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REMOVAL OF ORGANIC POLLUTANTS FROM ABATTOIR WASTEWATER USING ELECTRO-COAGULATION

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ABSTRACT

Electrocoagulation technique was employed for removal of organic matters in abattoir wastewater. The experiments were carried out using batch apparatus with monopolar iron (Fe) plate anode and cathode employed as electrodes. The effect of various process variables such as current density (12.35 – 61.73 mA/cm^2), operating time of 15 to 60 minutes, initial pH of the wastewater (3.0 – 10.0) and inter-electrode spacing of 1.0 to 3.0 cm was investigated by keeping the background electrolyte constant at 1500 mg/L of Na_2SO_4. The efficiency of the process was evaluated using current efficiency and power consumption while the kinetic of the process was evaluated. It was found that the optimum condition for the process was: 61.73 mA/cm^2 current density, inter-electrode spacing of 1.0 cm, and pH of 7. The power consumption with reference to COD removal increased from 3.88 to 7.11 % and 3.81 to 9.77 kWh/kg within current density of 12.35 to 61.73 mA/cm^2. The Electrocoagulation process is deduced to be pseudo second order process with rate constant of 0.744 L.min/mg.

Keywords: electro-coagulation, abattoir, wastewater, COD, NTU

INTRODUCTION

The continuous drive to increase meat production for the protein needs of the ever increasing world population has some environmental pollution problems attached. The pollution arises from activities in meat processing as a result of failure in adhering to Good Manufacturing Practices (GMP) and Good Hygiene Practices (GHP) (Akinro *et al.*, 2009). Abattoir waste just like any other waste can be detrimental to humans and the environment if definite precautions are not taken. In meat processing industry, slaughter houses are littered with non-meat products and wastes that constitutes nuisance and public health risks associated water pollution as well as infestation of flies and other disease vectors (Osibanjo and Adie, 2007). Wastewater from abattoir is a mixture of the processing waters from both slaughtering line and cleaning of the guts, which causes a large variation in the concentration of organic matters. The contributors of organic load to these effluents are paunch, feaces, fat and lard, grease, undigested food, blood, suspended material, urine, loose meat, soluble proteins, excrement, manure, grit and colloidal particles. The major environmental problems associated with abattoir wastewater are the large amount of suspended solids and liquid waste containing various types of organic materials. These materials are mainly amino acids and other organic nitrogenous compounds which are responsible for the colours and offensive odours. These substances generate highly offensive odour as a result of biodegradation processes (Gauri, 2006; Asselin *et al*., 2008; Tezcan Ün *et al.*, 2009). Therefore treatment of wastewater from slaughter houses is very important for

prevention of high organic loading to water bodies, reduction or total elimination of microorganism associated with the degradation processes.

Conventional methods used for treatment of wastewaters are ultra filtration, membrane, adsorption, solvent extraction, evaporation, fine screening, sedimentation, coagulation–flocculation, trickling filters and activated sludge processes (Pant and Singh, 2013). Some of these methods are very cumbersome, inefficient for treatment of abattoir effluent, and in most cases involve inventory of large volume of chemicals that leave their traces in water, etc. Coagulation is one of the most important physiochemical operations used in water treatment. This is a process used to cause the destabilization and aggregation of smaller particles into larger colloidal particles. Water contaminants such as ions (heavy metals) and colloids (organics and inorganics) are primarily held in solution by electrical charges. The colloidal systems could be destabilized by the addition of ions having a charge opposite to that of the colloid. The destabilized colloids can be aggregated and subsequently removed by sedimentation and/or filtration. Coagulation can be achieved by chemical or electrical means. Chemical coagulation is becoming less acceptable today because of the higher costs associated with chemical treatments involving the large volumes of sludge generated, inventory of large volume of chemicals and the hazardous waste categorization of metal hydroxides (Matteson *et al.*, 1995; Lin *et al.*, 1998; Chen *et al*. 2000; Mollah *et al.*, 2001).

