Symbiosis

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www.symbiosisonlinepublishing.com
ISSN Number: 2572-3162

International Journal of Scientific Research in Environmental Science and Toxicology

Research Article

Open Access

Application of Electrocoagulation on Adsorption of Styrene Acrylate Polymer from Aqueous Solutions

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Received: August 17, 2018; Accepted: August 23, 2018; Published: September 03, 2018

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Abstract

In this paper, the feasibility of electrocoagulation technique for the adsorption of Styrene acrylate SA from aqueous solution has been studied. The results showed that SA and COD removal were (99.2% and 95.9 %), (99.4% and 97.1%) and (99 % and 93.1 %) by using iron Fe, stainless steel S-S and aluminum Al electrodes at 8 min respectively. The adsorption equilibrium were analyzed by Langmuir and Freundlich isotherm models. It was found that the data fitted to Freundlich (R^2 = 0.944) better than Langmuir (R^2 = 0.674) model. The adsorption of SA exhibited pseudo first order with rate constant (0.932, 0.913 and 0.942 min-1) using Fe, S-S and Al electrodes. The consumption of electrical energy for SA at optimum conditions as follows: (0.283, 0.243 and 0.18 KWh/m^3) using Fe, S-S and Al electrodes respectively.

Keywords: Styrene acrylate; Electrocoagulation; Water Treatment; Electrode; Adsorption; Kinetics;

Introduction

The environmental occurrence of polymers is identified as an important pollution related issue, because of the estimated volumes involved, and because they are difficult and time consuming to remove [1]. The World Health Organization (WHO) has reported a 20%-40% increased risk of certain types of cancer (in particular lung cancer) for those who come into regular contact with, or work with paint while Danish researchers point to the added possibility of neurological damage. By far, the most important environmental impact from paints is the release of volatile organic compounds (VOCs) during the drying process after the coating is applied [2]. Styrene acrylate copolymer (SA) is one of the old industrial synthetic in paint using as washable decorative final coat and added to water based latex paint formulations to provide water whitening resistance, improved washability, and enhanced film formation [3]. Styrene acrylate have small acute toxicity, can cause slight irritation in eye , skin and Inhalation of product vapor or mist can cause irritation of the nose, throat, and lungs. Headache and nausea are also possible [4]. Several treatment procedures have been reported for the degradation of some types of polymers from water e.g. thermal degradation, biodegradation, photodegradation, photo-oxidation, microelectrolysis system [5, 6, 7, 8, 9] . Electrochemical processes have been proposed and they have received increasing attention in the last years. Electrocoagulation (EC) has gained recognition as a powerful water treatment technology to remove colloidal species from water. The EC process is an amalgamation of different processes including oxidation, coagulation, flocculation and flotation of water [10].

The objective of the current work is to study the efficiency of electrochemical process on adsorption of styrene acrylate and chemical oxygen demand (COD) in aqueous solution using stainless steel SS , iron Fe and aluminum Al electrodes , study the rate and order of reaction for polymer removal and isotherm modeling.

Experiment Chemicals

Two representative polymers were selected for the synthetic polymer aqueous solutions Where the manufacturer of the emulsion polymer styrene acrylate (Sizerco. for paint production) were purchased from (Gaza Strip-Gaza city) commercial. Sodium chloride (NaCl), potassium chloride (KCl), sodium sulfate (Na_2SO_4), sodium carbonate (Na_2CO_3), sodium fluoride (NaF), sodium hydroxide (NaOH) and sulfuric acid (H_2SO_4), were of analytical grade and purchased from Merck. Distilled water was used for the preparation of solutions. Standard solutions of potassium dichromate ($K_2Cr_2O_7$), sulfuric acid (H_2SO_4) reagent with Mercury sulfate ($HgSO_4$), silver sulfate (Ag_2SO_4) and sulfuric acid reagent were prepared to measure the COD.

