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REVIEW ARTICLE

TREATMENT OF PHARMACEUTICAL WASTE WATER BY ELECTRO-COAGULATION AND NATURAL COAGULATION PROCESS : REVIEW

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ABSTRACT

In the last years, the decontamination and disinfection of waters by means of direct or integrated electro-coagulation processes are being considered as a very appealing alternative due to the significant improvement of the electrode materials and the coupling with low-cost renewable energy sources. Many electro-coagulation technologies are currently available for the remediation of waters contaminated by refractory organic pollutants such as pharmaceutical micro-pollutants, whose presence in the environment has become a matter of major concern. Recent reviews have focused on the removal of pharmaceutical residues upon the application of other important methods like ozonation and advanced oxidation processes. Here, we present an overview on the electro-coagulation and natural coagulation (*Moringa Oleifera*) methods devised for the treatment of pharmaceutical residues from both, synthetic solutions and real pharmaceutical wastewaters. Electro-coagulation and Natural coagulation, which only isolate the pollutants from water, are firstly introduced. The fundamentals and experimental set-ups involved in technologies that allow the degradation of pharmaceuticals, like anodic oxidation, electro-oxidation with active chlorine, electro-Fenton, photo-electro Fenton and photoelectron catalysis among others, are further discussed. Progress on the promising electro-coagulation devised and further developed in our laboratory is especially highlighted and documented. The abatement of total organic carbon or reduction of chemical oxygen demand from contaminated waters allows the comparison between the different methods and materials. The routes for the degradation of the some pharmaceuticals are also presented.

Keywords : Pharmaceutical Waste Water, Electro-Coagulation, Natural Coagulation, Moringa Oleifera, Water Treatment.

1. INTRODUCTION

Wastewater produced from the pharmaceutical industries is hazardous and toxic, and also often has intensive color and disgusting odor. Most pharmaceuticals used for human medicine today were manufactured and recalcitrant. They survived throughout wastewater treatment process and finally were discharged into environment. The presence of pharmaceutical compounds in surface and ground water has been repeatedly reported. Many of those active substances were persistent and prone to transport. The impact of pharmaceutical chemicals on public health and environment has gotten increasing concern not only due to their acute toxicity but also their genotoxicity and mutagenic effects. Certain chemicals, especially some antibiotics, could neither be adsorbed nor be degraded by the sewage sludge. Meijie Ren et al, (2011) reported 8 pharmaceuticals in the raw and treated wastewater of 12 sewage treatment plants in Finland. Many of those active substances were persistent and prone to transport.

Hospitals are known to be intensive consumers of water, thus generating significantly higher wastewater flows than conventional households (400–1200 L bed^{-1} d^{-1} vs. 100 L $capita^{-1}d^{-1}$). Moreover, hospital effluents constitute a very complex water matrix, loaded with microorganisms, heavy metals, pharmaceuticals, toxic chemicals and radioactive elements. The direct discharge of these effluents into urban sewerage systems without preliminary treatment constitutes a potential risk to the environment, since conventional sewage treatment plants (STPs) have not been really designed for this specific purpose. Expected concentrations in hospital effluents are in the range of 5–50 g/L, although a high variability has been observed. According to the information gathered between 1997 and 2002 in 15 European countries, hospital care consumption as a proportion of total anti-biotic consumption can be quite significant ranging from 6.4% up to 17.8% .This proportion was reported to be as high as 26% in Germany, which appears to be the cause of the high concentrations (up to 100μg/L) reported for several antibiotics, such as b-lactams, fluoroquinolones, sulfona-mides and trimethoprim in different Sonia Suarez et al, (2009).

After intake, these pharmaceutically active compounds undergo metabolic processes in organism. Significant fractions of the parent compound are excreted in un-metabolized form or as metabolites (active or inactive) into raw sewage and waste-water treatment systems. Sewage treatment plant effluents are discharged to water bodies or reused for irrigation, and bio-solids produced are reused in agriculture as soil amendment or disposed to landfill. Thus body metabolization and excretion followed by wastewater treatment is considered to be the primary pathway of pharmaceuticals to the environment. Aleksandra Jelic et al,

(2011) reported the disposal of drug leftovers to sewage and trash is another source of entry, but its relative significance is unknown with respect to the overall levels of pharmaceuticals in the environment.