An electrocoagulation (EC) is a primary technique for treatment of various wastewaters from industry, agriculture or urban areas (Moreno-Casillas *et al.*, 2007**;** Merzouk *et al.*, 2009; Zongo *et al.*, 2009). An electrocoagulation (EC) process has attracted a great attention on treatment of industrial wastewaters because of the versatility and environmental compatibility. This technique has several advantages as compared to conventional methods in terms of use of simple equipment, ease of operation, cost effective, fewer inventories of chemicals, and environmental benign (Savas *et al.*, 2007). Electrocoagulation can often neutralize ion and particle charges, thereby allowing contaminants to precipitate, reducing the concentration below the chemical precipitation method, and can reduce or replace the use of expensive chemical agents (metal salts, polymer) (Rebhun and Lurie, 2009; Larue and Vorobiev, 2003).

Electrocoagulation is a complex process occurring via series of steps. When current is passed through electrochemical reactor, it must overcome the equilibrium potential difference, anode over potential, cathode over potential and potential drop of the solution. The anode over potential includes the activation over potential and concentration potential, as well as the possible passive over potential resulted from the passive film at the anode surface, while the cathode over potential is principally composed of the activation over potential and concentration over potential. Reactions at electrode surfaces, formation of coagulants in aqueous phase, adsorption of soluble or colloidal pollutants on coagulants are responsible for the removal of pollutants (Rebhun and Lurie, 1993; Rajeshwar and Ibanez, 1997; Larue and Vorobiev, 2003).

Generally, aluminum and iron are used as an electrode material in the electro-coagulation process. In the iron electrode, the most acceptable mechanisms proposed for electro-coagulation is

At the anode electrode

$$4Fe_{(s)} \rightarrow 4Fe^{2+}_{(aq)} + 8e^{-} \qquad (1)$$

$$4Fe^{2+}_{(aq)} + 10H_2O_{(aq)} + O_{2(g)} \rightarrow 4Fe(OH)_{3(s)} + 8H^{+}_{(aq)} \qquad (2)$$

While at the cathode

$$8H^{+}_{(aq)} + 8e^{-} \rightarrow 4H_{2(g)} \qquad (3)$$

And the overall reaction

$$4Fe_{(s)} + 10H_2O_{(aq)} + O_{2(g)} \rightarrow 4Fe(OH)_{3(s)} + 4H_{2(g)} \qquad (4)$$

The iron anode is oxidized to Fe^{2+} which undergo electrolytic oxidation, and various species of monomeric ions, $Fe(OH)_3$ and polymeric hydroxide complex such as: $Fe(H_2O)_6^{3+}$, $Fe(H_20)_5^{2+}$, $Fe(H_2O)_4(OH)^{2+}$, $Fe(H_2O)_8(OH)_2^{4+}$ and $Fe_2(H_2O)_6(OH)_4^{4+}$ are generated in the aqueous medium (Rebhun and Lurie, 1993; Larue, and Vorobiev, 2003). The ions counteract the ionic species and are therefore responsible for neutralization of the

charges. These counter ions are responsible for the reduction of the electrostatic interparticle repulsion so that Van der Waal's attraction predominates hence coagulation occurs which approach to the zero net charge. The surfaces of the solid hydroxides and oxyhydroxides are responsible for adsorption of contaminated contents in the abattoir (Rebhun and Lurie, 1993; Lin and Chen, 1997; Larue and Vorobiev, 2003; Can *et al.,* 2003**;** Moreno-Casillas, *et al.,* 2007).

The objectives of this study are to examine feasibility of electrocoagulation in removing organic pollutants in abattoir wastewater and to determine the optimal operational conditions for the process. Operating parameters such as current density, treatment time, initial pH, and electrode spacing were conducted in laboratory scale. The efficiency, cost effectiveness and kinetics of the process were evaluated.

MATERIALS AND METHODS

Collection of Materials

The abattoir wastewaters were collected from slaughterhouse at Ilara-Mokin, Ondo State, Nigeria. Sample collected at discharge point was screened to remove hair and solid larger particles using muslin cloth and was stored in sterilized, dried, cleaned and airtight Amber bottle. After collection, the samples were transferred immediately to the laboratory in iceboxes within 2 hours and were analyzed. Analysis of raw wastewater samples was performed for various physical, chemical and biological parameters by Standard Method for Water and Effluents. The quality of the raw abattoir wastewater was analysed as shown in Table 1.

