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Removal of Basic Dye Bromophenol Blue from aqueous solution by Electrocoagulation using Al – Fe Electrodes: Kinetics, Equilibrium and Thermodynamics Studies

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ABSTRACT

Electrocoagulation (EC) in a batch cell with Al anode and Fe cathode in monopolar parallel (MP) connection was used for the removal of basic dye, Bromophenol Blue (BPB). The effects of current density, pH, temperature and initial dye concentration, on the process were investigated. Equlibrium data were analyzed using four model equations: Langmuir, Freudlinch, Temkin and Dubinin–Radushkevich. Data obtained from the time dependent electrocoagulation removal of BPB were analyzed with pseudo-first-order, pseudo-second-order and Elovic kinetic models. The study showed that the process depend on current density, temperature, pH and initial dye concentration. The process attained equilibrium after 15 minutes at 30 ^oC, all the isotherm models fitted the data with $R^2 > 0.9$. The maximum removal capacity Q_m value of 166.50 mg g^{-1} was obtained for the study while the first order kinetic model best described the process based on the lower values of %SSE. The calculated thermodynamics parameters (ΔG^o, ΔH^o and ΔS^o) indicated that the process is spontaneous and endothermic in nature.

Keywords: Electrocoagulation; Iron and Aluminium Electrodes; Bromophenol blue; kinetics; thermodynamics; isotherms.

INTRODUCTION

The discovery of synthetic dyes marks the beginning of tremendous change in the manufacturing industries connected with dye usage either as a raw materials or final products. Synthesis of dyes involved the use chemicals that are toxic, carcinogenic and sometimes explosive [1]. The residual dyes from various industrial effluents such as: textile, paper and pulp, dye and dye intermediates, pharmaceutical, tannery and kraft bleaching industries are considered as organic coloured pollutants [2 – 5]. These industries utilize large quantities of variety of dyes which residues lead to large amount of coloured wastewaters, toxic and even carcinogenic, posing serious hazard to aquatic living organisms. Most dyes used in industries are stable to light, heat and oxidation, they are not biologically degradable and are also resistant to aerobic digestion [6], and even when they degrade they produce toxic and hazardous products [7].

Dyes used in the industries are classified into three classes: (a) anionic (direct, acid, and reactive dyes); (b) cationic (all basic dyes) and (c) non-ionic (dispersed dyes). Bromophenol Blue is a

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basic dye of triphenylmethane derivative (Figure 1); it is structurally similar to fluoresceins and xanthenes that are widely used as industrial dyes for foods, drugs, cosmetics, textiles, printing inks, or laboratory indicators. Some of these compounds have been reported to be genotoxic [8], hence, treatments of such dye-laden effluents is important before discharge into aquatic environment because they may eventually return to food chain.

Removal of these dyes from industrial wastewaters is a crucial process, from both economic and environmental points of view [9]. Effective electrochemical techniques which include; electro-oxidation, electrochemical reduction, electro-coagulation, electro-flotation and [10], have been developed for the treatment of organic pollutants in wastewater with higher efficiency than any of biological, physical and chemical process [11, 12]. Electrocoagulation has been known for some time as a process capable of fractionating a number of organic substances in a rather efficient manner by electrochemical coagulation. The coagulants are generated in-situ by electro oxidation of the anode, mostly iron or aluminum because of their availability and relatively low cost. Electrocoagulation is accomplished in a three step processes as follows: (1) Electrolytic reactions at surface of electrodes, (2) Formation of coagulants in aqueous phase and (3) Adsorption of soluble or colloidal pollutants onto coagulants and removal of them using sedimentation or flotation of flocs when hydrogen gas bubbles were produced at the cathode [13]. Combinations of electrocoagulation with flocculation (electrocoagulation /electroflotation) have also been studied extensively in the the field of removal of dye in the laboratory and pilot scale [14 – 17].