Although pharmaceutically active compounds had been detected previously in effluent from landfills and sewage-treatment plants (STPs) these more recent investigations indicated that some pharmaceutically active compounds are nearly ubiquitous at low concentrations in water bodies that receive STP effluent. Paul E.Stackelberg et al, (2004). As a consequence there are no specific rules or regulations for many industrial effluents, increasing efforts to provide treatment to liquid, solid and gaseous residues have stimulated the development of new technologies. Marcela Boroski et al, (2009).

These contaminants include antibiotics, other prescription drugs, non-prescription drugs, animal and plant steroids, reproductive hormones, personal-care products, detergent metabolites, flame retardants, products of oil use and combustion, and other extensively used chemicals, collectively referred to as organic wastewater contaminants (OWCs) .The frequent occurrence of these compounds in streams (Kolpin et al., 2002) , some of which are used as sources of drinking water, gives rise to concern over the potential for these compounds to occur in drinking water and, thus, to affect human health through chronic exposure.

Access to safe drinking water is a human right. Solution to this global problem is aimed to develop simple, effective, low-cost and easy to use technologies able to reduce organic, inorganic and microbiological water contamination. Coagulation represents a feasible and effective treatment due to its capacity to remove suspended particles of the water through the addition of certain chemicals known as coagulants. The most common ones are alum ($AlCl_3$), ferric-chloride ($FeCl_3$) and poly aluminum chloride (PAC). In spite of the effectiveness of these chemicals as coagulants are well-recognized, its application is not possible in poor areas of developing countries due to high cost and low availability of these products. Recently, concerns associated with the use of these coagulants such as detrimental effects on human health, production of large sludge volumes (toxic in some cases) and impact on the environment, question or even disregard its usage. There is also strong evidence linking aluminum based coagulants to the development of neurodegenerative illnesses as senil dementia (Rondeau et al., 2001) and with Alzheimer's disease in human beings (Gauthier, 2000). Poly-electrolytes are also questionated due to the toxicity and carcinogenetic potential of the monomers used for their synthesis, as in the case of poly-acryl amide, or due to the possible interference of the residual product in water with disinfection products. B. García-Fayos et al (2010).

In fact, it seems probable that most urban wastewater is contaminated with medicinal compounds (Jones et al., 2005). This pollution arises from emission from production sites, direct disposal of over plus drugs in households and hospitals, excretion from urine or feces after drug administration to humans and animals and water treatments in fish farms. The STP effluents then contain bio recalcitrant un-metabolized and metabolized pharmaceutical residues that are released in the receiving surface waters, mainly rivers (Klavarioti et al., 2009). Pharmaceuticals released in to the environment may impose toxicity potentially on any level of the biological hierarchy, although their effects on living beings are not yet well documented (Kümmerer, 2009). For example, it is usually accepted that some pharmaceuticals may cause long-term, irreversible changes to the micro-organisms genome, even at low contents, which therefore increases their resistance to them Esplugas et al., 2007; Klavarioti et al., 2009. Further-more, these pollutants often occur as complex mixtures, giving rise to 'drug cocktails' whose toxicity has been seldom predicted, as in the case of beta-blockers (Cleuvers, 2005). On the other hand, some pharmaceuticals have also been classified as endocrine disrupting compounds (EDCs) since they cause harmful effects on the human endocrine system (Esplugas et al., 2007; Klavarioti et al., 2009; Rahman et al., 2009). Ignasi Sirés et al, (2011).

