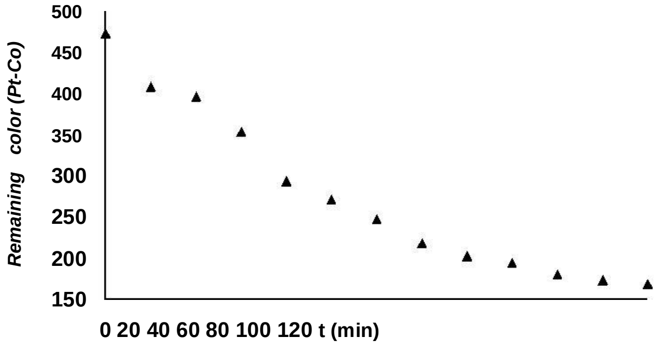

Figure 6. Remaining color as function of contact time of the wastewater treated in the ozone-electrocoagulation process.

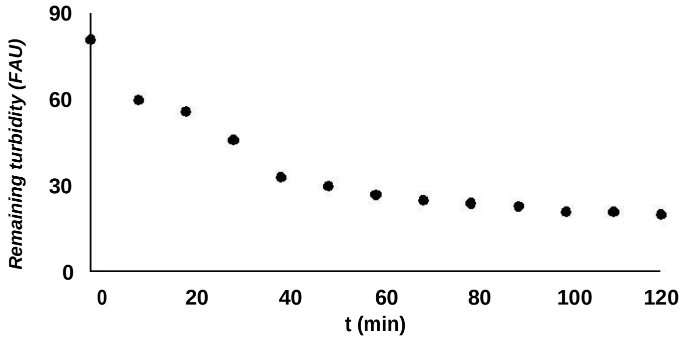

Figure 7. Remaining turbidity as function of contact time of the wastewater treated in the ozone-electrocoagulation process.

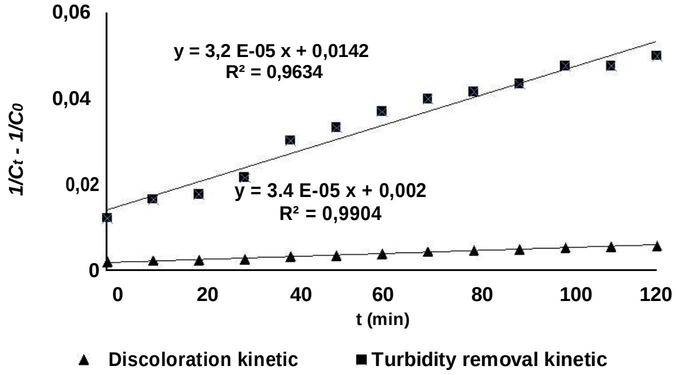

Figure 8. Kinetics of discoloration and turbidity of the wastewater treated in the ozone-electrocoagulation process

Figures 6 and 7 illustrate the disappearance of the concentration of color and turbidity versus time, respectively, which was fast in the first 70 min of reaction. Afterwards, the disappearance rate of color and turbidity was slower.

Using data obtained from equation 2; figure 8 shows that the second-order kinetics fitting curve followed well the experimental data for discoloration and turbidity removal, and the square of the correlative coefficient (r^2) of the experimental results was 0.9904 for the discoloration kinetic and 0.9634 for turbidity removal kinetics. The slope of the linear plot represents the second-order rate constants, which were $3.4 \text{ X } 10^{-5}$ L mol^{-1} min^{-1} and $3.2 \text{ X } 10^{-4}$ L mol^{-1} min^{-1} respectively.

The discoloration kinetic study as functions of ozonation time was investigated by Santana *et al*. in a synthetic water containing Reactive Orange 122; they state that using ozone constitutes an efficient technology for color removal [19]. Secula *et al*. report that electrocoagulation of synthetic wastewater containing indigo carmine dye obeys a second order reaction, which agrees with our results [4]. Durante *et al*. reported that when advanced oxidation processes (AOPs), such as ozonation or electrooxidation are applied in series with electrocoagulation (EC), a complete removal of the recalcitrant fractions of Cr in a synthetic wastewater, can be successfully achieved [16].

3.6 UV–Vis spectra of the wastewater in the ozone-electrocoagulation process

The spectrum for the raw wastewater (▲) presents a baseline with two absorbance peaks; the first at 290 nm and the second at 655 nm, which are associated with the contaminants in this matrix (2308 mg/L COD) and the color of the sample (630 Pt-Co).

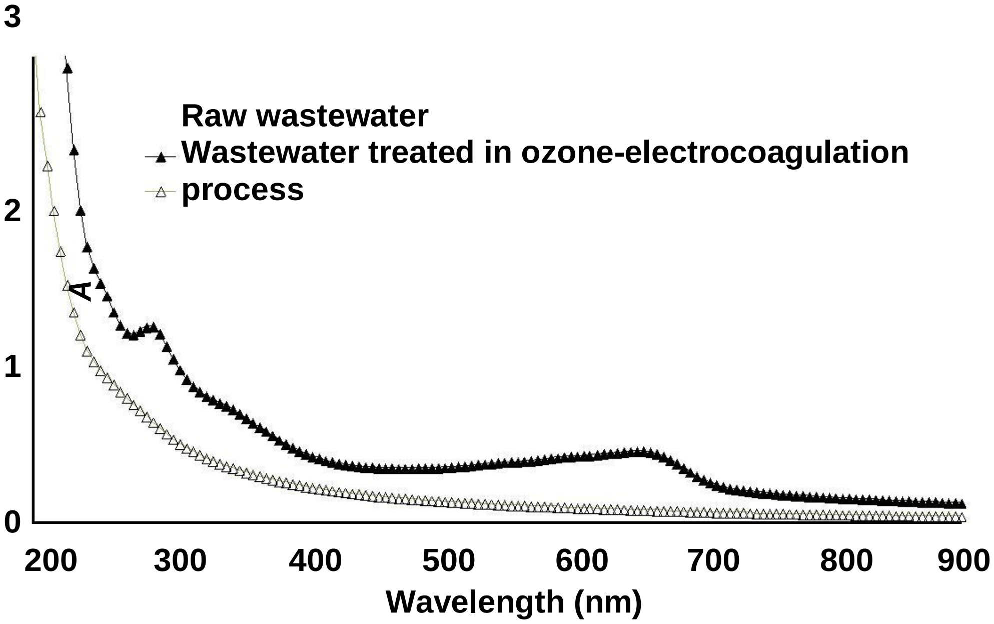

Figure 9. UV–Vis spectrum of the raw wastewater and treated wastewater in ozone-electrocoagulation process.

For 120 minutes of reaction, the wastewater treated in the ozone-electrocoagulation process (Δ) showed the highest efficiency in removing color (64.27%), turbidity (75.30%) and COD (36.85%) together with a decrease in the baseline and a decrease in the two absorbance peaks; as shown in figure 9. The oxidation of organic contaminants, the degradation of indigo carmine dye and the removal of inorganic contaminants were indicated by the decrease in the absorption band at 290 nm, 655 nm and baseline, respectively.

Song *et al*. presented the UV–vis spectra of the discoloration efficiencies of C.I. Reactive Blue 19 in synthetic water by applying a simultaneous electrocoagulation ozonation process; they found that this process is a promising alternative for treatment of wastewater with a high content of recalcitrant reactive dyes [20]. Cristóvão *et al.* investigated the degradation of a mixture of textile dyes, in synthetic water. The discoloration was appraised as a percentage of the absorbance reduction at the wavelength of maximum absorbance as total color removal based in spectrum. A significantly high discoloration was achieved indicating the applicability of this method for textile wastewater treatment [21]. These results agree with our results presented in Figure 9.