Experimental Setup

The studies were conducted in a lab-scale batch system, which composed of an electrolytic cell, a DC power supply, magnetic stirrer, rheostat, ammeter, and multimeter. An electrolysis cell was made of 1000 mL glass beaker and pair of iron plate as both anode and cathode with the dimension of 2[(120×30)+(30×3)+(120×3)] mm [(Length×Width)+ (Width ×Thick)+ (Length ×Thick)].The effective surface area of each electrode are 82cm^2.

Experimental Procedure

A screened raw abattoir wastewater was transferred into the electro-coagulator. The electrolytic cell used was 1000 mL glass beaker reactor with working volume 400ml equipped with magnetic stirrer operating at 50 rpm. The Direct Current (DC) power supply of 12V, 5.0A capacity was used and the current was controlled by a Rheostat and measured by Ammeter. The electrode pair previously pickled in acid and washed with distilled water was dipped in the wastewater to a depth of 8.0 cm and electrode spacing of 1.0 cm apart at first. The effective area of the electrode pair was 82.0cm^2 using iron electrodes, and conductivity of the solution was increased by addition of 1500 mg/L Na_2SO_4. Samples were taken at selected interval, filtered and analyzed for colour and COD which was used for monitoring the removal efficiencies. The parameters were determined using Standard Methods for Water and Effluents analysis. The efficiency of pollutant removal, R was evaluated using the expression;

$$\%R = \frac{C_0 - C}{C_0} \times 100 \qquad (5)$$

C_0 is the concentration of raw pollutants; C is concentration of pollutant after electrolysis.

The efficiency of the electrochemical coagulation process and its cost effectiveness can be evaluated in terms of two parameters using current density (Moreno-Casillas *et al.*, 2007; Chaturvedi, 2013). The current efficiency (CE) and power consumption (EC) usually evaluated at different current densities. The CE and EC of electrocoagulative operation can be calculated using equations (5) and (6):

$$CE = \left(\frac{F \times V_R \times \Delta_{COD}}{8It} \right) \times 100 \qquad (6)$$

$$EC = \frac{VIt}{\Delta_{COD} \times V_R} \qquad (7)$$

where change in Δ_{COD} is change in the COD; applied current (I) in Ampere; electrolysis time (t); applied cell voltage (V), volume of the reactor (V_R) and Faraday's constant (F) in C/mol.

The kinetics of the process was evaluated from the removal efficiency of COD with respect to time using linear-pseudo second order equation

(Moreno-Casillas *et al.*, 2007; Bayar *et al.*, 2011)

$$\frac{t}{c} = \left[\frac{1}{c_{\max}}\right] t + \left(1/k_z\right) c_{\max}^2 \quad (8)$$

Where c is the COD removed at time t, c_{max} is the maximum COD removed, k_z is the reaction rate constant and t is the electrolysis time. Figure 5 show the plot of pseudo - second – order rate equation for the COD removal " t/c" versus " t".

RESULTS

Some physicochemical parameters of the sample was determined and the result is presented in Table 1.

Removal of organic pollutants was coducted using electrocoagulation technique in laboratory batch scaleand the results are presented.

Effect of Current Density on Removal of Organic Matter

Different values of current density ranging from 12.35 to 61.73 mA/cm^2 at constant time of 30 mins were used to treat the wastewater. The results are shown in Figure 1. The effect of current density in Figure 1 shows that the pollutants removal efficiency increased directly with increased current densities at constant pH of 7, addition of 1500 mg/l of Na_2SO_4 as supporting electrolyte, and electrode spacing of 10.0 mm. The operational and cost effectiveness were evaluated from the removal efficiency of the pollutant and the value obtains are shown in Table 2.