The above considerations reflect the need for the complete removal of pharmaceuticals and their metabolites from aquatic systems to avoid their potential toxicity and other possible dangerous health effects. These pollutants cannot be totally destroyed in the STPs with conventional techniques like bioremediation and physicochemical treatments including coagulation, volatilization, adsorption, sedimentation and filtration (Jones et al., 2005; Rahman et al., 2009; Suárez et al., 2008). In most STPs, disinfection of final effluents is mandatory and chlorination and/or UV irradiation are applied, but both techniques exhibit low oxidation ability and the trace organic pollutants are refractory to their action (Khetan and Collins, 2007; Suárez et al., 2008). Recent research has then focused on the application of electro-coagulation followed by natural coagulation process, which are widely applied for the disinfection of reclaimed water, for treating pharmaceutical residues and pharmaceutical wastewaters. Electro-coagulation followed by natural coagulation processes environmentally friendly chemical, electrochemical methods based on the in situ production of hydroxyl radical (•OH) as main oxidant, that it is able to non-selectively react with most organics via hydroxylation or dehydrogenation until their total mineralization. Several reviews have extensively described the use of O_3, chemical AOPs (O_3/H_2O_2, Fenton's reagent (Fe_2+/H_2O_2), ultrasound and wet-oxidation) and photochemical AOPs (O_3/UV, H_2O_2/UV, photo-Fenton (Fe_2+/H_2O_2/U V)) and UV /solar TiO_2 photo-catalysis, alone or combined with physicochemical or biological treatments, for the decontamination of synthetic and real wastewaters with drugs (Esplugas et al., 2007;Ikehata et al., 2006; Klamerth et al., 2010; Klavarioti et al., 2009),chemical and pharmaceutical industrial wastewaters (Bloecher, 2007), urban wastewater (Suárez et al., 2008) and drinking water (Rahm an et al., 2009). In contrast, only few papers have summarized some data on the performance of electrochemical advanced oxidation processes (EAOPs) like anodic oxidation (AO), electro-Fenton (EF), and photo-electro-Fenton (PEF) to remove pharmaceuticals (Brillasetal. 2008, 2009; Garrido et al., 2007; Klavarioti et al., 2009).

2. EMERGING TRENDS: PHARMACEUTICAL WASTE WATER TREATMENT

Coagulation/flocculation processes can be used to treat several types of waters and wastewaters, being among the most commonly treated the supply waters A. Masion et al (2000), M. Franceschi et al (1999) the urban wastewaters, and wastewaters coming from different types of industries, such as those produced in the textile D. Georgiou et al (2003), chemical M.H. Al-Malack et al (1999), pharmaceuticall L.G. Torres et al (1997), metalworking P. Canizares et al and petrochemical A.A. Hafiz et al (2005) factories. Commonly, the conventional coagulation/flocculation processes involve three stages. In the first stage, chemical reagents are added to the wastewater, and these reagents produce the destabilization of the pollutants (or the formation of particles with reduced solubility from the pollutants). The aim of the second step is achieving the formation of solids with bigger size, and it is attained by a soft mix that allows the collision between particles and their aggregation. The last stage consists of the separation of the solids by settling or dissolved air flotation.

An alternative to the conventional process is electro-coagulation, which consists of the in situ generation of coagulants by the electro-dissolution of a sacrificial anode, usually of aluminum or iron P. Ca nizares et al (2009).In this process, a proper design of the electrochemical cell allows carrying out the three stages previously mentioned in a single compartment G. Chen, X et al (2000). Thus, the electro-dissolution of the sacrificial anode to the wastewater leads to the formation of hydrolysis products. (hydroxo-metal species) that are effective in the destabilization of pollutants P. Canizares et al (2009) and/or in the formation of particles with reduced solubility that entrap the pollutants P. Canizares et al (2006) .In addition, the hydrogen can be collected and used as fuel in a fuel cell to produce energy. Other advantages reported in literature for the electrochemical process is the lower operating costs compared to the conventional process, due to the low electric current required M. Bayramoglu et al (2007), M. Kobya et al (2007). In both coagulation processes (conventional and electrochemical) it is common the use of aluminum or iron reagents as coagulants. When these reagents are added to the wastewater, different hydrolysis species are formed. On the contrary, ferric hydroxide precipitate shows a much lower solubility over a rather broad pH range and this limits the influence of the monomeric species on the coagulation results J. Gregory et al (2001). As well, in addition to these species, it is reported the formation of polymeric hydroxo-metallic ions, especially under high metal concentrations J.Y. Bottero et al (1980), J.Y. Bottero et al (1982). All these hydrolysis metal species can interact with different types of pollutants, achieving their removal from the wastewaters. These interaction processes are strongly related to the metal speciation, and they can be summarized into three main types:

- The metallic ionic monomeric species can neutralize the charge of the pollutants by adsorption on their surfaces (or by binding to their ionized groups).
- The metallic ionic polymeric species can bind to several particles (or molecules) of pollutant at a time.
- The pollutants can be enmeshed into growing metallic hydroxide precipitates, or can be adsorbed onto their surfaces.