In this study, BPB was removed from aqueous solution in an electrochemical cell using Aluminum anode and Iron cathode in monopolar parallel connection. The following reactions were envisaged at the electrodes:

Anodic reaction:

$$M \rightarrow M^{n+} + ne^- \tag{1}$$

$$2H_2O \rightarrow 4H^+ + O_2 + 4e^- \tag{2}$$

Cathodic reaction:

$$M^{n+} + ne^- \rightarrow M \tag{3}$$

$$H_2O + 2e^- \rightarrow H_2 + 2OH^- \tag{4}$$

From the eqns. 1 – 4 above, the metal ions (M^{n+}) produced immediately undergo further spontaneous reactions producing corresponding hydroxides and polyhydroxides having strong affinity for dispersed particles as well as counter ions bringing about the coagulation [18]. The gases evolved at the electrodes separate particles and coagulant aggregates by lifting them up through a flotation-like process while accelerating collisions between particles and coagulant by inducing more mixing [19]. The effect of current density, initial dye concentration, electrolyte concentration, pH and temperature were studied. Adsorption kinetics of electrocoagulants was analyzed with pseudo-first-order, pseudo-second-order, and Elovic kinetic models. The diffusion mechanism was analyzed with intraparticulate diffusion model while the equilibrium adsorption behaviour was analyzed by fitting the equilibrium data with Langmuir, Freudlinch, Tempkin, and Dubinin–Radushke isotherm models. Thermodynamic parameters such as free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) were also determined to understand the heat efficiency of the electrocoagulation process.

MATERIALS AND METHODS

Dye solution preparation

Bromophenol Blue (BPB) (3',3",5',5"-Tetrabromophenolsulfonphthalein Sodium (Fig. 1), CAS 115-39-9, Product No. – 020015) was a product of Central Drug House, Delhi, India. 1000 mgL^{-1} aqueous solution of BPB was prepared with de-ionized water as the stock solution and was further diluted with de-ionized water to obtain the working standard solutions. The pH of the solution was adjusted when necessary with aliquots of HCl and NaOH (1.0 $molL^{-1}$) before the commencement of the experiment. The conductivity of the solution was maintained with NaCl solution as electrolyte.

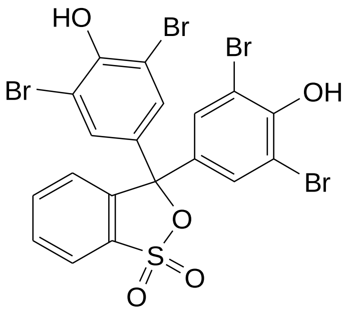

Fig. 1. Structure of Bromophenol Blue

Experimental Apparatus and Procedures

The electrocoagulation cell consists of a 0.6 L glass cell fitted with a polycarbonate cell cover with slots to introduce the electrodes, thermometer and electrolyte, the aluminum and iron electrodes of dimension 4.5 x 7 x 0.3 cm with inter electrode distance of 2 cm were fully immersed in the 0.5 L solution of the dye (Figure 2). A regulated direct current (DC) was supplied from a rectifier (0 - 2 A, 0 – 35 V; Applab 7711 multi-output). The temperature of the electrolyte was controlled to the desired value with a variation of ±1 ^oC by adjusting the temperature knob on the IKA RCT Basic magnetic hotplate stirrer and allowed to equilibrate before the commencement of the experiment. The electrocoagulation process commenced by switching on the DC generator having filled the cell with the appropriate dye solution.

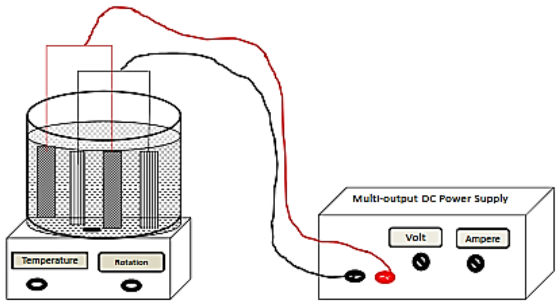

Fig. 2. Laboratory Scale Electrocoagulation Cell

Analytical Procedure

The concentrations of the dye in solutions were estimated using spectrophotometer (UV-VIS –NIR VARIAN 500 Scan CARY). FTIR of BPB and residual dye were obtained using FTIR spectrophotometer (TENSOR 27 Bruker Optik GmbH, Germany) in order to compare the dye obtained from the coagulation with the original BPB dye.

Effect of current density

Current density is an important factor among the various operating variables, which strongly influences the performance of electrocoagulation process. The amount of coagulants generated is related to the time and current density [20]. In order to investigate the effect current density on the removal of BPB, series of experiments were carried out on solutions containing 50 mg L^{-1} BPB, at 30 ^oC, pH 7.0 and electrolyte concentration maintained with 2 g L^{-1} NaCl, while the current density was varied between 0.12 to 0.59 Am^{-2}. Sample solutions were withdrawn and the residual dye concentrations were determined.