Effects of EC Treatment Time

The effect of treatment time was determined at current adjusted to 5.0A constant at 15, 30, 45, and 60 min interval. The effect of time was studied at constant current density of 61.73 mA/cm^2, 1500 mg/L Na_2SO_4, and electrode spacing of 1.0cm. The result is shown in Figure 2.

The kinetics of the process was derived from the removal efficiency of COD with respect to time (Fig.2) and the result obtained is shown in figure 3.

Effect of Electrode Interspace

The effect of electrode spacing (10.0, 20.0, and 30.0 mm) was investigated. In each EC run the treatment time was kept constant at 60 minutes with constant current density of 61.73 mA/cm^2, initial pH of 7, and addition of 1500mg/L Na_2SO_4. The result is shown in Figure 4.

Table 1: Characteristics of Raw abattoir wastewater against Standard/guidelines

Parameters	Raw Wastewater
pH	6.78
Temperature (^{O}C)	32.5
Conductivity (µs/cm)	3,120
Turbidity (NTU)	16,00
Total Dissolved Solid (mg/l)	650.5
Total Suspended Solid (mg/l)	1,020
Chemical Oxygen Demand (mg/l)	2,240
Odour	offensive
Colour	Dark red

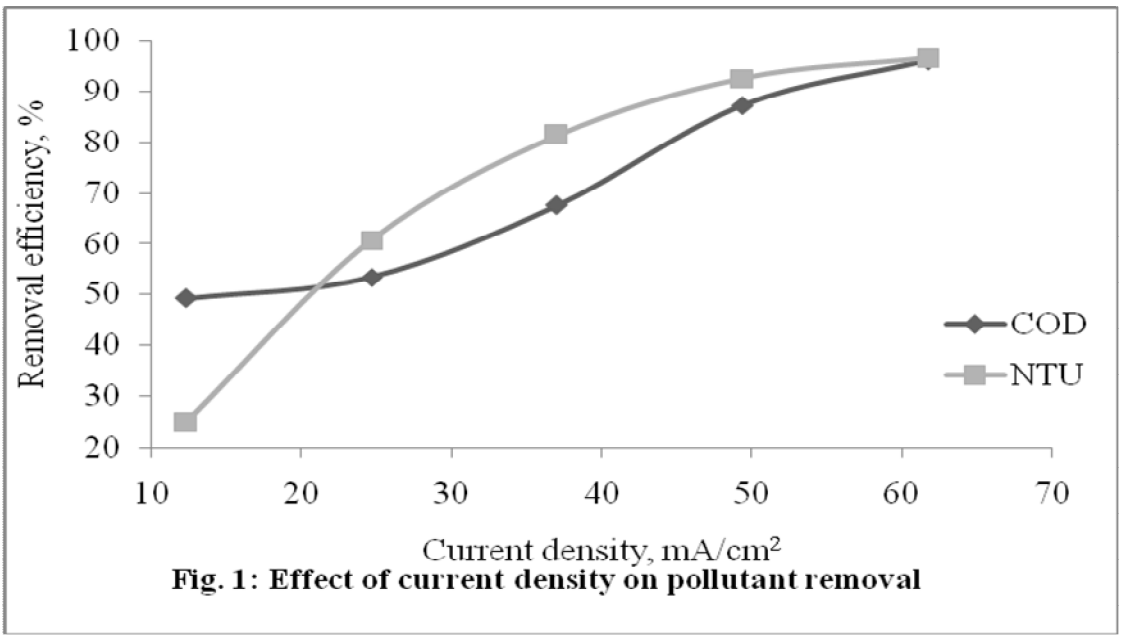

Fig. 1: Effect of current density on pollutant removal

Table 2: Operational and cost effectiveness of the process

Current density (mA/cm^2)	Current efficiency (%)	Power Consumption (kWh/kg of COD)
12.35	3.88	3.81
24.69	4.11	7.03
37.04	5.21	8.33
49.39	6.74	8.60
61.73	7.41	9.77

