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Experimental and kinetic study on the treatment of synthetic and real pharmaceutical wastewater by electrocoagulation

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In this research, the probability of using the electrocoagulation process as a method of pharmaceutical removal from synthetic and real industry wastewater was demonstrated. Batch experiments were performed using a simple laboratory scale electrochemical reactor with aluminium as anode and stainless steel as cathode, respectively. The effects of main operating parameters such as current density, initial pH, electrolyte concentration and inter-electrode distance have been studied. Kinetic equilibrium stu-dies have shown that the pseudo-first order equation is better suited to the aluminum hydroxide adsorption process with a strong correlation between experimental and theoretical data. The findings showed that maximum removal of total organic carbon (TOC) (66%) and chemical oxygen demand (COD) (62.5%) was achieved for real industry wastewater.

Keywords: Electrocoagulation, Total organic carbon (TOC), synthetic and real pharmaceutical wastewater.

Introduction

The availability and nature of water consistently have played an essential role in determining not only where the people can live but also their quality of life. From overall water resources, only 2.5% freshwater is available for human uses[1]. The scarcity of freshwater resources to meet water demand problems is getting more severe because of exhaustive depletion of water resources[2]. In India, one-third of total water pollution occurs through the industrial discharge of effluents, solid waste, and other hazardous waste[3]. Over the past decades, the Indian pharmaceutical sector has consistently been attracted to a growth rate of 15% to 20%[4]. Wastewater produced from the pharmaceutical industry is toxic and hazardous, also often intense color and unpleasant odor[2]. Wastewater is the main route of entry of pharmaceuticals into the environment. Their detection in the aquatic environment represents a significant concern in terms of their adverse effects on the environment and human health[3]. Paracetamol is a common drug in various pharmaceutical formulations because of its analgesic and antipyretic properties[4]. Pharmaceutical wastewater is generally classified as one of the main complex and toxic industrial wastewaters with high TOC, COD, biological oxygen demand (BOD), total suspended solids (TSS) and odor[5]. Although the volume of incompletely treated wastewater from the pharmaceutical industry is low, it contains non-biodegradable organic matter. In India, the Central Pollution Control Board (CPCB) sets standards for the discharge of pollutants from the pharmaceutical manufacturing industry to receiving bodies[6].

Investigation of characteristics of wastewater is important to estimate the quality of wastewater. The conventional wastewater treatment processes for various compounds present in pharmaceutical waste water appear to be ineffective[7]. But, the electrochemical treatment process is the most effective method for the treatment of all kinds of organic and inorganic compounds. This technology has many advantages such as compactness in the model, less area requirement, economically affordable, highly removal efficient of non-biodegradable compounds and reduction of secondary pollutants. Different electrochemical technologies can be used for the treatment of wastewater. They are electrocoagulation (EC), electro-floatation, electro-sorption, and electrochemical oxidation[8]. EC as a safe and environmentally friendly technique[9,10,] which is considered as an alternative technique for the treatment of various industrial effluents like textile[11], heavy metal[16], tannery[12], sewage[13] and pharmaceutical wastewater[5]. EC is an electrochemical process used by sacrificial metal electrodes to produce the coagulant agent that destabilizes the pollutants and particulate the suspension and ultimately aggregates the destabilized content into flocs[14,15]. Aluminum and iron are the most widely used electrode materials in the EC process. Compared with iron electrodes, aluminum electrodes were more useful for the removal of COD, with a removal efficiency of over 90%. The coagulants produced by EC are formed by metal ions reactions, usually Fe^{2+} or Al^{3+}, with electrolysis-formed OH^- ions forming metal hydroxide coagulants[9]. These coagulants destabilize the surface charges of the suspended solids, breaking up the colloid or emulsion. In the meantime, the coagulant forms a sludge layer that covers the solid particles that are suspended. The H_2 gas released during the electrolysis process raises the resultant sludge to the surface of the water[16].

In this work, the possibility of using aluminium-based EC to remove TOC from real and synthetic pharmaceutical wastewaters efficiently is investigated by systematically measuring the effects of conductivity, pH, current density and interelectrode distance.