Oxidation processes are the most widely used effective tools for pharmaceutical wastewater treatment. However, some pharmaceuticals, especially the anthropogenic origins, could extremely resist oxidation. Thus, it is definitely necessary to take coagulation as pretreatment step for the removal of refractory products from pharmaceutical wastewater. Electro-coagulation (EC), as a burgeoning and environmental friendly wastewater treatment technique, has showed tremendous achievements on dealing with special problems. Many studies optimized the EC process for galvanic wastewater treatment I. Heidmann et al (2009) , removing Cu, Zn and Cr from electroplating wastewater N. Adhoum et al (2004), N. Daneshvar et al (2006), C.B. Diaz et al (2006), O. Abdelwahab et al (2009). Many benefits of EC have been showed in comparison with conventional coagulation techniques, including higher efficiency, simpler equipment, more flexible operation, less sludge, and no additional reagents. However, high energy consumption and anode passivation phenomenon have limited further application of EC technology. Fortunately the advent of pulse technique brought a significant impact on the electrochemical processes; it could not only save energy but also showed higher activity and efficiency during the process J. Zhou et al (2011), K. Xie et al (2010), A. Molina et al (2010).

Coagulation–flocculation and flotation are physico-chemical processes that can be applied at different stages of water treatment: (i) pre-treatment of industrial effluents before entering municipal sewer systems (Jain et al., 2001; Liu and Lien, 2001; Gautam et al., 2007); (ii) primary treatment of urban wastewater (Mels et al., 2001); (iii) tertiary treatment of urban wastewater (Chuang et al., 2006); and (iv) drinking water treatment plants, which typically combine coagulation with sand filtration, sorption by activated carbon and disinfection by ozone or chlorine. Sonia Suarez et al (2009).

The electro-coagulation process (EC) using metallic electrode is a technique used to remove organic and suspended materials from several types of effluent matrix. The fundament of the EC/metallic electrodes is the generation of Mn^{+} species in the metallic anode, which can suffer hydrolysis or form polymeric compounds; these species can absorb organic materials by charge or surface effects, leading the contaminants to coagulate. Depending on the formed flocks' characteristics, the hydrogen bubbles formed by water reduction in the cathode can promote the flotation of the aggregated pollutants. The EC process is highly dependent on physical–chemical characteristics of the effluent (nature, composition and concentration of the pollutants, solution conductivity, pH, electrolysis cell design (size/area and electrodes distance), electrolysis time, current and electrodes material). Several advantages are attributed to EC such as the contaminants removal rate, small apparatus size, easy maintenance and low equipment operation costs. Furthermore, there is no need of adding chemical agents, which can generate secondary pollution.

Continual improvements in analytical equipment and methodologies enable the determination of pharmaceuticals at lower and lower concentration levels in different environmental matrices. investigated the occurrence and distribution of pharmaceuticals in soil irrigated with reclaimed water Gielen et al., (2009); Kinney, (2006); Ternes et al., (2007) and soil that received biosolids from urban sewage treatment plants Carbonell et al., (2009); Lapen et al., (2008). Aleksandra Jelic et al (2011) indicated that the applied wastewater treatments are not efficient enough to remove these micro-pollutants from waste-water and sludge, and as a result they find their way into the environment.

Several studies investigated and reported on Cleuvers, et al (2004); Nentwig et al., (2004); Schnell et al., (2009) systems that use an activated sludge process are still widely employed for wastewater treatment, mostly because they produce effluents that meet required quality standards (suitable for disposal or recycling purposes), at reasonable operating and maintenance costs. However, this type of treatment has limited capability of removing pharmaceuticals from wastewater (Kasprzyk-Hordern et al., (2009); Wick et al., (2009). Most of the studies on the fate of pharmaceuticals in WWTPs focused only on the aqueous phase, and concentrations of the compounds in sludge were rarely determined mainly due to the demanding efforts required in the analysis in this difficult matrix Lillenberg et al, (2009), Lindberg et al. (2010); McClellan and Halden, (2010), Radjenovic et al (2009).