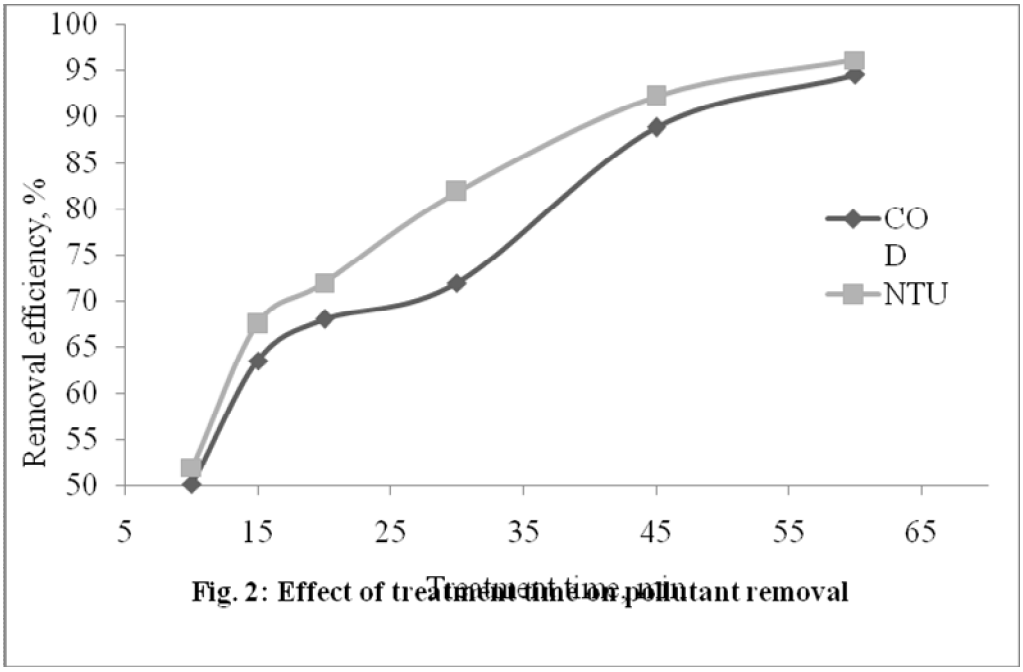

Fig. 2: Effect of treatment time on pollutant removal

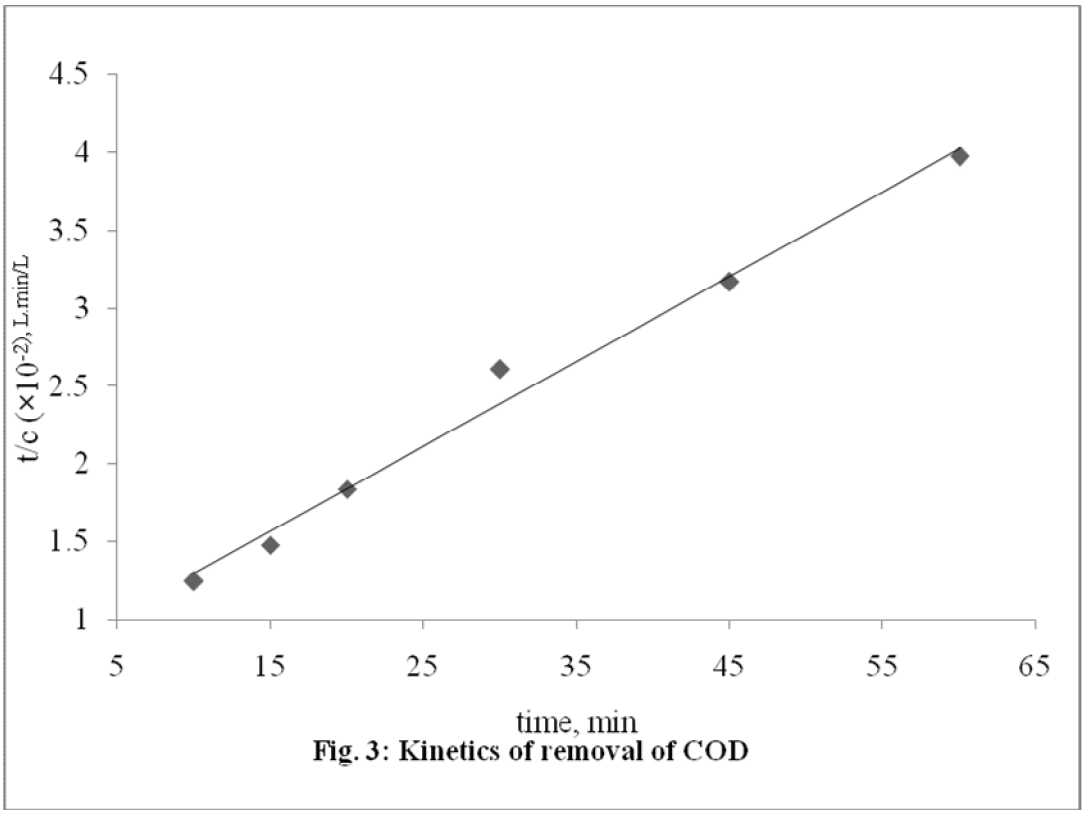

Fig. 3: Kinetics of removal of COD

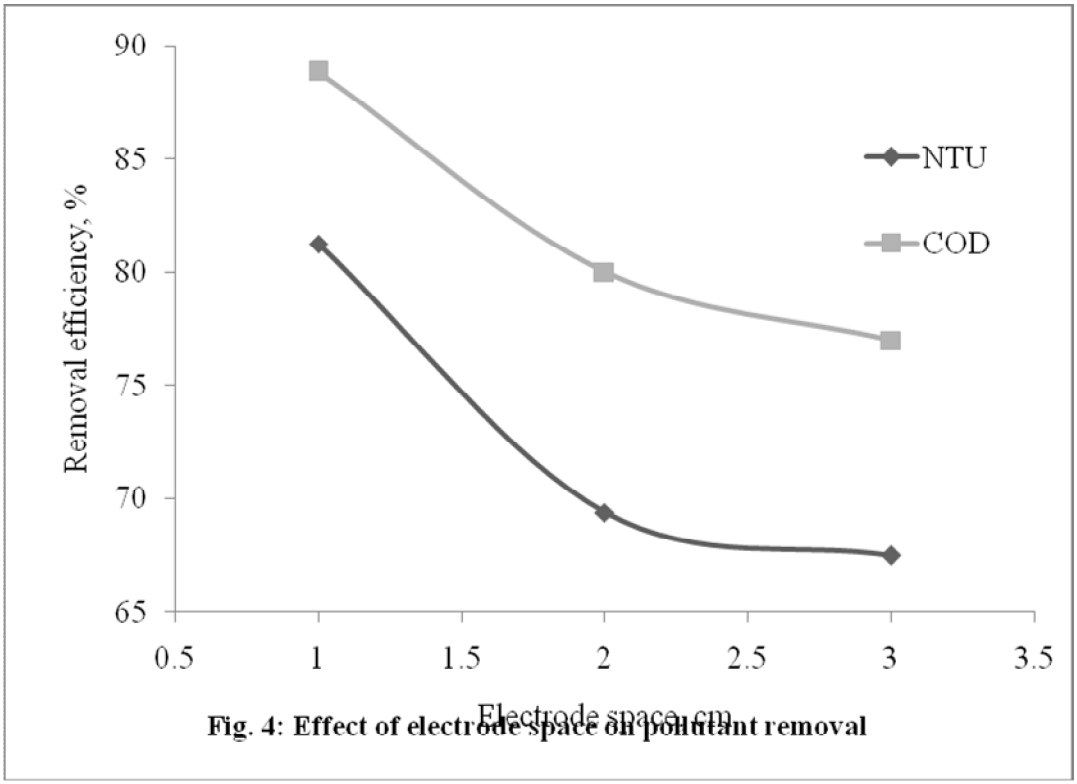

Fig. 4: Effect of electrode space on pollutant removal

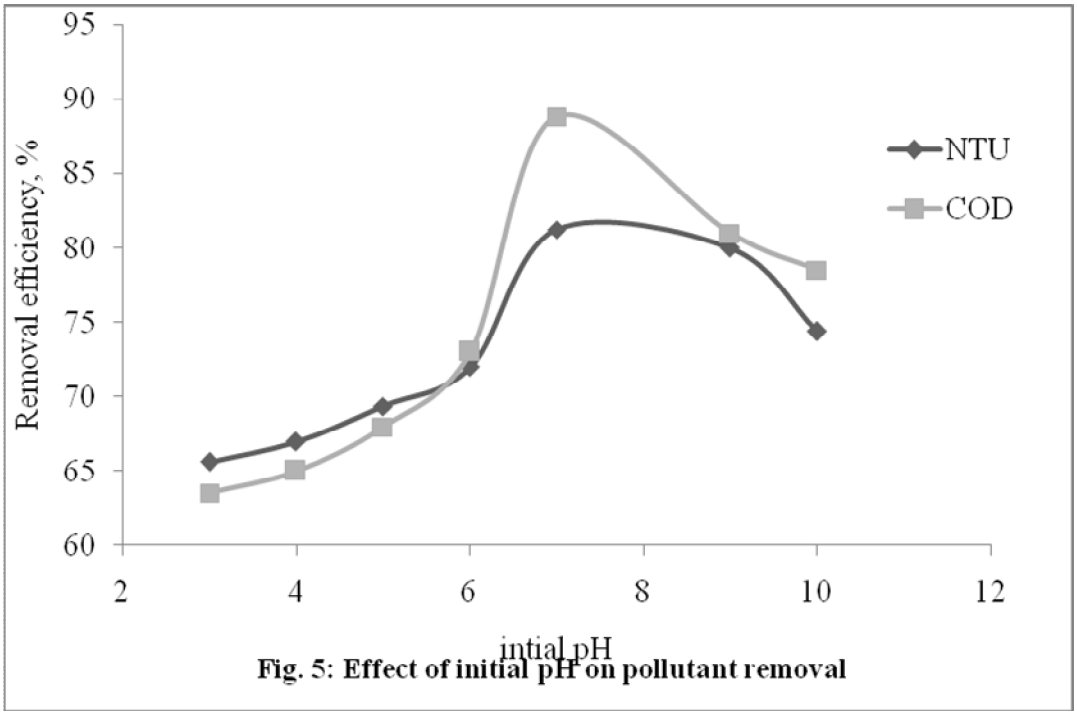

Fig. 5: Effect of initial pH on pollutant removal

Effect of Initial pH on Pollutant Removal

The initial pH of the wastewater was adjusted for each experiment by using 1.0 M sodium hydroxide or 1.0 M sulphuric acid within the pH range of 3.0 to 10. The result is shown in Figure 5.

DISCUSSION

Operating current density is a critical factor in electro-coagulation process; it is one of the most operational parameters that can be controlled directly. Current density directly determines both coagulant dosage and bubble generation rates, which strongly influenced both solution mixing and mass transfer at the electrodes (Larue and Vorobiev, 2003). The performance of the process was studied under various quantities of the current density (1.0 – 5.0 A). Thus current densities ranging from 12.35 to 61.73 mA/cm^2 were investigated to establish the impact of coagulant dosage generated on the pollutants removal efficiency. The effect of current density in Figure 1 shows that the pollutants removal efficiency increased directly with increased current densities at constant pH of 7, addition of 1500 mg/l of Na_2SO_4 as supporting electrolyte, and electrode spacing of 10.0 mm. The COD removal increased steadily from 49 % to 95 % as current density increased within a working range of 12.35mA/cm^2 to 61.73 mA/cm^2. The colour removal increased from 25 % to 96 % within the studied current density.