Equipment's and Procedures

Stock solutions of polymer 500 mg/L for styrene acrylic were prepared by dissolving an accurate quantity of the polymer in distilled water and suitably diluted o the required initial concentrations. The amount of polymers required to prepare the stock solution was calculated using the following equation

$$M_1 \times V_1 = M_2 \times V_2 \qquad (1)$$

the electrocoagulation unit consists of an 100 ml electrochemical reactor with an effective surface area of 4 cm2. The electrodes were 2 cm × 1 cm. The electrode were positioned vertically and parallel to each other using iron or aluminum or stainless steel electrode as anode or cathode. The anode is connected to the positive pole and the cathode to the negative pole of the direct current power supply. Magnetic stirrer controller with a sufficient magnetic stirring (50-100 rpm) was used. DC power supply, model (DZ040019) EZ Digital CO. Ltd. (Korea). The polymer concentration was determined using a double - beam UV-Vis spectrophotometer, model UV 1601 is from Shimadzu (Japan) at 291 nm. Hot Plate, model (HB502), BIBBY STERILIN LTD. (U.K.). A pH meter model AC28, TOA electronics Ltd., (Japan). Water bath model SB-650, Tokyo Kikakkai CO. Ltd., (Japan). A closed reflux titrimetric unit was used for the COD determination. Chemical Oxygen Demand (COD), HANNA instruments, Termo reactor, model C9800 Reactor in Hungary-Europe.

Analysis

The remaining pollutants of styrene acrylate polymer concentration were measured with the double-beam UV-Visible spectrophotometer at λmax= 291 nm using calibration curve with standard error ± 0.5%. The COD was determined using a closed reflux colorimetric method at λmax = 600 nm. The equation used to calculate the polymer removal efficiency in the treatment experiments was:

$$\%E = [(A_o - A) / A_o] \times 100 \quad (2)$$

Where Ao and A are absorbance values of polymer solutions before and after treatment respectivily with respect to their λmax. The calculation of COD removal efficiency after EC treatment was performed using the following formula [11]

$$\%CR = [(C_o - C) / C_o] \times 100 \quad (3)$$

Where Co and C are concentrations of polymer solutions before and after electrocoagulation.

Result and Discussion

Electrocoagulation is a complex process that may be effected by different parameters such as electrolysis time, current density, initial pH, type of supporting electrolyte, electrolyte concentration, initial polymer concentration and temperature.

Effect of Current Density (mA/cm^2)

To investigate the effect of current density on the styrene acrylic and COD removal efficiency, a series of experiments were carried out at time 8 min, SA concentration of 200 mg/L, pH 7.3, interelectrode distance of 1 cm, NaCl concentration of 2 g/L and temperature of 20°C using Fe, S-S and Al electrodes. Figure 1

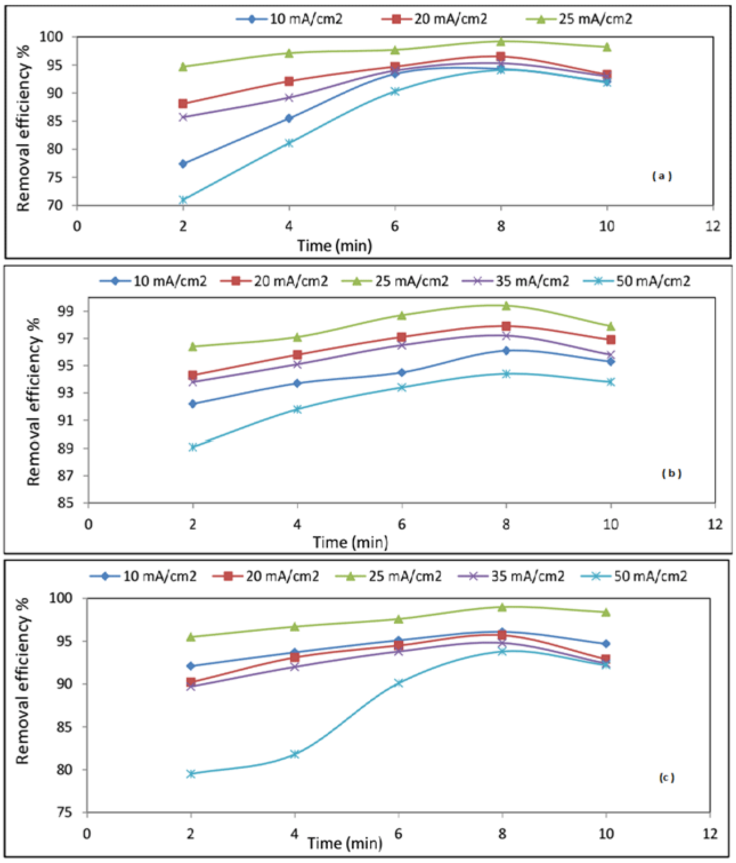
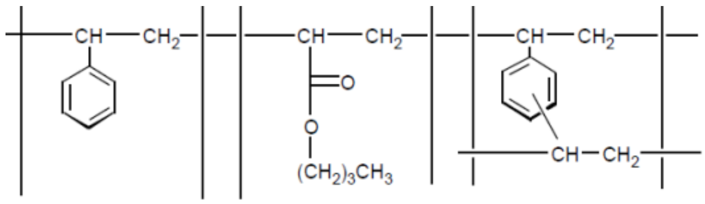