Michael Lea indicates that *Moringa oleifera* seeds coagulate 80.0% to 99.5% turbidity (surrogate for suspended fine particles) and color (surrogate for natural organic material), efficiently leading to an aesthetically clear supernatant. As a safer indicator, this was concurrently accompanied by a 90.00% to 99.99% bacterial load reduction (fecal coliforms), with bacteria concentrated in the sediment sludge. *Moringa* flocculants released from the crushed seed kernels have been characterized as basic polypeptides with a molecular weight between 6 and 16 kDa and an isoelectric pH of 10 to 11. They bind suspended particles in a colloidal suspension, forming larger sedimenting particles (flocs) that include pathogenic microorganisms Madsen et al., (1987). These findings highlight the importance of widespread dissemination of this rudimentary water treatment protocol (Basic Protocol 2 and Support Protocol 1) among the rural and peri-urban marginalized poorest of poor communities, contributing to improving equity, social justice, and the overall quality of life through the provision of potable water.

It is desirable a progressive replacement of these chemical coagulants with alternative coagulants and flocculants preferably from natural and renewable sources. Biopolymers would be of great interest since they are natural low-cost products, characterized by their environmentally friendly behaviour, and presumed to be safe for humans health. Even though, scientific community is researching new natural coagulant sources as Nirmali seeds (Strychnos potatorum), tannin, cactus and specially Moringa oleifera (Ying, 2010). Despite of promising results of Moringa oleifera seeds as a coagulant in the clarification of turbid water, research about its coagulant activity under real conditions and modification of 2 main quality parameters of the water treated are scarce. This study evaluates the performance of Moringa oleifera seeds in treating low turbidity surface waters in terms of physico-chemical and microbiological contamination removal, and compares it with the most common coagulant in drinking water treatment, PAC. B. García-Fayos et al (2010).

The history of the use of natural coagulants is long. Natural organic polymers have been used for more than 2000 years in India, Africa and China as effective coagulants and coagulant aids at high water turbidities. They may be manufactured from plants seeds, leaves and roots (Kawamura 1991). These natural organic polymers are interesting because comparative to the use of synthetic organic polymers containing acrylamide monomers, no human health danger and the cost of these natural coagulants would be less expensive over to the conventional chemicals like since it is locally available most rural communities. A number of effective coagulants from plant origin have been identified: Nirmali, Okra, red bean, sugar and red maize (Gunaratna et al. 2007), Moringa oleifera (Jahn 1988), Cactus latifera and seed powder of Prosopsi juliflora (Diaz et al. 1999). Natural coagulants have bright future and are concerned by many researchers because of their abundant source, low price, environment friendly, multifunction and biodegradable nature in water purification.

3. MATERIAL AND METHODS FOR ELECTRO-COAGULATION AND NATURAL COAGULATION OF PWW

A bench-scale reactor of 12.5 L with a virtual volume of 10 L was made of plexus glass and used throughout the experiments (Fig. 2).The distance between anode and neighboring cathode could be adjusted. The electrodes were polished and immersed in 1% W HCl (1) Pulse generator; (2) reaction tank; (3) pump; (4) electrodes, to the experiments, and weighed before and after the reaction. A Pulse current was supplied and record the cell voltages. After that the COD and the concentrations of BH of the wastewater at a wavelength of 340 nm was determined.

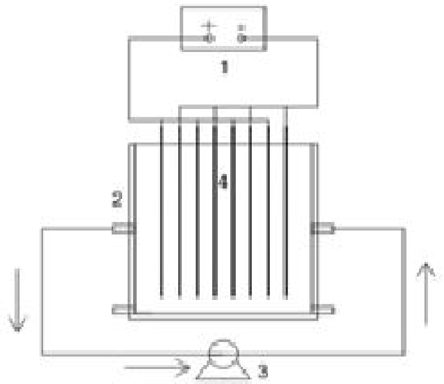

Fig. 1 : Schematic Representation of Pulse Electro-Coagulation

Source- Meijie Ren et al (2011)

Marcela Boroski et al (2009) investigate the EC apparatus consists of a pair of iron electrodes (dimensions: 12.50 cm × 2.50 cm × 0.10 cm of thickness), area approximately 31.25 cm 2, with the electrodes distanced by 2.0 cm. Electrodes were connected to a dc power supplier. The investigation of the desirable electro-coagulation time was carried out on a batch-type system by using 500 mL of original samples (as collected from the factory) at pH of 4.0, 5.0, 6.0, 7.0 and 10.0.After EC, part of the coagulated flocks settled down at the bottom of the vessel and part of the coagulated flocks flowed carried by hydrogen bubbles; these coagulated materials were separated.