The operational and cost effectiveness of the process was valuated from the current density using equations 6 and 7. The current efficiency (CE) and power consumption (EC) were evaluated at different current densities ranging from 12.35 to 61.73 mA/cm^2. The CE and EC of electrocoagulative operation were calculated using Equations (5) and (6) respectively (Bayramoglu *et al*., 2003; Moreno-Casillas *et al*., 2007; Hernandez *et al*., 2009; Bazrafshan *et al*, 2012a,b,c). The effect of the current density on COD removal and power consumption (Table 2) shows that increase in current density (12.35 to 61.73 mA/cm^2) of the electrochemical cell results in increasing the percentage COD removal. This is due to production of more coagulants which removes the pollutants. It can further observed that the power consumption marginally increased from 3.81 to 9.77 kWh/kg of COD with correspondingly in current efficiency (3.88 % to 7.11 %) within the studied current density. This implies that there is slight increase in the operating cost of the treatment process due to increase in power consumption with increasing the current efficiency.

The efficiency of removal of colour and COD as a function of operating time shows that operating time has an effect on the pollutant removal. In each case, voltage across the electrodes was measured by a multimeter. When the operating time increased from 15 to 60 minutes the COD removal increased rapidly from 50% to 95%. The colour removal also increases steadily from 52% to 96% within the studied time. The colour removal efficiency increased steadily from 52 - 96 % as time increased from 15 - 60 minutes. The result of this study is in accordance with the earlier reports on electrocoagulation of molasses, removal of dye and heavy metals using electrocoagulation (Merzouk *et al.*, 2009; Gadd *et al.*, 2010; Saravanan *et al.*, 2010). The straight line of the plot shows in figure 3 obtained using equation 8 shows a good agreement with the pseudo - second – order kinetic model for different removal rates. The correlation coefficient (R^2) for the pseudo - second – order equation was 0.99. This suggests that the COD removal rate is most appropriately represented by a pseudo - second – order process. The reaction rate constant, k_z from the plot was 0.744 L.min mg^{-1}.

Inter-electrode spacing is a vital parameter in EC process for the removal of pollutant from effluent (Bukhari, 2008). The colour and COD removal as a function of inter-electrode spacing as presented in Fig. 4. The results reveal that the removal efficiency of EC process for colour and COD increased as the inter-electrode spacing decreased. Maximum removal efficiency was observed at an inter-electrode spacing of 1.0 cm.

It has been reported by other investigators that pH is an important parameter influencing the performance of the electrochemical process (Contreras, 2009; Kobya *et al.*, 2003). Figure 5 illustrates the removal of colour and COD as a function of initial pH. As the reaction progress the pH changes as hydroxides ions are generated. From the figure it could be observed that initial pH has effect on the pollutant removal efficiency. When the initial pH changed from 3.0 to 7.0 the removal of COD increased from 63 to 88 % and then gradually decreased to 78 % at pH of 10. The colour removal from 65 to 81% as pH increased from 3 to 7 and thereafter decreased to 74 % at pH of 10. This

observation has been reported due to various species of monomeric ions and polymeric hydroxy iron complexes generated during the reaction which are the primary coagulants.

CONCLUSION

In this study, the electrocoagulation treatment of abattoir wastewater by EC using iron plate electrodes was investigated. Effects of current densities, treatment time, electrode spacing, and initial pH of solution have been investigated. It can be concluded that the setup in static mode is effective for the treatment of abattoir wastewaters in particular reference to COD and colour. According to the results obtained from the above experiments, an increase in current density of 12.35 – 61.73 mA/cm^2 lead to 49 – 95% and 25 – 96% COD and colour removal respectively. The treatment time caused increase in COD of 50 – 95% and 52 – 96% colour removal in the wastewater. It was also established that, smaller gap between the electrodes favoured coagulants generated. With reference to initial pH of the wastewater, increase in pH from 3 – 7 lead to rise in COD removal from 63 to 88% COD removal and thereafter decrease to 74% at pH of 10. The efficiency of the process shows that power consumes increase slightly from 3.88 to 7.11% while the current efficiency increase from 3.81 to 9.77kWh/kg of COD. Kinetically, the process is pseudo second order reaction with correlation coefficient of 0.99 with the reaction rate constant, k_z from the plot of 0.744 L.min mg^{-1}

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