Materials and methods:

Chemicals and materials:

The chemicals used in this experiment, such as paracetamol, H_2SO_4, NaOH, and NaCl, were purchased from Sigma-Aldrich, which were of 98% purity.

Synthetic and real pharmaceutical wastewater:

Preparation of synthetic wastewater of paracetamol was done by 1.3 g of paracetamol (650 mg Tablets) powder, which was transferred into a volumetric flask and diluted for 1000 ml using distilled water[4]. Then the resulting solution was mixed well. To adjust the initial pH of the sample, dilute H_2SO_4 and NaOH solution was used. The conductivity is provided by the addition of NaCl electrolyte in experiments. Real wastewater was collected from the pharmaceutical industry (Orchid Pharma Ltd., Chennai, India). The initial characteristics of the synthetic and real pharmaceutical wastewater are summarized in Table 1.

Table 1. Synthetic and real pharmaceutical wastewater characteristics

Sl. No.	Characteristics	Synthetic wastewater	Real wastewater
1.	TOC (mg L^{-1})	1106	2300
2.	COD (mg L^{-1})	1350	3250
3.	pH	7.8	6.73
4.	Phosphate (mg L^{-1})	–	350.86
5.	Chloride (mg L^{-1})	–	52.07

Experimental setup and procedure:

Batch experiments were carried out in a 500 ml heat-resistant glass beaker, and two electrodes, aluminum as anode and stainless steel as cathode with identical dimensions (11 cm×5 cm×0.3 cm) with rectangular shapes were placed in parallel and vertically. The electrode distance was maintained at 3 cm during electrolysis. The electrodes were rubbed with sandpaper to polish the active surface before each experiment. All the samples were centrifuged at 3,000 rpm for 10 min by using a centrifuge (HERMLE Z326-K).

The removal efficiency of Total organic carbon (TOC) was calculated by

$$R(\%) = \frac{TOC_o - TOC_t}{TOC_o} \quad (1)$$

Analytical methods:

In this work, analysis of the wastewater sample such as TOC and COD was done after electrocoagulation experiments. TOC analyses were performed by TOC Analyzer (Shimadzu). The COD removal percentage and pH were measured by the APHA standards method.

Results and discussion

Effect of initial pH:

The initial pH of the wastewater plays an important role in this process as it affects the solution conductivity, hydroxide speciation. To identify the influence of pH on TOC removal in the electro-coagulation process, studies were carried out by adjusting the pH from 2–12 for synthetic wastewater (TOC-1100 mg L^{-1}) and real wastewater (TOC-2300

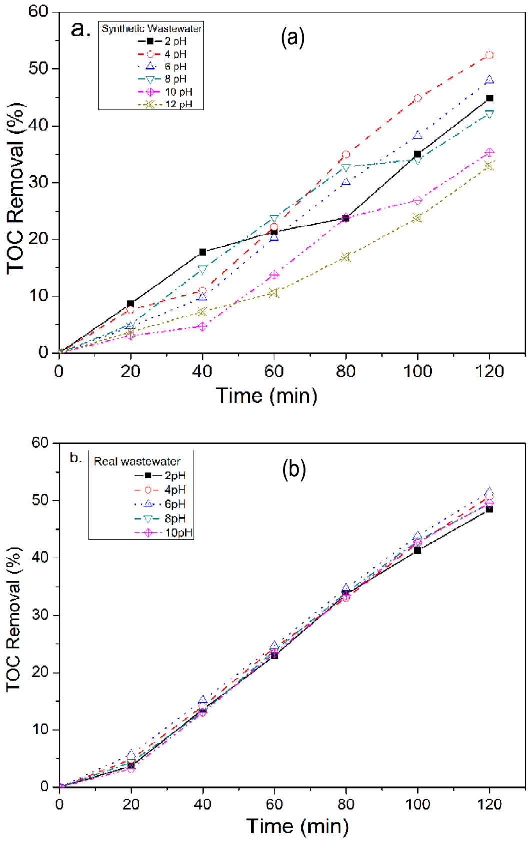

Fig. 1. TOC removal at variable pH for (a) synthetic and (b) real wastewater.