The effluent after EC treatment executed at optimized operational conditions was submitted to the photo-catalysis with UV artificial irradiation Experiments were conducted in order to establish optimum photo-catalysis conditions such as pH, time, catalysts and hydrogen peroxide concentration. Measurements of pH, conductivity, turbidity, dissolved oxygen, chemical oxygen demand (COD), biochemical oxygen demand (BOD), organic and ammonia nitrogen, sulfate, phosphate, nitrite, nitrate and chloride of effluents samples were performed.

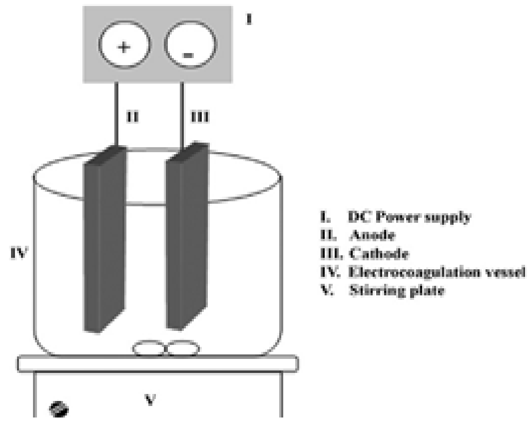

Fig. 2 : The Electro-Coagulation Apparatus

Source- Marcela Boroski et al (2009)

Pablo Canizares et al (2009) the electro-coagulation experiments have been carried out in a bench-scale plant with a single compartment electrochemical flow cell Aluminum electrodes were used as the anode and cathode. Both electrodes were square in shape (100 mm side) with a geometric area of 100 cm^2 each and with an electrode gap of 9 mm. The characterization of the hydrolyzed aluminum species generated has been carried out by ferron method. Monomeric species react almost instantaneously with ferron, whereas polymeric species have a much slower reaction rate with this compound.

Coagulation is a traditional physicochemical treatment of phase separation to precipitate colloidal and ionic species by adding coagulating agents such as Fe^{3+} or Al^{3+} ions in the form of chloride salts. Similar effects can be achieved by electro-coagulation (Chen, 2004), where a current is applied to dissolve Fe (or steel) or Al anodes immersed in the polluted water to release the corresponding metal ions yielding different Fe(II) (and/or Fe(III)) or Al(III) hydroxide species depending on the pH of the medium. These species act as coagulants or destabilizing agents that neutralize charges and separate colloids and ionic products from the wastewater by sedimentation, producing some sludge. The coagulated particles can also be separated by electro-flotation when they are attached to the bubbles of H^2 gas evolved at the cathode, being transported to the solution surface where they can be withdrawn.

When an iron or steel anode is used in EC, Fe2+ is dissolved in the wastewater from the anodic oxidation of Fe by reaction(1) , whereas H2 gas is generated at the cathode from proton reduction in acid medium by reaction(2) or water reduction in alkaline medium by reaction (3) :

$$Fe \rightarrow Fe^{2+} + 2e^- \quad (1)$$

$$2H^+ + 2e^- \rightarrow H_{2(g)} \quad (2)$$

$$2H_2O + 2e^- \rightarrow 2OH^- + H_2 \quad (3)$$

The in soluble Fe $(OH)_2$ precipitates at pH N 5.5, remain in g in equilibrium with Fe^{2+} up to pH 9.5 or with monomeric species such as $Fe(OH)^+$, $Fe(OH)_2$, and $Fe(OH)_3$ at higher pH values. In the presence of O_2, dissolved Fe^{2+} is oxidized to insoluble $Fe(OH)_3$ by reaction(4):