3.7 Cyclic voltammetry

Figure 10 shows the voltammograms of the raw and treated wastewater obtained by starting the potential scan in the positive direction, where the results show an oxidation process and a reduction process in the raw wastewater detectable at potentials lower than those corresponding to oxygen evolution due to pollutants present; also, a capacitive current is noted that can be related to degradation of the dye. When cyclic voltammetry was applied to the wastewater treated after the process of ozone-electrocoagulation, the peaks do not appear, indicating that pollutants in the raw wastewater have already been oxidized.

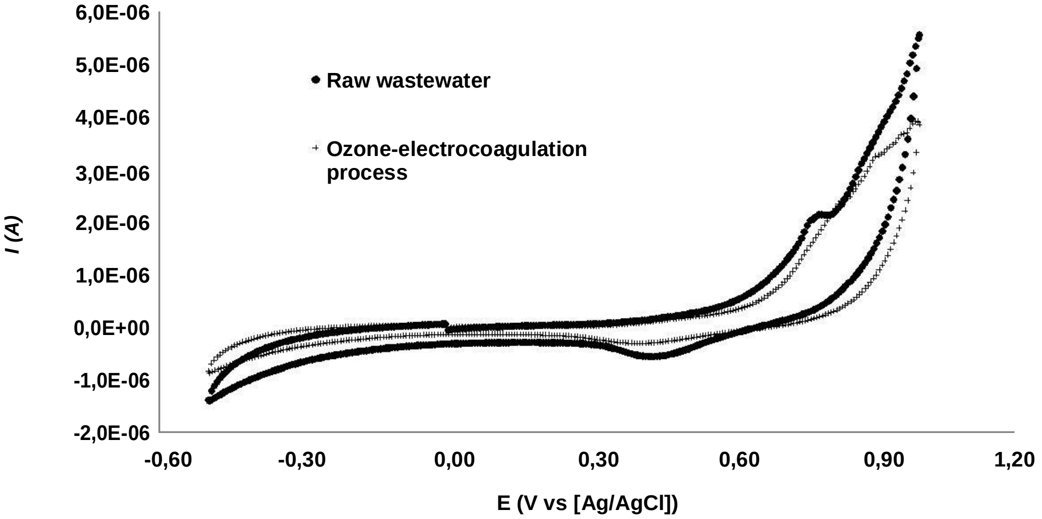

Figure 10. Cyclic voltammograms recorded at the CPE within the −0.6 to 1.2V potential window at $0.1Vs^{-1}$ scan rate.

Zhang *et al.* present the cyclic voltammogram of high discoloration efficiency of methyl red in synthetic water by synergistic effect of electrocoagulation and electrooxidation, they report that the Acid Red 2 can be oxidized, but not reduced, and the removal is related to its oxidation [22]. This agrees with the voltammogram that we present in Figure 10.

4. CONCLUSIONS

The effect of the integration of ozone and electrocoagulation treatments in the pulsed ozone-electrocoagulation process, resulted in increased removal efficiency of color, COD and turbidity compared with the efficiency obtained in treatments alone in the denim effluent researched; differences of 43.56%, 34.19% and 51.85% resulted respectively, compared to the less efficient process. The ozone process showed similar results to the integrated process for removing color and turbidity; though not so for COD removal. The lowest efficiencies of color removal and turbidity were obtained the through electrocoagulation process.

The reaction kinetics for the removal of color and turbidity in ozone-electrocoagulation pulses process were second-order indicating that the efficiencies obtained in the integrated process depend on the coupling of treatments (ozone and electrocoagulation).

The decrease in the intensity of the spectrum between the raw wastewater and the treated wastewater indicate the oxidation and removal of organic compounds in the integrated process. This result is consistent with the cyclic voltammogram obtained.

Given the physicochemical characteristics of the treated wastewater from the denim effluents, the hardness, chlorides, alkalinity, conductivity and TS could compete with the hydroxyl radicals by decreasing the efficiency of color, turbidity and COD removal in the treatments researched.

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2.3 Artículo 3 (Publicado)

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An integrated electrocoagulation and ozonation process for removal of indigo carmine dye from denim processing effluent

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ABSTRACT

The goal of this research was to improve the effectiveness of dye removal from textile wastewater by integrating electrocoagulation and ozone oxidation processes. Effluent from a denim dyeing facility where the primary -pollutant is the organic dye indigo carmine was treated to reduce color, turbidity, and chemical oxygen demand (COD). While ozonation alone only -removed 33% of the blue color, 34% of the turbidity, and 7% of COD, the integrated process removed 84, 92, and 8%, respectively. The UV-Vis spectra and cyclic voltammograms also show the improvement in water quality.

INTRODUCTION

In addition to color, the dyes present in textile industry wastewater also have a high organic load and a low biodegradability, due to the large stable molecules [1-3]. Of the 0.7 Mt of colorants produced annually in the world, 100,000 are dyes and about 20,000 of those are indigo-derivatives. Although indigo itself is insoluble in water, the reduced form and many useful derivatives are soluble. Additionally, its low affinity for fabric necessitates highly concentrated vats and significant residual dye in the waste stream [2]. Indigo carmine is the primary indigo derivative found in denim industry wastewater. This sulfonated form [1,4], also known as Acid Blue 74, Food Blue 1, or FD&C Blue 2, is a dark blue powder that is soluble in water, with molecular formula $C_{16}H_8O_8N_2S_2Na_2$ and molecular weight of 466 [1]. The content of dyes in effluents can block the penetration of light in rivers and lakes, thereby inhibiting the biological processes based on photosynthesis; these effluents may contain chemicals that are toxic, carcinogenic and mutagenic for multiple organisms and animals [1,5].

Conventional treatments of dyed wastewater include biological oxidation and adsorption [3]. Although it is less expensive than other methods, biological treatment is relatively ineffective for decolorization [2,3]. Adsorption on activated carbon is very effective in sequestering many types of contaminants onto the solid phase, but it is expensive and requires regeneration [3]. Alternative methods like electrocoagulation and oxidative processes like ozonation have shown promise in reducing the dye content in effluent, but have not been evaluated in an integrated system [3,5].

Electrochemical techniques are important for the treatment of textile wastewater because they present high efficiency, easy operation and environmental compatibility [5]; this process involves *in situ* generation of coagulants by electrolytic oxidation of a sacrificial anode (aluminum) by applying a direct current [1].

The most widely used electrode materials in electrocoagulation process are aluminum and iron. In the case of aluminum, important reactions are [6]:

Anode:

$$Al_{(s)} \rightarrow Al^{3+}_{(aq)} + 3e^- \qquad (1)$$

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Cathode:

$$3H_2O + 3e^- \rightarrow 3/2H_{2(g)} + 3OH^-_{(aq)} \qquad (2)$$

Al^{3+} and OH^- ions generated by electrode reactions (1) and (2) react to form various monometric and polymetric species which transform finally into $Al(OH)_{3(s)}$ according to complex precipitation kinetics.

$$Al^{3+}_{(aq)} + 3H_2O \rightarrow Al(OH)_{3(s)} + 3H^+_{(aq)} \qquad (3)$$

An advanced oxidation process (AOP) involves the generation of highly reactive intermediate species (•OH radicals) that initiate the oxidation of organic compounds [3]. The ozonation process belongs to the AOP group and is particularly attractive for the treatment of wastewater because ozone has a good solubility in water and is highly reactive toward organic compounds due to its decomposition into free radicals; these free radicals are available to react with organic compounds present in the wastewater such as dyes [7].