mg L^{-1}). The results on the effect of pH on the TOC removal efficiency as a function of time are shown in Fig. 1. It was observed that an increase in the pH range 2 to 6 in wastewater increases in hydroxide ion (OH^-) near the cathode and it would form aluminum hydroxides with a positive charge, e.g. $Al(OH)_2$, $Al(OH)_3$. The $Al(OH)_3$(s) flocks have large surface areas that supported the high adsorption of soluble (organic) and colloidal particles. The highest percentage of TOC removal was recorded for synthetic wastewater at pH 4 (52.50%) and real wastewater at pH 6 (53.50%).

Effect of current density:

The current density is directly proportional to the formation of aluminum flocs. An increase in the current density ratio (current to active electrode surface area) leads to an increase in the generation of ions on the electrode. To study the effect of current density on the TOC removal efficiency in synthetic and real wastewater, different current ranging (0.5 to 2 A) was chosen, and the results are shown in Fig. 2. The

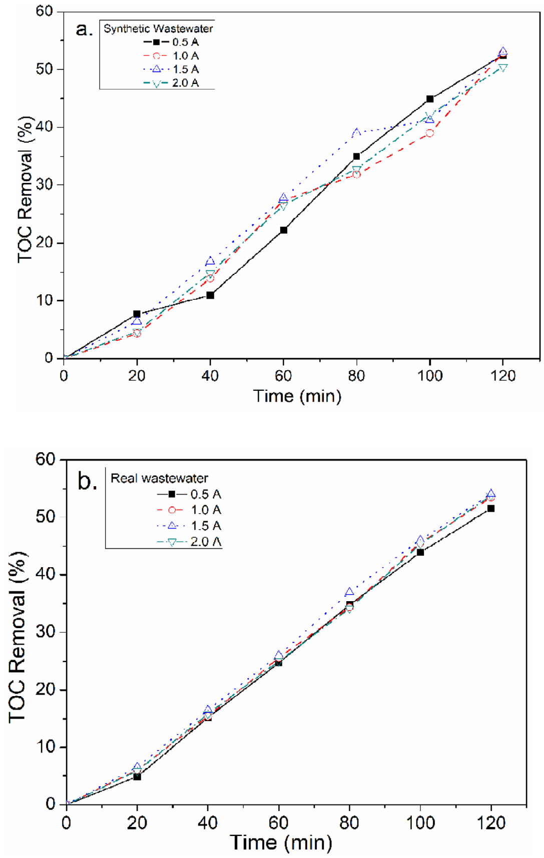

Fig. 2. TOC removal at different current density values: (a) synthetic and (b) real wastewater at optimum conditions.

TOC removal efficiency slightly increased from 52.5 to 53.07% in synthetic wastewater and 51.5 to 55.2% in real wastewater respectively up to 1.5 A. The TOC removal efficiency became constant for any further increase in current after 1.5 A. Therefore, it is considered as the optimal current density for this process.

COD reduction at optimum conditions:

The COD removal% from the wastewater was investigated as a function of reaction time at optimized operating parameters is shown in Fig. 3. The results reveal that maximum COD removal efficiencies were obtained as 60.8% and 62.5% for synthetic wastewater and real wastewater, respectively.

Adsorption kinetics:

Pseudo-first order kinetic model:

The adsorption kinetic data are analyzed using the

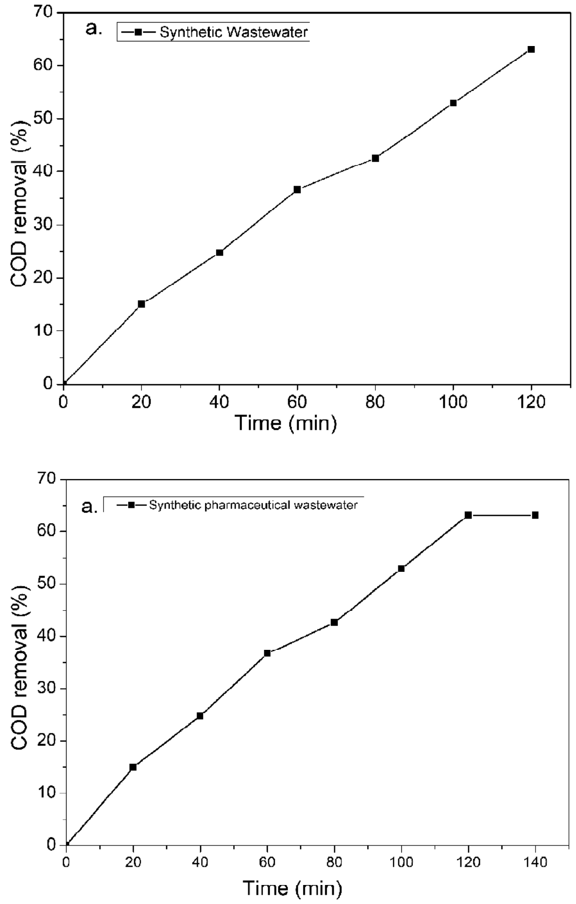

Fig. 3. COD removal% at optimized conditions for (a) synthetic and (b) real wastewater.

Lagergran rate equation. The first order is given by eq. (2):

$$\frac{dq}{dt} = K_1 (q_c - q) \tag{2}$$

where q_e and q are the amounts of TOC adsorbed at equilibrium and at time t, K_1 and K_2 are the rate constant (min^{-1}) of pseudo-first and second order adsorption.

$$\log (q_e - q) = \log q_e - \frac{K_1 t}{2.303} \tag{3}$$

The value of q_e is calculated using the below eq. (4):

$$q_e = \frac{V(C_o - C_e)}{W} \tag{4}$$

Pseudo-second order kinetic model:

The second order kinetic model is expressed as

$$\frac{dq}{dt} = K_2 (q_e - q)^2 \tag{5}$$

$$\frac{t}{q} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \tag{6}$$

where, q_e is TOC adsorbed per unit mass of adsorbent (mg g^{-1}), C_e is TOC concentration in solution (mg L^{-1}), C_o is the initial TOC concentration in solution, V is the volume of solution (L), and W is the mass of anode dissolved (adsorbent) (g).

The validity of the models was verified by linear equation analysis log ($q_e - q$) vs t. Where K_1 and predicted q_e are

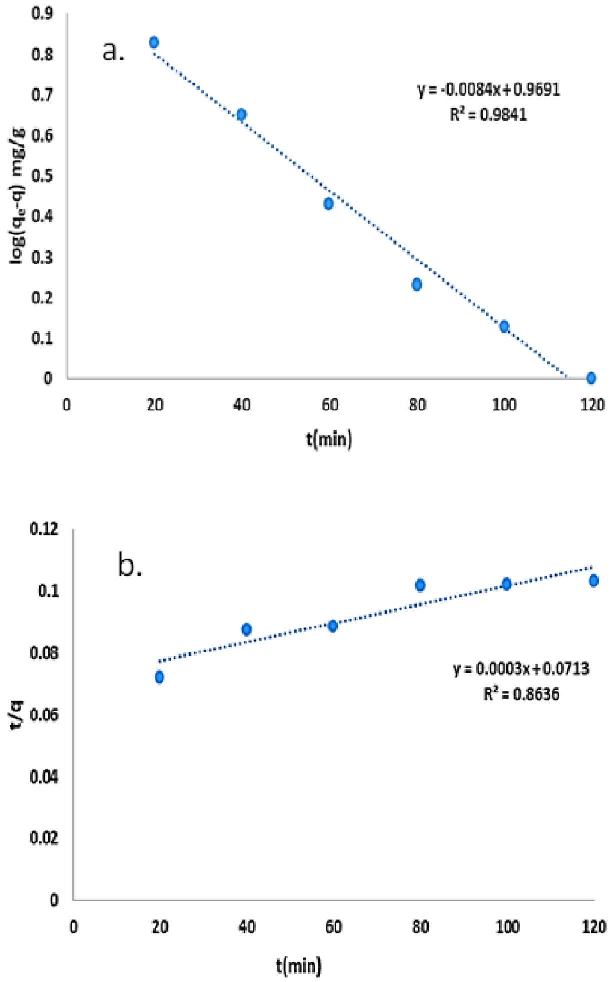

Fig. 4. (a) Pseudo-first order and (b) pseudo-second order kinetic model for synthetic wastewater at optimum conditions.