$$4Fe^{2+} + 10H_2O + O_{2(g)} \rightarrow 4Fe(OH)_{3(s)} + 8H^+. \quad (4)$$

4. COMPARATIVE STUDIES AND CHALLENGES

Comparison of Al and Fe Electrodes : Electrode materials have significant effects on the treatment efficiency of EC process N. Daneshvar et al (2007). High efficiency, easy to attain and non-toxic were the most important requirements for materials to be considered as electrodes P. Canizares et al (2007). Al and Fe were usually used as anodes in EC systems A.H. Essadki et al (2008), because they could generate hydroxides, oxy-hydroxides and polymeric hydroxides, which could successfully destabilize colloidal suspensions and emulsions, and form flocs that could be removed by sedimentation, filtration or flotation N. Daneshvar et al (2006). It showed that the removal efficiencies of COD and BH were significantly higher by using Fe electrode than by using Al electrode Meijie Ren et al (2011). With Fe electrode, the removal efficiency reached above 80% within 3.5 h, which was about twice as high as with Al electrode, the dissolution current efficiency was far higher for Al than for Fe electrode S. Zodi et al (2009).

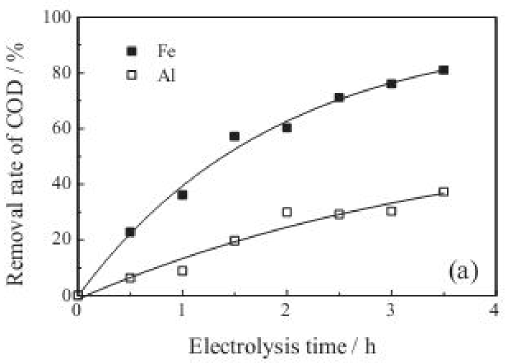

Fig. 3 : The Removal Efficiencies of COD and BH versus Time with Al and Fe Electrodes

Source Meijie Ren et al (2011)

Effect of Electrode Distance : Electrode distance played a significant role in the PE process. As showed in Fig. 7, the removal efficiencies of COD and BH ascended at first and then fell down with the increase of the electrode distance. The removal rates of COD and BH reached 68.0% and 72.0% separately at the optimum electrode distance of 2.0 cm. Short electrode distances inhibited the ion diffusion between electrodes, and reduced the coagulation efficiency, the electric resistance and voltage increased with the increase of the electrode distance, which caused higher energy consumption.

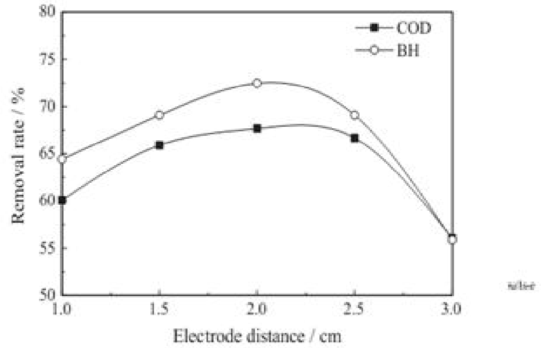

Fig. 4 : Effect of Electrode Distance on COD and BH Removal. Meijie Ren et al (2011)

Effect of Reaction Time : Electrolysis time was another vital factor affecting the treatment efficiencies of the PE process A.R. Khataee et al (2009). According to Faraday's law (Eq.(6)), the electrolysis time determined the total amount of Fe^{3+} and Fe^{2+} ions produced during the electrochemical process and subsequently affected the pollutant elimination efficiencies. Meanwhile, energy and material consumption ascended with the electrolysis time, so it was essential to determine the optimum reaction time.

$$\Delta M = \frac{MI\theta t_{PE}}{nF} \quad (6)$$

Where ΔM was the amount of iron dissolved (g); M was the molecular weight of the iron (g/mol); n was the number of electron moles (it should be 2 here); F was the Faraday constant (F).

Effect of pH : The effect of the initial pH on the EC treatment using iron electrodes (as cathode and anode) was investigated at constant $763 Am^{-2}$ current density and 30 min of electrolysis. The pH 6.0 was taken as optimum initial pH, which is employed for all subsequent EC experiments. At pH 6.0 the main Fen+ species formed in solution is $Fe(OH)^{2+}$ K. Xie, L et al (2010) , which can neutralize organic substances and suspended materials (usually presenting negative charge density) leading them to aggregation process.K. Xie, L et al (2010) At a pH higher than 10, the $Fe(OH)_4$ species is the main product; this species is not an effective coagulant agent.