Depending on solution pH, once dissolved in aqueous solutions, the oxidant rapidly reacts either through direct reactions with target chelating agents or through OH radicals. In acidic conditions, ozone undergoes selective electrophilic attack on the specific part of chelating agent that has C=C bonds or different electronegativity between its atoms and decomposes it into carboxylic acid and aldehydes as end products. Dissolved ozone accumulates and decomposes into the radicals in bulk water according to the following reactions [8]:

Initiation

$$O_3 + OH^- \rightarrow HO_2^- + O_2 \qquad (4)$$

$$O_3 + OH^- \rightarrow O_3^- + \bullet OH \qquad (5)$$

$$O_3 + OH_2^- \rightarrow \bullet OH_2 \qquad (6)$$

Propagation

$$HO_2\bullet \longleftrightarrow \bullet O_2^- + H^+ \qquad (7)$$

$$\bullet O_2^- + O_3 \rightarrow \bullet O_3^- + O_2 \qquad (8)$$

$$\bullet O_3^- + H^+ \longleftrightarrow \bullet HO_3 \qquad (9)$$

$$HO_3\bullet \rightarrow \bullet OH + O_2 \qquad (10)$$

Termination

$$\bullet OH + O_3 \rightarrow O_2 + HO_2 \qquad (11)$$

$$\bullet OH + H_2O_2 \rightarrow HO_2 + H_2O \qquad (12)$$

$$\bullet OH + HO_2^- \rightarrow HO_2 + OH^- \qquad (13)$$

$$\bullet OH + CO_3^{2-} \rightarrow OH^- + CO_3{}^{-}\bullet \qquad (14)$$

$$O_3 + CO_3^-\bullet \rightarrow (O_2 + CO_2 + O_2{}^-) \qquad (15)$$

Given the advantages of electrocoagulation and ozonation, in the present study, both processes are integrated into a batch reactor to increase the efficiency of color removal of an industrial effluent from the dyeing of denim.

MATERIALS AND METHODS

1. Wastewater Characterization

The wastewater samples used in this study were collected at the effluent of an industrial denim dyeing process, preserved and analyzed according to Standard Methods for characterizing conventional parameters [9]. The electrocoagulation and the integrated electrocoagulation-ozone processes were monitored for color, turbidity, and chemical oxygen demand (COD), as well as pH variation. A UV-Vis spectrum of the effluent was done on a Perkin Elmer Lambda 25. The color and turbidity were monitored at 465 and 860 nm wavelength, respectively using a HACH DR/4000U 110 spectrometer. COD was analyzed by the closed reflux colorimetric method. The pH during treatment was monitored with an OAKTON pH/CON 300 Series.

Cyclic voltammetry of initial and treated wastewater was carried out in a standard three-electrode cell using a Basi Electrochemistry Cell Stand EpsilonTM C-3 potentiostat at a scan rate of 100 mV s^{-1}. The working electrode was a circular carbon paste electrode (CPE) prepared in a 1:1 mixture of graphite (Alfa Aesar) and nujol oil (Aldrich). An Ag/AgCl electrode was used as the reference electrode and a glassy carbon electrode as the counter electrode.

2. AOPs

Advanced oxidation experiments were carried out with ozone in a laboratory scale reactor consisting of a 60 cm acrylic column with a 20 cm internal diameter. The reactor was a batch type reactor filled with 2.5 L of effluent. The ozone was supplied at the bottom of the reactor through a stone diffuser for 40 min. Samples were taken every 10 min and the excess ozone was led to a trap containing a solution of 0.1 M KI. Ozone was produced by a Lab21 ozone generator, providing 5.2 g O_3 h^{-1} using air (21% O_2) as feed to a flow of 0.283 Nm^3 h^{-1} and 1.4 kPa.

3. Electrocoagulation-ozone Integrated Process

The electrocoagulation-ozone integrated process was performed by coupling the ozonation simultaneously with an electrocoagulation process in the reactor previously described for AOPs.

Aluminum rectangular plates were used as the anode and cathode in the electrocoagulation process. The active surface area of the electrodes was 343 cm^2 and the ratio of surface area to volume was 0.137 cm^{-1}. A current of 0.1 A at 16 V DC was supplied to the system using a GW-1820 HD ISTEK GPR power source to obtain 0.292 mA cm^{-2} of current density, which remained constant throughout the experiment. Electrocoagulation was performed without additional electrolytes. A 30 mL sample was taken every 5 min during the 40 min of treatment. The samples were allowed to stand for 1 h and then analyzed.

RESULTS AND DISCUSSION

The wastewater showed the following initial values: 1075 mg L^{-1} COD, 308 Pt-Co color, 61 FAU turbidity, 3.66 pH, 1488 µS cm^{-1} for electrical conductivity, 304 mg L^{-1} chloride, 492 mg CaCO$_3$ L^{-1} total hardness, and 208 mg L^{-1} alkalinity.

1. Color Removal

For the electrocoagulation process the removal of color was rapid in the first 10 min, then increased gradually for the duration of the reaction with values of 9, 18, 19, 19, 19, 20, 20 and 20% at 5, 10, 15, 20, 25, 30, 35 and 40 min of reaction, respectively. Similar results were obtained with the ozone process up to 30 min. After 40 min of ozone treatment the color was reduced by 32%, but when it was coupled with electrocoagulation in the integrated process, the effectiveness rose to 84%, as shown in Fig. 1a. For the ozone process, -color -r-eduction can be attributed to the reaction of ozone with the unsaturated bonds of indigo carmine, leading to the breaking of bonds and dissociation of the rings, according to the Criegee mechanism [10]. In the process of electrocoagulation Al^{3+} and OH^{-} ions generated at the electrode surfaces react to form an aluminum hydroxide gelatinous solid [11], which destabilizes and agglomerates the particle suspension absorbing and precipitating dissolved contaminants [12]. The reaction- kinetics for the removal of color in the integrated process was first order, with an r^2 fit of 0.985.

Similarly, the removal of turbidity was more efficient in the integrated process than the ozonation alone. Ozonation reduced the turbidity by 34%, with the integrated process reduction by 92%.

2. COD Removal

After 40 min of treatment, the COD reduction for electrocoagulation and ozone processes were up to 5 and 7%, respectively; whereas it rose to 8% for the electrocoagulation-ozone integrated process (Fig. 1b). In the ozone process, oxidation activity of hydroxyl radicals is limited by the presence of inhibitors (hardness, chlorides, alkalinity, conductivity) so these ions terminate the chain reaction and inhibit the decomposition of ozone to hydroxyl radicals which cause an incomplete degradation of the organic matter of treated wastewater [11]. On the other hand, the aluminum hydroxide formed in the electrocoagulation process removes ions and organic compounds, absorbing precipitating dissolved contaminants [12] and resulting in a slightly increased efficiency of COD removal.

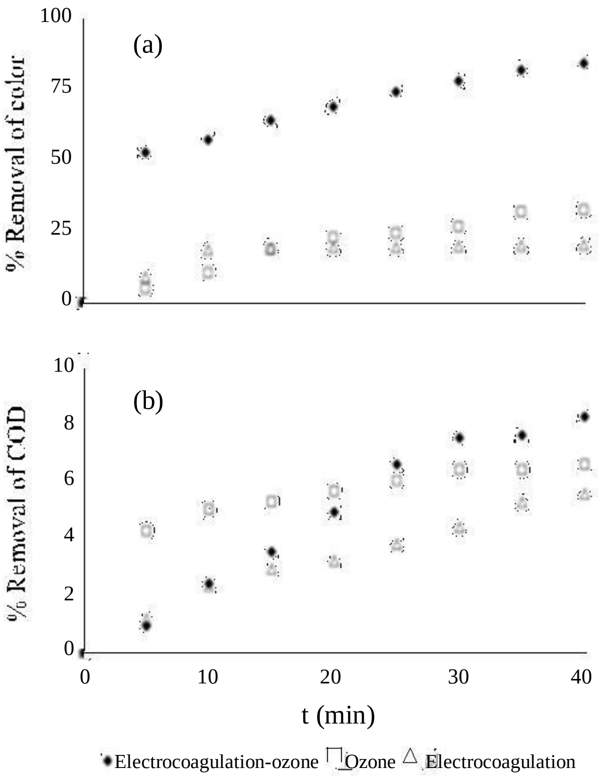

Fig. 1. Contaminant removal efficiency in wastewater treated in the different processes. (a) color, (b) COD.