Figure 1: Effect of current density on the efficiency of styrene acrylic adsoprtion using iron (a), stainless steel (b) and aluminum (c) electrodes respectively

Table 1: Chemical and Physical Properties of SA copolymer

Commercial Name	Styrene-acrylate copolymer, styrene acrylic copolymer and Styrene acrylic acid
Chemical structure	
Chemical formula	$(C_{10}H_{10}.C_8H_8.C_7H_{12}O_2)n$
IUPAC Name	Poly(2-propenoic acid, butyl ester, diethenylbenzene, and ethenylbenzene) mer
Physical Appearance	Milky with Bluish Emulsion
Degree of hydrolysis at pH=1-2 or pH=4-9 (25°C)	stable, <2% degradation over 2 weeks at 40°C and pH=1.2-9.0
Degree of purity	more than 99% (w/w)
λ_{max}	291 nm

and Table [Table 2a, 2b, 2c] show the effect of current densities for SA and COD removal efficiencies increased by increasing the current densities up to 99.2% and 95.9% for Fe electrodes, 99.4% and 97.1% for S-S electrodes and 99% and 93.1% for Al electrodes respectively. It can be indicated that the optimum current densities were 25 mA/cm^2 for all studied electrodes. Upon increasing current density, the amount of oxidized metal increased and amounts of metal hydroxide compounds for precipitation and adsorption of the matrix were also increased [12].

Effect of Initial PH

Experiments were carried out to evaluate the effect of pH, using solutions at initial pH varying in the range (3-11), a current density of 25 mA/cm^2, initial concentration of 200 mg/L, interelectrode distance of 1 cm, NaCl concentration 2 g/L, temperature of 20^{o}C, and time 8 min. Figure 2 and [Table 2a, 2b, 2c] show the SA and COD are high in neutral medium for all working electrodes. In general when pH increases the dissolved metal during the electrocoagulation process increases due to the formation of metal hydroxide species which adsorb the polymer molecules and causes the increase of the removal efficiency [13].

Effect type of Electrolyte

Figure 3 explain the effect of type of electrolyte on the SA and COD removal efficiencies at time 8 min, at current density of 25 mA/cm^2, pH of 7.3, inter-electrode distance of 1 cm and temperature of 20^{o}C. According to Figure 3 and [Table 2a, 2b, 2c] the SA and COD removal using NaCl electrolyte is better than other electrolytes (KCl, Na_2CO_3, NaF and Na_2SO_4).

Table 2 (a): Effect of current density, pH, type of electrolyte, concentration electrolyte, rubber concentration, and temperature on the efficiency of COD removal for Styrene Acrylate using iron electrode

Current density (mA/cm^2)	10	20	25	35	50
COD (%)	83.9	86.7	95.5	80.4	78
pH	3	5	7	9	11
COD (%)	60.3	75.2	95.9	79.3	86.7
Electrolyte	KCl	Na_2CO_3	NaCl	Na_2SO_4	NaF
COD (%)	93.4	87.7	95.9	92.4	94
[NaCl] (g/L)	0.5	1	1.5	2	2.5
COD (%)	69.5	79.8	83	95.9	90.2
[polymer] (mg/L)	50	100	150	200	-
COD (%)	46.1	52	93	95.9	-
Temperature (^{O}C)	10	20	30	40	-
COD (%)	79.8	95.9	86.7	82.1	-