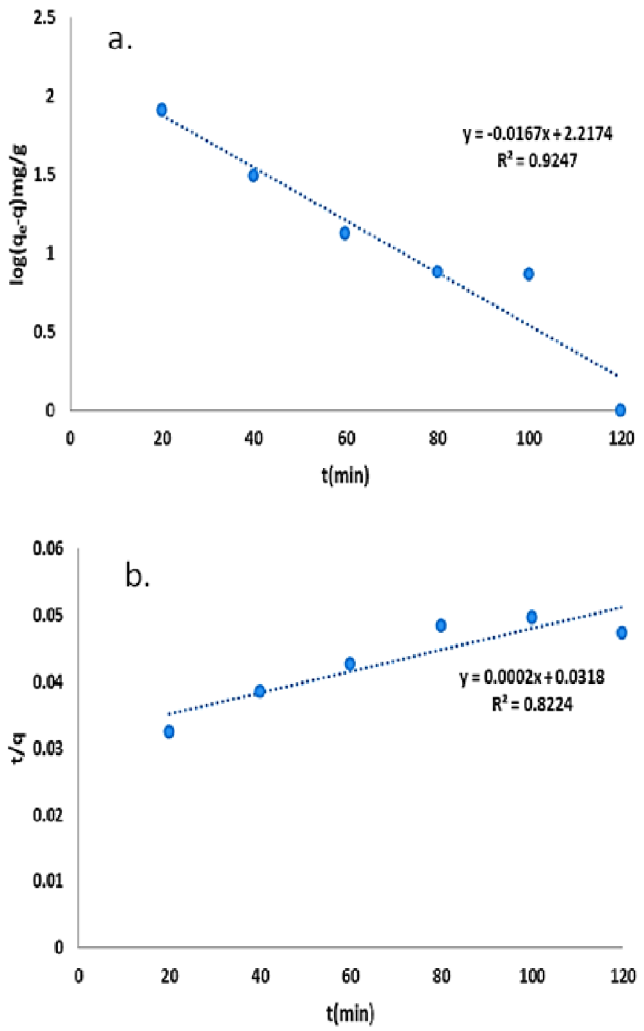

Fig. 5. (a) Pseudo-first order and (b) pseudo-second order kinetic model for real wastewater at optimum conditions.

determined from the slope and intercept, respectively, shown in Figs. 4(a,b) and 5(a,b). A straight line is obtained from the plots suggests the applicability of this pseudo-first order kinetic model and correlation factor has shown in Table 2.

Table 2. Kinetic studies of electrocoagulation process

Sl. No.	Models	Synthetic wastewater	Real wastewater
1.	Pseudo-first order (R^2)	0.9841	0.9247
2.	Pseudo-second order (R^2)	0.8636	0.8224

Conclusion

The present study demonstrated the applicability of the electrocoagulation process for the treatment of real and synthetic pharmaceutical wastewater containing paracetamol was investigated in this work. The result concluded that the EC process highly depends on the pH, current density, inter-electrode distance, and electrolyte concentration. TOC and COD removals of 63.2% and 60.8%, respectively, were observed at the optimized operating parameter of pH 4, inter-electrode distance 2 cm, electrolyte concentration 1.5 g L^{-1}, and current density 272.72 A m^{-2} (1.5 A) for the synthetic wastewater. TOC and COD removals of 66% and 62.5%, respectively, were observed at the optimized operating parameter of pH 6, electrolyte concentration 2.0 g L^{-1}, and current density 272.72 A m^{-2} for the real wastewater. The higher percentage of TOC removal in the real pharmaceutical wastewater study can be attributed to the formation of more flocks with a large surface area that has led to the high adsorption of soluble and colloidal particles.

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