3. pH Variation

There was no significant change in the pH values for the process with ozone, the pH remained close to the initial value of 3.7. For the electrocoagulation-ozone integrated process pH values decreased gradually to 2.7 after 30 min of reaction, remaining constant through 40 min.

4. Cyclic Voltammetry

Figure 2 shows the voltammograms of the raw and treated wastewater starting from the potential scan in positive direction. The results of cyclic voltammetry show both an oxidation and reduction process, and also show a capacitive current that can be related to the dye degradation. When cyclic voltammetry is applied to the treated wastewater after the electrocoagulation-ozone integrated process, the peaks do not appear, indicating that pollutants have been oxidized.

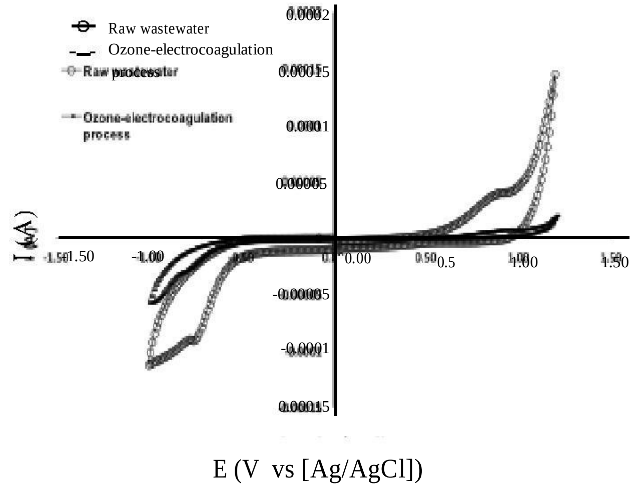

Fig. 2. Cyclic voltammograms over the window of potential from -1.5 to 1.5 V at a scan rate of 0.1 V s^{-1} with CPE working electrode.

5. UV-Vis Spectrum

The raw wastewater UV-Vis spectrum (Δ) has a baseline with two absorbance peaks, the first peak at 290 nm and the second at 665 nm, which are associated with the contaminants in the matrix (1075 mg L^{-1} COD) and the color of the sample (308 Pt-Co). For the first 40 min reaction, the treated wastewater in the electrocoagulation-ozone integrated process showed a decrease in the two absorbance peaks and at baseline, as shown in Fig. 3. The oxidation of organic contaminants, degradation of indigo carmine dye and the elimination of inorganic contaminants is indicated by the decrease in the absorption bands at 290, 655 nm, and the baseline, respectively.

CONCLUSIONS

The integrated electrocoagulation-ozone process resulted in increased effectiveness in the removal of color, COD, and turbidity as compared to the treatments with ozone or electrocoagulation alone in the denim processing effluent studied. The pH was maintained without significant changes during all treatments performed.

Spectra intensity decreases between raw and treated wastewater indicating the oxidation and removal of organic compounds in the integrated process. This result is consistent with cyclic voltammetry results.

Given the physicochemical characteristics of the treated wastewater, hardness, chlorides, alkalinity, conductivity, and total solids could compete with hydroxyl radicals decreasing the removal efficiency of color, turbidity, and COD in the processes studied.

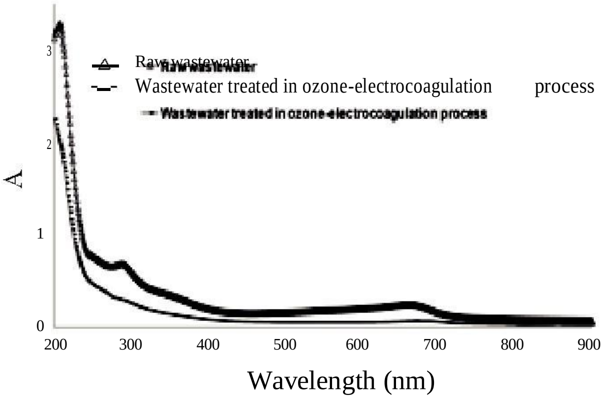

Fig. 3. Raw and integrated process treated wastewater UV-vis spectra.

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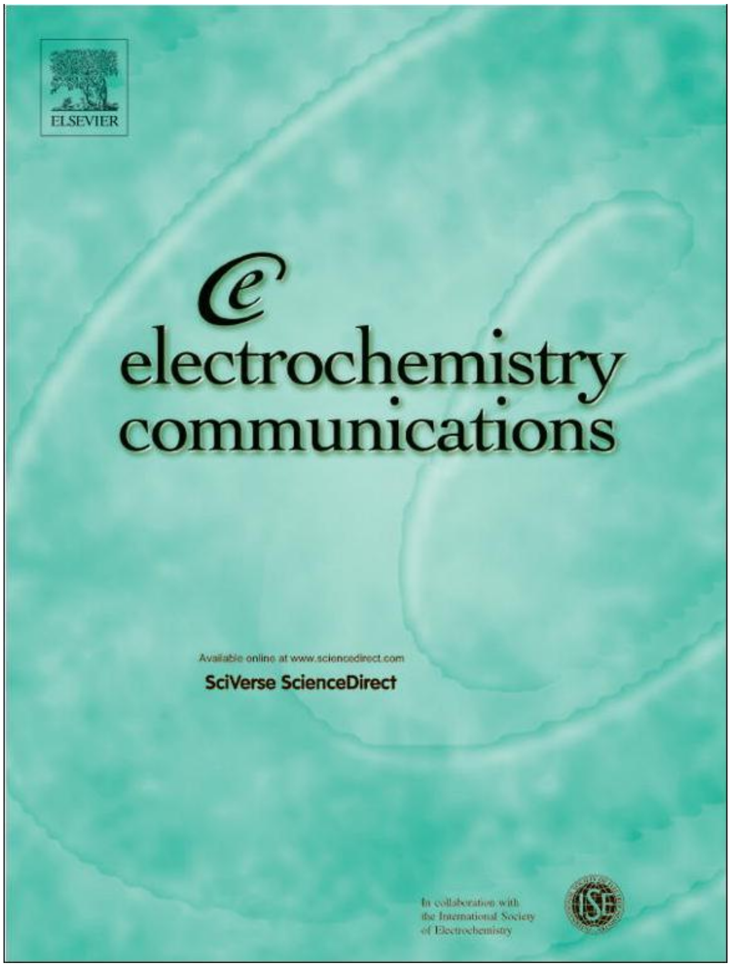

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Synergy of electrochemical oxidation using boron-doped diamond (BDD) electrodes and ozone (O_3) in industrial wastewater treatment

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abstract

This work evaluates the coupling of electrochemical oxidation and ozonation to reduce the high organic load of industrial wastewater quickly and effectively. Ozonation alone is shown to only reduce the COD of waste-water by about 45%. Electrochemical oxidation using boron-doped diamond electrodes reduces the COD by 99.9%, but requires over 2 h per 0.7 L batch. However, when the two processes are coupled, the COD is re-duced by 99.9% along with most color and turbidity in about an hour. The coupled process practically elimi-nates the COD, color, and turbidity without the addition of chemical reagents or changing the pH and doesn't generate any sludge, so it is both effective and environmentally friendly.