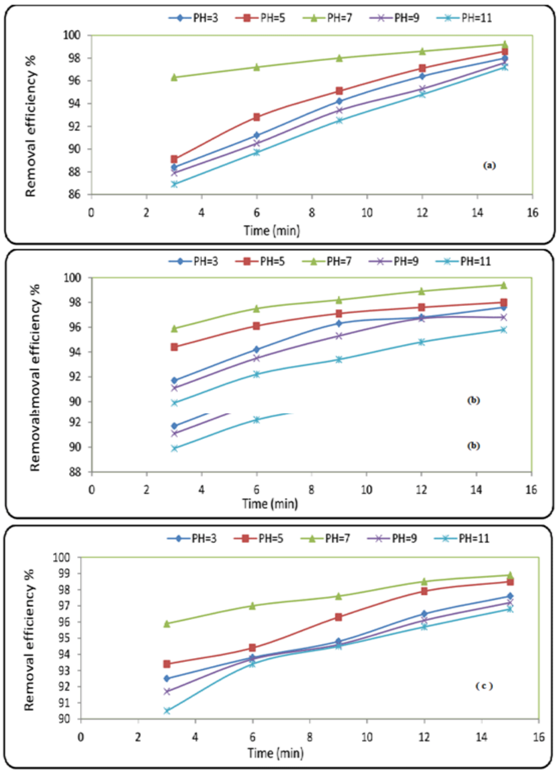


Figure 2: Effect of pH on the efficiency of styrene acrylic adsoprtion using iron (a), stainless steel (b) and aluminum (c) electrodes respectively

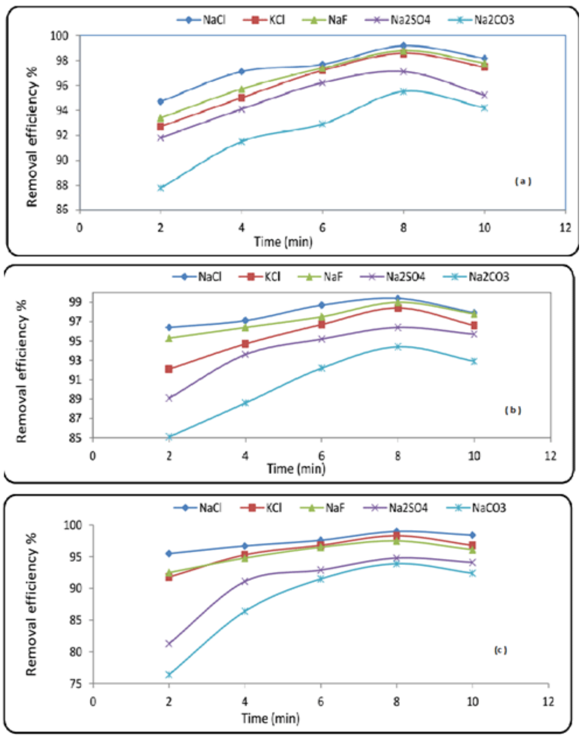


Figure 3: Effect type of electrolyte concentration on the efficiency of styrene acrylic adsoprtion using iron (a), stainless steel (b) and aluminum (c) electrodes respectively

Effect of Electrolyte Concentration(g/L)

AIn general, NaCl was used to increase the conductivity of the solution and to facilitate the EC process. The conductivity of the wastewater is adjusted to the desired values by adding NaCl [14]. Figure 4 and [Table 2a, 2b, 2c] represent the effect of electrolyte concentrations on SA and COD removal efficiencies at time 8 min, initial concentration of 200 mg/L, current density of 25 mA/cm^2, inter-electrode distance of 1 cm, pH of 7.3 and temperature of 20^{o}C. The figures show that the increasing the removal efficiencies with electrolyte concentration increased. The results obtained from the above figures indicate that 2 g/L NaCl was the maximum value for removal efficiencies.

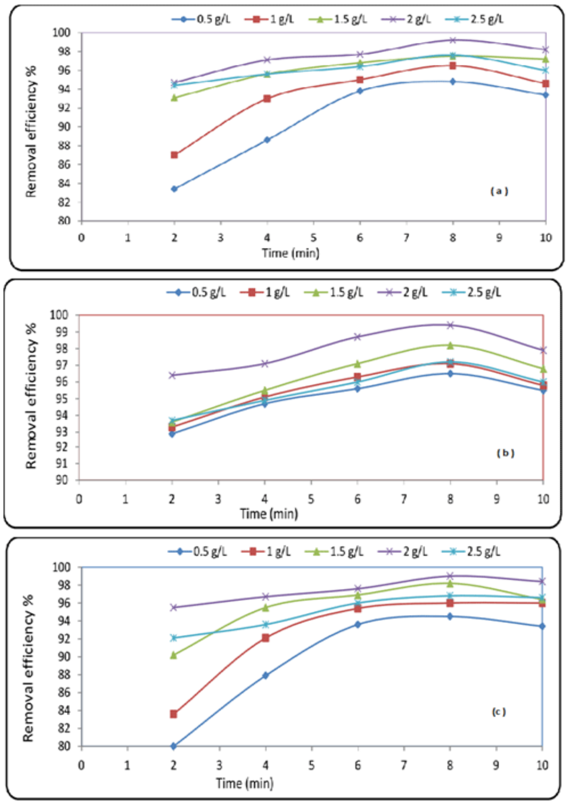


Figure 4: Effect of electrolyte concentration on the efficiency of styrene acrylic adsorption using iron (a), stainless steel (b) and aluminum (c) electrodes respectively