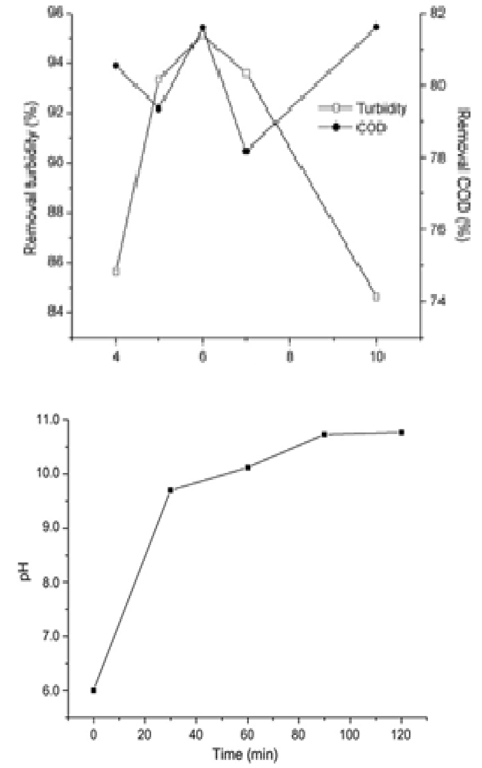

Fig. 5, 6 : COD and Turbidity Removals of EC-Treated Water At Several Initial pHs.

Source-Marcela Boroski et al (2009) pH Values Evolution During EC Time's Initial pH 6.0

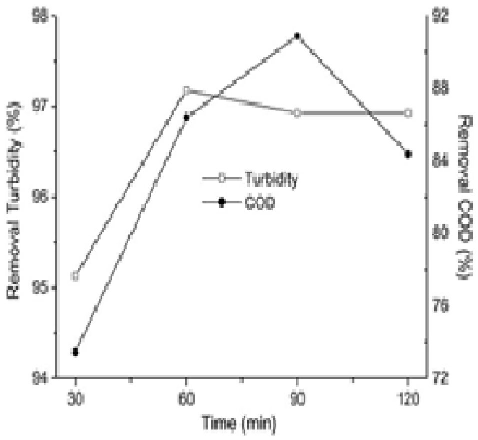

Fig. 7 : COD and Turbidity Removals of Water During EC. Initial pH 6.0

5. CONCLUSION

The treatment of pharmaceutical residues by means of several AOPs is progressively receiving greater attention due to their efficacy and/or efficiency. EAOPs, especially those based on the electro-coagulation, have been the most applied electrochemical processes for the treatment of synthetic aqueous solutions containing pharmaceutical residues .However, the formation of some refractory carboxylic acids requires the use of UV radiation from commercial lamps or sunlight and/or the use of high oxidation power anodes to take advantage of the anodic oxidation process based on the role of heterogeneous •OH. On the other hand, the real hospital and pharmaceutical wastewaters have been mostly treated by electrochemical oxidation with "non active" anodes such as BDD and electro-coagulation. The results showed that if we applied the combination of electro-coagulation followed by natural coagulation process it will improve the quality of the effluent with peptides residues, such as peptone fragments. The electro-coagulation removed the majority of the colloidal organic substances and suspended materials; however, refractory compounds still remained in this water effluent. In the sequence, by employing the natural coagulation, these refractory compounds were degraded up to mineralization (or at least to small and simple molecules). Such combined process of electro-coagulation and natural coagulation will be efficient and presents potential application in industrial scale. The majority of removal is evident during the filtration stage. These are encouraging results. The organic loading on any subsequent biological treatment stage would be much reduced.

Future work is planned to further explore this area by undertaking laboratory study of direct and dual filtration of wastewater as an effective primary treatment step before biological stabilization. There are issues to address and overcome before large-scale commercialization is possible, including: standardization of the products, securing compliance with relevant regulatory approvals (such as toxicological studies) and development of markets (local/regional/international). In-country processing will add a real value and stability to the products and their markets. This represents an exciting initiative and challenge for many countries. Multidisciplinary collaboration and rigorous economic analyses are essential elements for future and continued success.

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