1. Introduction

Industrial effluents are difficult to treat using traditional biological systems due to the high variations in their compositions. Unlike munic-ipal wastewater, industrial sources have higher organic load, color, and pH which fluctuate [1,2]. While traditional biological reactors are very effective in digesting the organic matter in municipal wastewater into carbon dioxide and water, the effectiveness drops considerably when treating industrial wastewater. Biological reactors typically only reduce 50% of the biochemical oxygen demand (BOD_5) and 35% of the chemical oxygen demand (COD) [3,4].

Due to the limitations of biological reactors, industrial wastewater is typically pretreated using physical–chemical processes such as co-agulation–flocculation. However, these processes generate large quantities of sludge and usually require pH adjustments and chemical reagents, all of which create their own environmental issues [5,6]. Co-agulation–flocculation is not efficient in the removal of dissolved (persistent) chemical pollutants.

In recent works we have shown that combining electrocoagulation and ozone produces synergistic effects in wastewater treatment [7,8]. However, the use of electrooxidation with boron-doped diamond (BDD) electrodes in conjunction with ozone for treating industrial efflu-ents has not yet been reported.

Both electrooxidation and ozonation are advanced oxidative pro-cesses based on the generation of hydroxyl radicals ($OH^{\bullet}$), which have high oxidation potential and degrade of a wide range of contam-inants. In particular, BDD electrodes have high anodic stability, a wide working potential window, and low stable voltammetric background current in aqueous media [9,10]. Therefore, the electrochemical be-havior of BDD electrodes have been investigated with the goal of de-veloping applications for wastewater treatment [11,12]. On the other hand, ozonation is an efficient and powerful oxidizing process well known for its degradation of organic compounds. The limitations to these processes are the time required for electrooxidation and the ef-fectiveness of ozonation, so neither alone is truly industrially practical.

Thus, this study evaluates the synergy of the two processes com-pared to the efficiency and effectiveness of the individual ones. The effectiveness is evaluated in terms of color, turbidity and chemical ox-ygen demand (COD) reduction. The influence of operating parame-ters such as time of treatment, current density, and initial pH is also evaluated.

2. Materials and methods

2.1. Wastewater samples

Wastewater samples were collected from the treatment plant of an industrial park, which receives the discharge of 144 different facil-ities. Therefore, the chemical composition of this effluent is rather

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complex. Samples were collected in plastic containers and cooled down to 4 °C, then transported to the laboratory for analysis and treatment. The pH of the raw wastewater is 8.24 and all treatment and testing were done at this value.

2.2. Electrooxidation reactor

A batch cylindrical electrochemical reactor was set up for the electrochemical process. The reactor cell contains a pair of BDD electrodes (BDD film supported on a niobium substrate), each electrode was 20.0 cm by 2.5 cm with a surface area of 50 cm^2. Batch volumes of 0.70 L were treated in the 1.00 L reactor. A direct-current power source supplied the system with 0.5, 1.0, and 1.5 A, corresponding to current densities of 10, 20, and 30 mA/cm^2.

2.3. Ozonation reactor

The ozone experiments were conducted in a 1.5 L glass reactor at 18 °C. Ozone was supplied by a Pacific Ozone Technology generator. The gas was fed into the reactor through a porous plate situated at the reactor bottom. The ozone concentration at the gas inlet and out-let of the reactor was measured by redirecting the flow to a series of flasks containing 0.1 M potassium iodide. The mean concentration of ozone in the gas phase was 5±0.5 mg/L and was measured imme-diately before each run. Ozonation experiments were carried out at the pH of raw wastewater and samples were taken at regular inter-vals to determine COD.

2.4. Synergy of electrooxidation/O_3 process

For the combined system the pair of BDD electrodes from the electrooxidation reactor was installed in the ozone reactor. Ozone was introduced at the same rate and the BDD electrodes were given the same current densities as in the individual reactors. Treated sam-ples were taken at the same intervals and were analyzed in the same way.

2.5. Methods of analysis

The initial evaluations of the electrochemical, ozonation, and inte-grated treatments were determined by analysis of the COD (mg/L), color (Pt–Co scale), and turbidity (NTU scale). COD was determined by the open reflux method according to the American Public Health Association (APHA). Following this method, samples are refluxed with potassium dichromate and sulfuric acid for 2 h. Once the opti-mal conditions were found the raw and treated wastewater samples were analyzed using the standard methods for the examination of water and wastewater procedures. [13].

3. Results and discussion

3.1. Electrooxidation treatment

The COD reduction (%) as function of electrooxidation treatment time on the raw wastewater is shown in Fig. 1. The maximum COD re-duction of 99.9% was observed at 140 min of treatment.

3.2. Ozonation treatment

Ozone was introduced into the sample at a concentration of 5± 0.5 mg/L and the COD was measured as a function of time. As shown in Fig. 2, the maximum COD reduction was 45% at 120 min of treatment time.

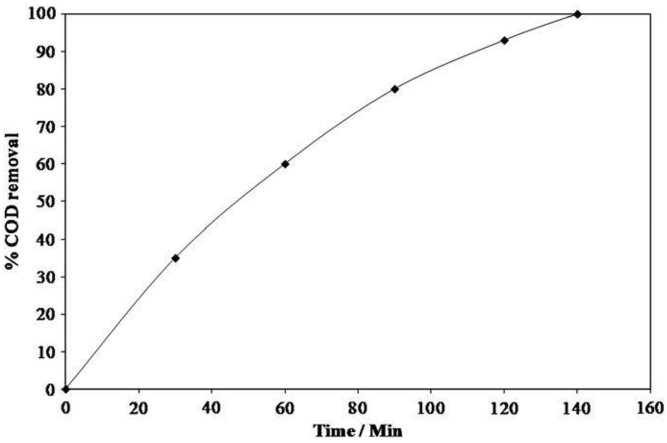

Fig. 1. COD removal as a function of electrooxidation treatment time at 10 mA/cm^2.

3.3. Synergy of electrooxidation/O_3 process

The effect of coupling electrooxidation and ozonation processes was studied through a series of experiments using the COD reduction as a function of treatment time for the raw wastewater. In Fig. 3 the effect of variation on the current density values is also described. The maximum COD reduction of 99.9% occurs at 60 min.

A comparative graph of the COD reduction as a function of treat-ment time among the three treatments indicates that ozone is not as effective and electrooxidation takes longer than the coupled pro-cess (Fig. 4).

The UV–vis spectra of the raw and treated wastewater are shown in Fig. 5. The raw wastewater shows considerable absorbance in the visible range of 300 to 630 nm which confirms that it is highly col-ored. However, this color is effectively removed by the coupled treatment.

The reduction in the values of some physicochemical parameters of the raw and treated wastewater is shown in Table 1.

As shown in Table 1, the coupled process reduces and practically eliminates the organic pollutants in the wastewater. The high levels of COD, color, and turbidity are effectively reduced without any addi-tion of chemical reagents and without adjusting the pH. The coupled process also increases the efficiency of the organic removal by reduc-ing the treatment time. Thus the two processes act synergistically in the coupled process.