Table 2 (b): Effect of current density, pH, type of electrolyte, concentration electrolyte, rubber concentration, and temperature on the efficiency of COD removal for Styrene Acrylate using stainless steel electrode

Current density (mA/cm^2)	10	20	25	35	50
COD (%)	85.6	93.6	97.1	86.7	79.3
pH	3	5	7	9	11
COD (%)	82.7	90.8	97.1	86.2	90.2
Electrolyte	KCl	Na_2CO_3	NaCl	Na_2SO_4	NaF
COD (%)	92.1	74.8	97.1	81.1	96.2
[NaCl] (g/L)	0.5	1	1.5	2	2.5
COD (%)	81.6	82.1	85.6	97.7	83.3
[Polymer] (mg/L)	50	100	150	200	-
COD (%)	36.5	64.2	72	97.7	-
Temperature (^{O}C)	10	20	30	40	-
COD (%)	85.6	97.7	87.3	78.7	-

Effect of Initial Styrene Acrylate Concentration (Mg/L)

To observe the effect of initial SA concentration on SA and COD removal efficiencies by EC, experiments were carried out for four different SA concentration from 50 to 200 mg/L for 8 min, a current density of 25 mA/cm^2, inter electrode distance of 1 cm, pH of 7.3, NaCl concentration 2 g/L and temperature of 20^{o}C. Figure 5 and [Table 2a, 2b, 2c] show the percentage removal efficiencies of SA and COD for different initial SA concentration. The results indicate that by increasing initial SA concentrations, the SA and COD removal efficiencies increased. For example SA removal efficiency increases from 89.8% to 98.2% as SA concentration changes from 50 to 200 mg/L using Fe electrodes.

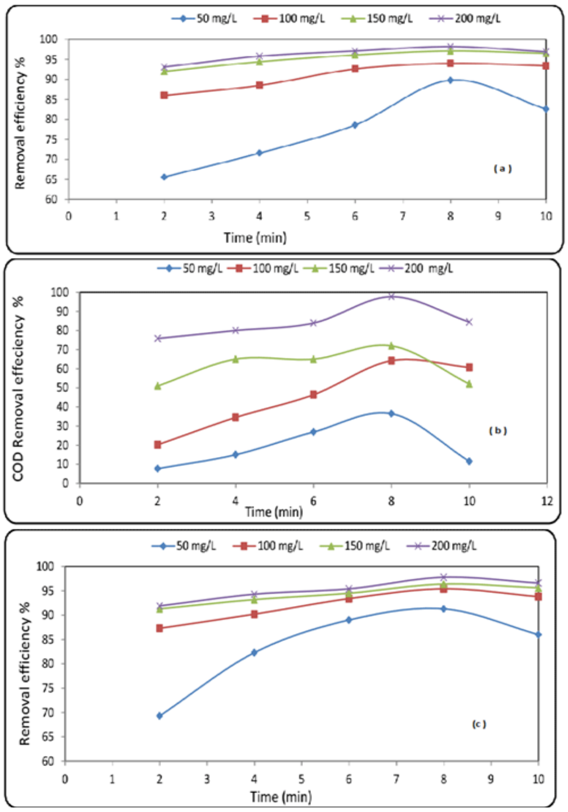


Figure 5: Effect of initial concentration on the efficiency of styrene acrylic adsoprtion using iron (a), stainless steel (b) and aluminum (c) electrodes respectively

Effect of Temperature (^{o}C)

Figure 6 and [Table 2a, 2b, 2c] show the effect of temperature on SA and COD removal efficiencies at 8 min, initial concentration of 200 mg/L, current density of 25 mA/cm^2, inter electrode distance of 1 cm, pH of 7.3 and at NaCl concentration of 2 g/L. The results from above figures indicate that the increasing temperature above 30^{o}C has a negative effect on removal efficiencies of SA and COD, where at 20^{o}C SA COD removal reached to (99.2% and 95.9%), (99.4% and 97.1%) and (99% and 93.1%) using Fe, S-S and Al electrodes respectively.

Effect of Electrolysis Time

The polymer removal efficiency directly depends on the concentration of hydroxyl and produced metal ions on the electrodes which increase by increasing time of electrolysis [15]. The optimum removal efficiencies for SA and COD electrolysis time was 8 min using Fe, S-S and Al electrodes and removal efficiencies reached a maximum value of 99.2%and 95.9 %) , (99.4 % AND 97.1 %) and 99 % and 93.1%) respectively at optimum condition.