Previous research [14] indicates that the oxidation of organics with concomitant oxygen evolution assumes that both organic oxidation

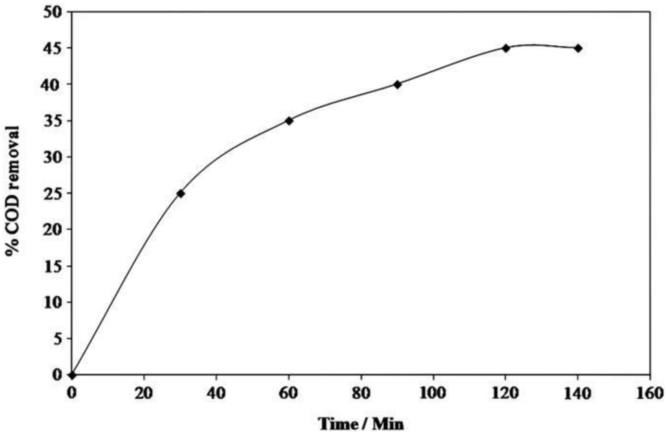

Fig. 2. COD removal as a function of ozonation (5±0.5 mg/L) treatment time.

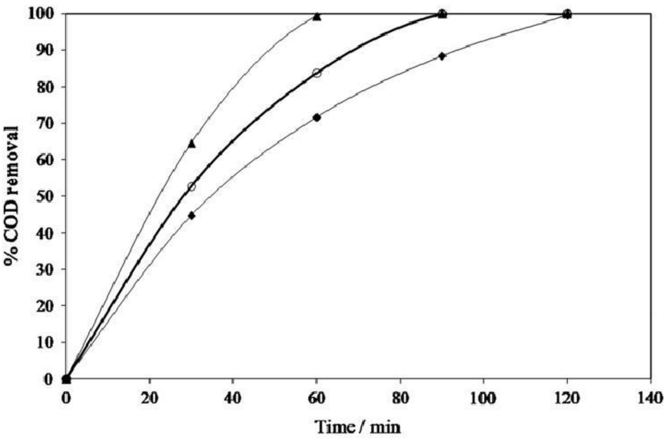

Fig. 3. COD removal when coupling electrooxidation and ozonation processes at three different current densities (▲) 30 mA/cm^2 (○) 20 mA/cm^2 (♦) 10 mA/cm^2.

and oxygen evolution take place on a BDD anode surface via intermedi-ation of hydroxyl radicals, generated from the reaction with water shown in Eqs. (1) and (2):

$$BDD \text{ þ } H_2O \rightarrow BDDðOH^{\bullet}Þ \text{ þ } H^{þ} \text{ þ } e^{-} \qquad ð1Þ$$

$$BDDðOH^{\bullet}Þ \text{ þ } R \rightarrow BDD \text{ þ } mCO_2 \text{ þ } nH_2O: \qquad ð2Þ$$

Reaction (2) is in competition with the side reaction of hydroxyl radical conversion to O_2 without any participation of the anode sur-face as indicated in Eq. (3)

$$BDDðOH^{\bullet}Þ \rightarrow BDD \text{ þ } 1{=}2O_2 \text{ þ } H^{þ} \text{ þ } e^{-}: \qquad ð3Þ$$

The ozone contribution can be attributed to the electrophilic na-ture of the direct attack by O_3 molecules (Eq. (5)) and the indirect at-tack via $OH^{\bullet}$ radicals in the ozonation process (Eq. (6)).

According to Tomiyasu et al. [15] the ozonation effect may be ini-tiated by the following reactions:

$$O_3 \text{ þ } H_2O \rightarrow 2HO^{\bullet} \text{ þ } O_2 \qquad ð4Þ$$

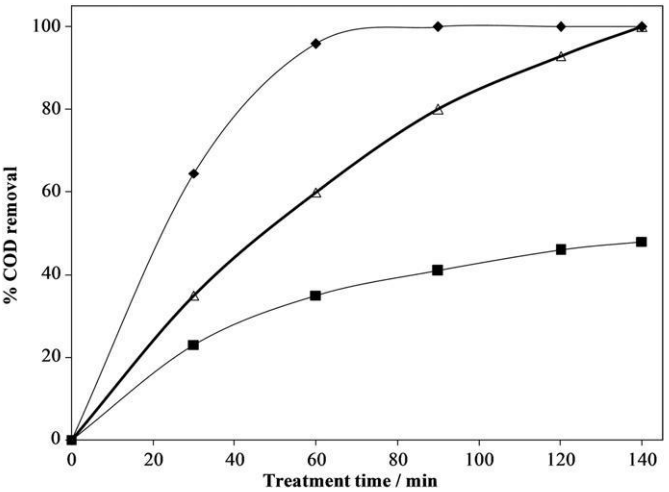

Fig. 4. COD removal as a function of treatment time of (♦) coupled, ( ) electrooxidation and (■) ozone treatment.

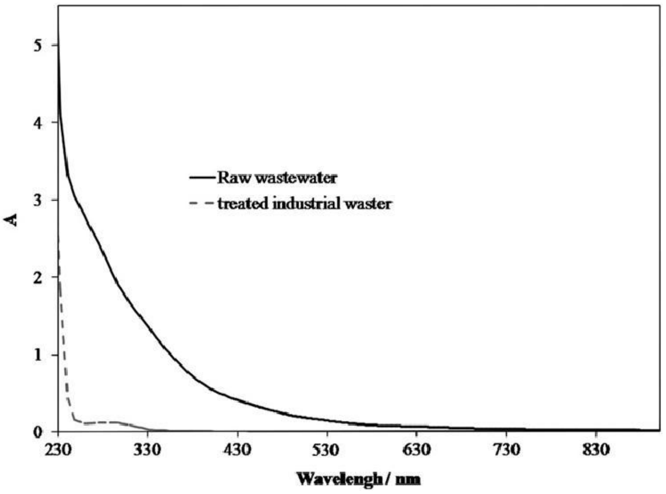

Fig. 5. UV–vis spectra of the (——) raw and (- - - -) treated industrial wastewater. The parameters of the coupled treatment were 30 mA/cm^2 and 5±0.5 mg/L of ozone.

$$O_3 \text{ þ } OH \rightarrow O_2^{\bullet -} \text{ þ } HO_2^{\bullet} \qquad ð5Þ$$

$$O_3 \text{ þ } OH^{\bullet} \rightarrow HO_2^{\bullet} \text{ þ } O_2: \qquad ð6Þ$$

According to the literature, the pH value of the solution signifi-cantly influences ozone decomposition in water since basic pH causes an increase of ozone decomposition. At pH b 3 hydroxyl radicals do not influence the decomposition of ozone. For 7 b pH b 10, the typical half-life of ozone is 15 to 25 min. [16].

4. Conclusions

The combination of electrooxidation and ozonation processes re-sults in a synergy that greatly enhances the rate and extent of remov-al of COD, color, and turbidity from a chemically complex industrial effluent. Electroxodiation alone reduces the COD to less than 1% of the initial, but requires a relatively long time of 140 min. On the other hand, ozonation alone only reduces it to 45%. When the coupled electrooxidation–ozonation process is used a maximum 99.9% of COD is removed in only 60 min under the optimal conditions: pH 8.24, with 5±0.5 mg/L of ozone concentration, and 30 mA/cm^2 of current density. While electrooxidation efficiency usually increases with in-creasing current density, the coupled process is more efficient at a rel-atively low (mA/cm^2) current density.

Acknowledgments

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Table 1
Physicochemical parameters of the raw and treated industrial wastewater.

Parameter	Raw wastewater	Treated wastewater
COD/mg L^{-1}	534	b1
Color/Pt–Co units	880	b50
Turbidity/NTU	52	b5

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CAPÍTULO 3

DISCUSIÓN GENERAL

Artículo 1: Treatment of soft drink process wastewater by ozonation, ozonation-H_2O_2 and ozonation-coagulation processes.