Inter-Electrode Distance

Long distance between anodes and cathodes require high electrical energy for motion of ions. This is due to longer travel path that increased the resistance of motion of ions and the situation is reversed in the case of short distance between each electrode. Inter-electrode spacing of 1.0 cm had the low energy consumption and high removal efficiency.

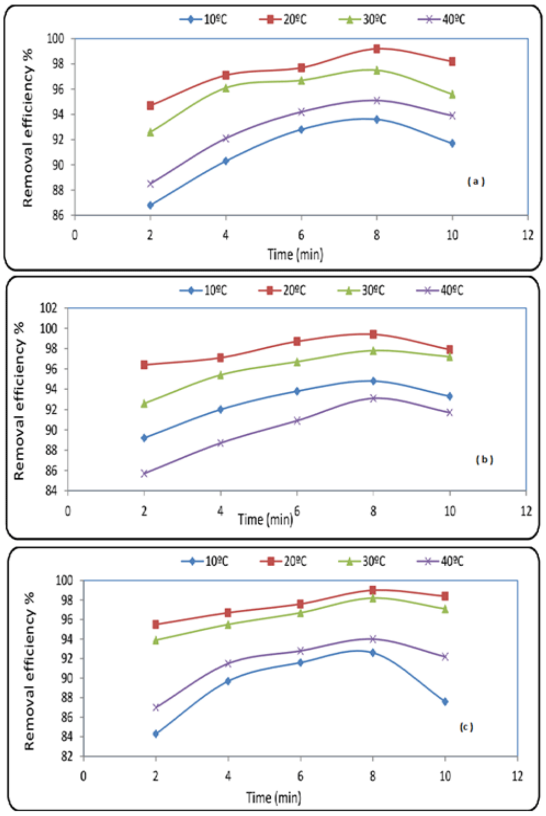


Figure 6: Effect of temperature on the efficiency of styrene acrylic adsoprtion using iron (a), stainless steel (b) and aluminum (c) electrodes respectively

Table 2 (c) : Effect of current density, pH, type of electrolyte, concentration electrolyte, rubber concentration, and temperature on the efficiency of COD removal for Styrene Acrylate using aluminum electrode

Current density (mA/cm^2)	10	20	25	35	50
COD (%)	89	84.4	93.1	70.1	47.1
pH	3	5	7	9	11
COD (%)	77.2	82.4	93.1	66.2	52.5
Electrolyte	KCl	Na_2CO_3	NaCl	Na_2SO4	NaF
COD (%)	91	68.5	93.1	71.1	71
[NaCl] (g/L)	0.5	1	1.5	2	2.5
COD (%)	62.6	77	83.9	93.1	77
[polymer] (mg/L)	50	100	150	200	-
COD (%)	53.8	84.5	79	93.1	-
Temperature (^{O}C)	10	20	30	40	-
COD (%)	76	93.1	89.6	79.3	-

Kinetic Studies of SA Copolymer

Kinetic studies: Figure 7 represent the SA removal using EC method of which exhibited pseudo first order with good correlation coefficient 0.932, 0.913 and 0.942 using Fe, S-S and Al electrodes according to following equation

$$LnA_t / A_o = -Kt \quad (4)$$

Where A_o, A_t, t and k are the SA absorbance at initial time reaction, SA absorbance after reaction, time of reaction (min), and reaction rate constant (min^{-1}) respectively. The straight lines in plots show a good agreement of experimental data with the kinetic models for different removal rate.

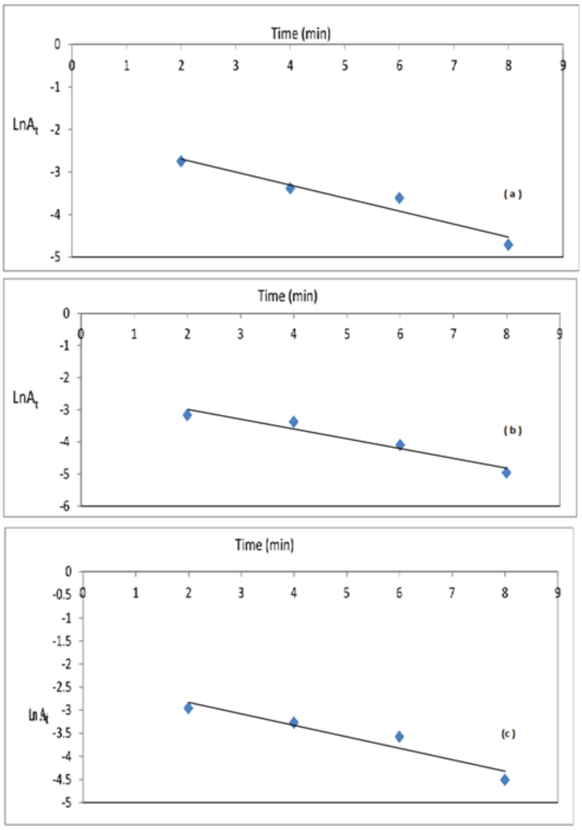


Figure 7: Relation between Ln At against the time for styrene acrylic adsoprtion using iron (a), stainless steel (b) and aluminum (c) electrodes respectively

Isotherm Modeling

Langmuir Adsorption Isotherm

This describes quantitatively the formation of a monolayeradsorbate on the outer surface of the adsorbent, and after that no further adsorption takes place. Thereby, theLangmuir represents the equilibrium distribution of metal ions between the solid and liquid phases. According the equation (5-6) two adsorption isotherms viz., Langmuir and Freundlich models were applied to establish the relationship between the amounts of SA adsorbed onto the iron hydroxides and its equilibrium concentration in the electrolyte containing contaminant ions. Figures [8 &9] represent the Freundlich and Langmuir Isotherms studies of equilibrium.

$$1/q_e = 1/q_m + 1/(q_m K_L C_e) \quad (5)$$

where qe ($mg.g^{-1}$) is amount adsorbed at equilibrium, Ce ($mg.L^{-1}$) equilibrium concentration, qm is the Langmuir constant representing maximum monolayer adsorption capacity and KL ($L.mg^{-1}$) is the Langmuir constant related to energy of adsorption [16]. The values of qmax and KLwere computed from the slope and intercept of the Langmuir plot of 1/qe versus 1/Ce. The essential features of the Langmuir isotherm may be expressed in terms of equilibrium parameter RL, which is a dimensionless constant referred to as separation factor or equilibrium parameter [17]

$$RL = 1/(1+(K_L+C_o) \quad (6)$$

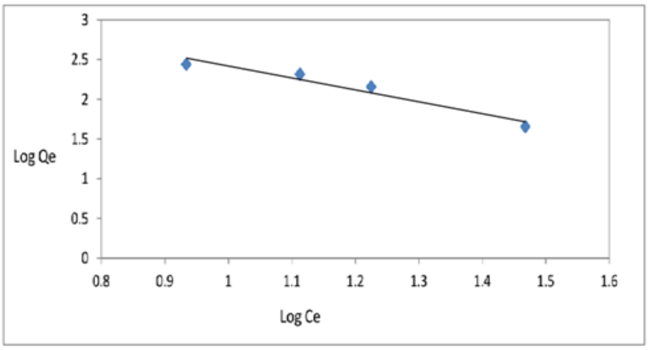


Figure 8: Freundlich plot (log qe vs. log Ce). for styrene acrylic adsorption using S.S electrodes

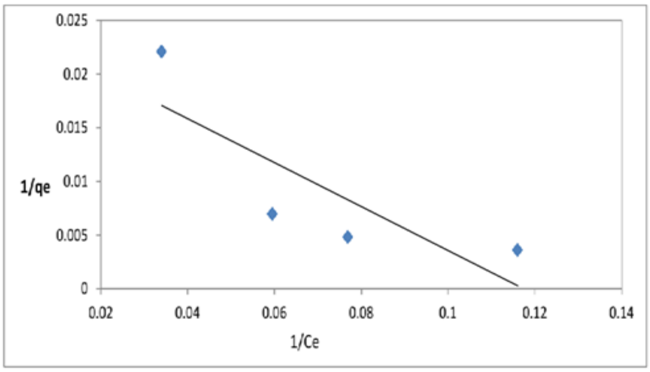


Figure 9: Langmuir plot (Ce/qe) vs. (Ce) for styrene acrylic adsorption using S.S electrodes

Where:

C_o = initial concentration , K_L = the constant related to the energy of adsorption (Langmuir Constant). R_L value indicates the adsorption nature to be either unfavourable if R_L>1, linear if R_L =1, favourable if 0< R_L<1 and irreversible if R_L =0