En esta investigación se estudió el tratamiento del agua residual del proceso de fabricación del refresco mediante oxidación con ozono. También se utilizó un esquema integrado secuencial de ozono – peróxido – coagulación para reducir los contaminantes presentes. Se evaluó efecto del ozono y del coagulante junto con la eficiencia del tratamiento integrado en las condiciones óptimas; observándose que había una mejor eliminación de color y turbidez en el proceso integrado acompañado por una reducción de la DQO. Los espectros de absorbancia de los productos oxidados se compararon mediante espectroscopia UV - VIS para indicar el nivel de oxidación de las aguas residuales. También se determinó la cinética de la decoloración y la eliminación de la turbidez con el mejor tratamiento. El mismo tratamiento integrado se aplicó a la muestra tomada del efluente final del sistema de lodos activados, obteniendo una eficiencia de eliminación de DQO del 100% en los primeros minutos de la reacción. El tratamiento integrado aplicado al agua residual de la fabricación de refrescos es el más eficiente para la eliminación de turbidez y color y representa una opción ventajosa para eliminar estos contaminantes debido a que su remoción se llevó a cabo en minutos en comparación con la duración de los procesos fisicoquímicos y biológicos tradicionales que requieren horas o días.

Artículo 2: Integrated Advanced Oxidation Process (Ozonation) and Electrocoagulation Treatments for Dye Removal in Denim Effluents.

Esta investigación tuvo como objetivo estudiar la eliminación del colorante índigo carmín utilizado en el proceso industrial del teñido de mezclilla. Para este fin se al agua residual los procesos de ozonación y electrocoagulación por pulsos así como el proceso integrado ozono – electrocoagulación por pulsos. Después de aplicarse el tratamiento con ozono se obtuvo una eliminación de color y turbidez muy superiores al tratamiento de electrocoagulación. Sin embargo; usando el proceso integrado estas eficiencias de remoción fueron obtenidas en un tiempo mucho menor. La sinergia asociada a la integración de ambos procesos resultó en un aumento en la eficiencia de la eliminación del color, COD y turbidez en comparación con los resultados obtenidos con los tratamientos individuales. La disminución en la intensidad del espectro UV-VIS entre el agua residual cruda y el agua residual tratada indican la oxidación y eliminación de contaminantes removidos que se llevaron a cabo en el proceso integrado. Este resultado es consistente con los voltamperogramas cíclicos obtenidos.

Artículo 3: An integrated electrocoagulation and ozonation process for removal of indigo carmine dye from denim processing effluent.

El objetivo de esta investigación fue mejorar la eficiencia de la eliminación del color del agua residual de la industria textil mediante la integración de los procesos de oxidación con ozono y electrocoagulación aplicando corriente continua. El efluente estudiado corresponde a una planta de teñido de mezclilla donde el contaminante primario es el colorante índigo carmín. El proceso con ozono no fue tan eficiente como el proceso acoplado con electrocoagulación el cual mejoró notablemente la eficiencia obtenida en la eliminación de DQO, color y turbiedad. Los espectros de UV-Vis y el voltamperograma cíclico obtenido muestran también la eliminación y oxidación de contaminantes en agua residual tratada.

Artículo 4: Synergy of electrochemical oxidation using boron-doped diamond (BDD) electrodes and ozone (O_3) in industrial wastewater treatment.

En este trabajo se evalúa el acoplamiento del proceso de ozono con la oxidación electroquímica para reducir la elevada carga orgánica de las aguas residuales industriales con rapidez y eficacia. Los resultados obtenidos en el proceso con ozono muestran que solo se pudo reducir el 45% de DQO. La oxidación electroquímica usando electrodos de diamante dopados con boro reducen la DQO en un 99%, pero este proceso requiere mas de 2 h para 0.7 L por lote. Sin embargo, cuando se acoplan los dos procesos, la DQO se reduce a 99% junto con la mayor parte de color y turbiedad en 60 min. El proceso integrado elimina prácticamente toda la DQO, color y turbidez en el agua residual en estudio sin la adición reactivos químicos o la modificación del pH y genera muy pocos lodos por lo que es una tecnología eficaz y amigable con el medio ambiente.

CAPÍTULO 4

CONCLUSIONES

Dadas las características físico-químicas de las aguas residuales industriales tratadas procedentes de los procesos de la fabricación de refrescos, de la industria textil y de Reciclagua los cloruros, carbonatos, bicarbonatos, dureza y ST compiten con los radicales hidroxilo disminuyendo la eficiencia de remoción de DQO en los tratamientos estudiados.

Los experimentos de oxidación química con ozono acoplado a los procesos de electrocoagulación y electro-oxidación resultaron en una sinergia que incrementó la eficiencia en la remoción de la DQO, color, turbidez, ST y sólidos sedimentables en relación con los procesos terciarios de tratamiento de aguas residuales industriales no acoplados.

La disminución en la intensidad de los espectros entre el agua residual cruda y el agua residual tratada en los diferentes procesos acoplados estudiados indican la oxidación de los contaminantes en las aguas residuales tratadas.

La disminución en la intensidad de los espectros entre el agua residual cruda y el agua residual tratada indican la oxidación y eliminación de compuestos orgánicos en el proceso integrado. Este resultado es consistente con los voltamperogramas cíclicos obtenidos.

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ANEXO

Mexico

64th Annual Meeting
of the International Society of Electrochemistry

8 to 13 September, 2013
Queretaro, Mexico

CERTIFICATE OF ATTENDANCE

This is to certify that **Marco Antonio García Morales** participated with the Poster presentation entitled
Synergy of electrochemical oxidation using boron-doped diamond (BDD) electrodesand ozone (O3) in industrial wastewater treatment
(Authors: Marco Antonio García Morales, Gabriela Roa Morales, Carlos Barrera Diaz, Verónica Martínez Miranda)
at the 64th Annual Meeting of the International Society of Electrochemistry
on 8 to 13 September, 2013 in Queretaro, Mexico.

Dr. Yunny Meas
Co-Chair, Organizing Committee
64th Annual ISE Meeting in Queretaro, Mexico

Evento Científico Mex-Esp

CIATEC

Otorga el presente

RECONOCIMIENTO

a:

Marco Antonio García Morales

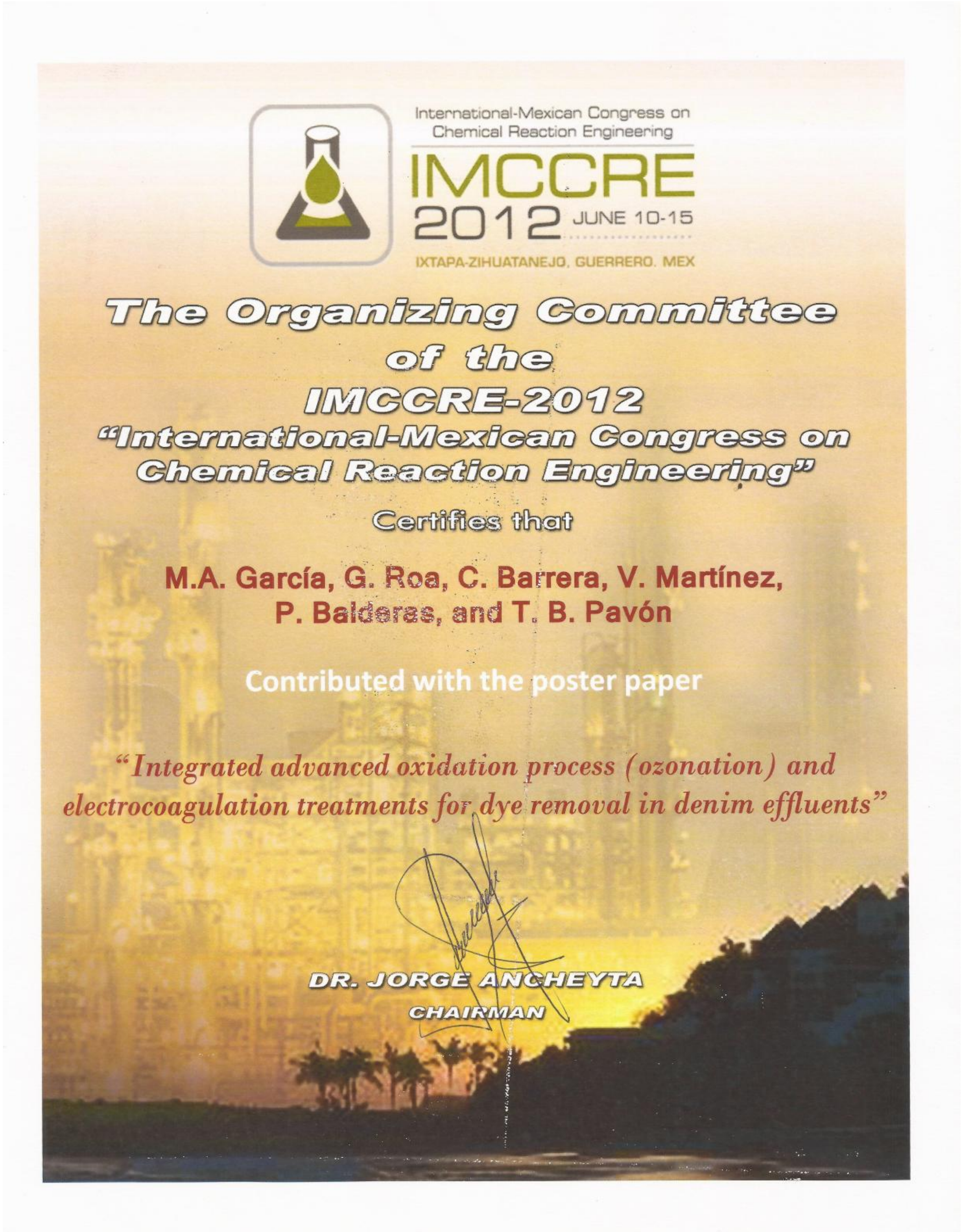
Por su valiosa participación en el evento
Científico México - España
Actualización en la aplicación de "PROCESOS AVANZADOS DE OXIDACIÓN"
fotoquímicos y electroquímicos
para llevar a cabo el tratamiento de agua
celebrado el miércoles 29 de mayo del presente año.

León, Guanajuato México a 29 de mayo del 2013.

Dr. Ricardo Jaime Guerra Sánchez
DIRECTOR GENERAL DE CIATEC, A. C.

Dr. Juan Manuel Peralta Hernández
PRESIDENTE DEL COMITÉ ORGANIZADOR

PAO-CON-06



International-Mexican Congress on Chemical Reaction Engineering

IMCCRE 2012 JUNE 10-15

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of the
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"International-Mexican Congress on Chemical Reaction Engineering"

Certifies that

M.A. García, G. Roa, C. Barrera, V. Martínez, P. Balderas, and T. B. Pavón

Contributed with the poster paper

"Integrated advanced oxidation process (ozonation) and electrocoagulation treatments for dye removal in denim effluents"

DR. JORGE ANCHEYTA
CHAIRMAN

XXXIII Encuentro Nacional y
II Congreso Internacional de la **AMIDIQ**

San José del Cabo, BCS, México. Del 01 al 04 de Mayo del 2012.

"LA INGENIERÍA QUÍMICA Y LA SUSTENTABILIDAD"

La Academia Mexicana de Investigación y Docencia
en Ingeniería Química, A.C. Otorga el presente

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a

Garcia Morales Marco Antonio, Roa Morales Gabriela, Barrera Diaz Carlos Eduardo, Martinez Miranda Veronica, Navarrete Rubio Giovanna, Rebollo González René.

Por la presentación del trabajo titulado:

"PROCESO INTEGRADO DE OXIDACIÓN AVANZANDA (OZONACIÓN) – ELECTROQUÍMICO PARA LA ELIMINACIÓN DE COLOR DE AGUA RESIDUAL INDUSTRIAL DEL TEÑIDO DE LA MEZCLILLA"

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y The Electrochemical Society

otorgan la presente

Constancia

A

M.A. García Morales, G. Roa Morales, C.E. Barrera Días, V. Martínez Miranda

Por la presentación del trabajo

Electrocoagulación integrada con oxidación avanzada para la eliminación de color en un efluente industrial del teñido de la mezclilla

en el ***XXVII Congreso de la Sociedad Mexicana de Electroquímica***
y el ***5th Meeting of the Mexican Section of the ECS***
celebrado del 11 al 15 de junio de 2012, en la ciudad de Toluca, México.

Dr. Norberto Casillas Santana
Presidente de la SMEQ

M. en A.P. Guadalupe Santamaría González
Directora de la Facultad de Química, UAEM

Dr. Carlos E. Barrera Díaz
Co-Presidente del Congreso

Dr. Bernardo A. Frontana Uribe
Co-Presidente del Congreso

UNIVERSIDAD AUTÓNOMA
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INSTITUTO DE
METALURGiA

La Universidad Autónoma de San Luis Potosí
a través del Instituto de Metalurgia

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CONSTANCIA

A **Marco Antonio García Morales**

Por su participación en el CURSO:

"Ingeniería Electroquímica"

Con una duración de 25 h,
impartido en el período del 18 al 22 de Junio de 2012,
en las instalaciones del Instituto de Metalurgia

Dra. María Isabel Lázaro Báez
Directora del Instituto de Metalurgia

Prof. José M. Bisang
Instructor del Curso

La Universidad Autónoma del Estado de México
a través de la Facultad de Química

otorga la presente

Constancia

a

Marco Antonio García Morales

por su participación como asistente al curso taller:
"Cálculo de Distribución de Corriente y Potencial"
que se llevo a cabo en el Centro Conjunto de Investigación en Química Sustentable
CICQS, UAEM—UNAM los días 2 y 3 de julio de 2012 con una duración de 12 hrs.

Toluca, México; a 3 de julio de 2012

Patria, Ciencia y Trabajo
"2012, Año Internacional de la Energía Sostenible para Todos"

M. en A.P. Guadalupe Ofelia Santamaría González
Directora

U. A. E. M.
FACULTAD DE QUIMICA
DIRECCION

Benemérita Universidad Autónoma de Puebla

Facultad de Ciencias Químicas

Instituto de Ciencias

Otorga la presente:

Constancia

A: Marco Antonio García Morales

Por su participación en la Jornada Binacional
“Materiales y Procesos de Aplicación Ambiental”

Realizado en la Facultad de Ciencias Químicas, del 29 de agosto al 2 de septiembre del año en curso.

“PENSAR BIEN, PARA VIVIR MEJOR”
H. Puebla de Zaragoza, 2 de septiembre de 2011

DIRECCION

M.C. BERTHA ALVARADO HIDALGO
DIRECTORA

Universidad de Guanajuato

La Universidad de Guanajuato

UNIVERSITY OF Southampton
School of Engineering Sciences

a través de

Posgrado en Química y Universidad de Southampton

otorga el presente reconocimiento a

MARCO ANTONIO GARCÍA MORALES

Por su asistencia al curso titulado

"Tecnología Electroquímica y Almacenamiento de Energía"

Celebrado en Guanajuato, Gto., del 6 al 8 de junio de 2011.
Con una duración de 20 horas
Con valor curricular

Martín Picón N

Dr. Martín Picón Núñez
Director de DCNE
Universidad de Guanajuato

Carlos Ponce de León

Dr. Carlos Ponce de León Albarrán
Profesor-Investigador de School of Engineering Sciences
University of Southampton