Freundlich Adsorption Isotherm

This is type of adsorption includes considerations of surface heterogeneity and exponential distribution of the active sites and their energies. The isotherm is adopted to describe reversible adsorption and is not restricted to monolayer formation. This isotherm typically fits the experimental data over a wide range of concentrations. The linearized and logarithmic expression of the Freundlich model is [18]

$$\text{Log } q_e = \text{Log } K_f + 1/n \text{ Log } C_e \qquad (7)$$

where kf (mg/g) and n (dimensionless) are constants that account for all factors affecting the adsorption process, such as the adsorption capacity and intensity. Te Freundlich constants Kf and n are determined from the intercept and slope, respectively, of the linear plot of log qe versus log C_e. Adsorption isotherms were obtained in terms of equations (5) and (7) by using experimental adsorption results in these equations. The values q_m, b, K_F, R_L and n are summarized in Table 3

Table 3: Parameters of Langmuir and Freundlichr isotherm constants and correlation coefficients using SS electrodes

Isotherm	R^2	Constnt	Value
Langmuir	0.777	q_m (mg /g)	41.66
		K_L	0.1176
		R_L	0.0409
Freundlich	0.954	K_F (mg /g)	8279
		n	0.667
		1/n	0.944

Electrical Energy Consumption

In an electrochemical process, the most important economical parameter is energy consumption Ec (KWh/m^3) [19-20] . This parameter is calculated from the following expression.

$$Ec = I\ Vt / volume \times 1000 \quad (8)$$

Where V, I, t and Volume stand for average voltage of the EC system (V), electrical current intensity (A), reaction time (h) and treated solution volume (m^{3}) respectively .

Mass of Loss From Anode Electrode

The loss of mass can calculated using Faraday's law of electrolysis by equation [21]

$$m = I.A.M.t / V.Z.F \quad (9)$$

where m is the mass of the anode material dissolved (g), I the current density ($A\ m^{-2}$), A the active electrode area (m^2), M the molar mass of the anode material ($g\ mol^{-1}$), t electrolysis time (s), V volume of the reactor (m^3), z the number of electrons transferred, and F the Faraday's constant (96,485 $C\ mol^{-1}$). the maximum possible mass of Fe and Al electrochemically generated from sacrificial anodes in Table [4] at optimum condition for each process.

Comparison Between the Electrocoagulation and Other Method Reported in Literature for Removal Efficiency of Polymers and COD

The percentages of adsorption for each method using in literature and the electrochemical method in this work were represented in the Table 5. It is clear that the electrochemical degradation is the best.

Table 4: mass of loss from Fe and Al electrode

SA polymer	Fe^{+2} (Kg/m^3)	Fe^{+3} (Kg/m^3)	Al^{+3} (Kg/m^3)
value	1.39×10^{-4}	9.28×10^{-5}	4.4×10^{-5}

Table 5 : Comparison between the Electrocoagulation method for adsorption efficiency styrene acrylic copolymer with other methods

Type of degradation	Reference	Removal %	Time
ultrasonic irradiation	(Saien et al., 2010)	91%	30 min
Electrocoagulation (S-S electrodes)	This study	97.1%	8 min
Electrocoagulation (Fe electrodes)	This study	95.9 %	8 min
Electrocoagulation (Al electrodes)	This study	93.1 %	8 min

Conclusion

The present study attempted to investigate the applicability of an electrocoagulation method in the treatment of SA polymer in aqueous solutions. The effects of initial pH, initial polymers concentration, current density, type of electrolyte, salt concentration, and temperature were investigated on removal efficiency and COD. The following conclusions are drawn up based on the results :

- The adsorption of SA polymers in aqueous solution using different electrodes was affected by different types of parameters such as current density, initial pH, initial type electrolyte, salt concentration, initial polymer concentration and temperature
- SA and COD removal were (99.2% and 95.9 %), (99.4% and 97.1%) and (99 % and 93.1 %) by using Fe, S-S and Al electrodes at 8 min, electrical energy consumption (0.283, 0.243 and 0.18 KWh/m^3) using Fe, S-S and Al electrodes respectively for SA with typical operating conditions: current density 25 mA/cm^2, pH 7.3, NaCl concentration 2 g/L, polymer concentration 200 mg/L, inter-electrode distance 1.0 cm and temperature 20 ^{o}C using all electrodes.
- The results were concluded that the electrode material play an important role in electrocoagulation method for treatment of polymer in aqueous solution.
- The SA adsorption was best fitted by the Freundlich adsorption isotherm, and the results were in good agreement with the experimental data

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