Effect of Initial Dye Concentration and Contact Time

The effect of initial dye concentration and contact time were investigated by performing electrocoagulation on dye solution with known initial concentrations of 10, 20, 30, 40 and 50 mg L^{-1} at constant temperature of 30 °C, current density 0.59 Am^{-2}, pH 7.0 and electrolyte concentration maintained with 2 g L^{-1} NaCl. Samples were withdrawn and analyzed for the residual dye from the aqueous at preset time intervals.

Effect of pH on electrocoagulation process

pH plays an important role on electrocoagulation process of dye by influencing the chemistry of the coagulant, dye molecule and that of electrochemical process in the solution. To investigate the effect pH, on the removal of BPB, series of experiments were carried out on solutions with initial pH varied between 3 and 11. The pH was adjusted with 0.1M NaOH or 0.1M HCl and measured using pH meter. The concentration of the solutions, current density and temperature were held constant at 50 mg L^{-1}, 0.59 $Am^{-2}$and 30 °C respectively.

Effect of electrolyte concentration

Electrolyte concentration play significant role in the process of electrocoagulation, to investigate the effect electrolyte concentration on the electrocoagulation removal efficiencies of BPB, experiments were performed on solutions containing BPB (50 mg L^{-1}), at current density of 0.59 Am^{-2} and pH 7, while the concentrations of NaCl were varied between 1 to 5 g L^{-1}.

Equilibrium Studies

The equilibrium studied was carried out on different concentrations as the process was then allowed to attain equilibrium, the sample solutions were then withdrawn while the concentration of the residual dye in the solution determined using UV-VIS-NIR spectrophotometer. The amount of dye coagulated at equilibrium, Q_e (mg g^{-1}), was calculated using equation 5 below:

$$Q_e = \frac{(C_o - C_e)V}{W} \tag{5}$$

where C_o (mg L^{-1}) is the initial concentration and C_e (mg L^{-1}) is the concentration of the dye at equilibrium in the liquid-phase. V is the volume of the solution (L) while W is the mass of the coagulant which can be estimated from Faraday Law according to the equation 6:

$$W = \frac{MIt}{nF} \tag{6}$$

M is the molar mass (g mol^{-1}) of the elements, I is the current (ampere), t is the electrocoagulation time in seconds, n is the number of electrons involved and F is Faraday's constant (96485.3 C mol^{-1}).

The percentage dye removal as colour removal:

$$\%Colour\ Removal = \frac{(Abs_o - Abs_e)x100}{Abs_0} \tag{7}$$

where Abs_o, is the blank absorbance and Abs_e is the absorbance at equilibrium.

Electrocoagulation Kinetics Studies

Since the amount of coagulant can be estimated for a given time, the pollutant removal can be modelled using an adsorption phenomenon. The procedures for the kinetics studies were basically identical to those of equilibrium tests. The aqueous samples were taken at preset time intervals, and the concentrations of the dye were similarly determined. The amount of dye removed at time t, Q_t (mg g^{-1}), was calculated using Equation 8:

$$Q_t = \frac{(C_o - C_t)V}{W} \tag{8}$$

where C_o (mg L^{-1}) is the initial concentration and C_t (mg L^{-1}) is the concentration of the dye at time t in the liquid-phase. V is the volume of the solution (L), and W is the mass of $Al(OH)_3$ calculated as stated in eqn. 6 above. In order to investigate the mechanisms of the adsorption process, pseudo-first order, pseudo-second-order and Elovich models respectively were applied to describe the kinetics of adsorption of BPB to $Al(OH)_3$ generated during the electrocoagulation process. A model is adjudged best-fit and selected based on statistical parameters.

EQUILIBRIUM DATA ANALYSIS

Adsorption Isotherms:

The equilibrium data from this study the coagulated and the remaining dye in the solution were described with the six adsorption isotherm models. These are models by Langmuir [21], Freudlinch [22], Temkin [23], Dubinin and Radushkevich [24]. The acceptability and suitability of the isotherm equation to the equilibrium data were based on the values of the correlation coefficients, R^2 estimated from linear regression of the linearized form of the equation using Microsoft excel 2000 package.

Langmuir Isotherms

The Langmuir isotherm equation is based on the following assumptions that the entire surface of adsorbent has the same activity for adsorption, no interaction between adsorbed molecules and the adsorption occurs by the same mechanism with less than one complete monomolecular layer on the surface. The Langmuir equation is given by equation (8) [21]:

$$Q_{eq} = \frac{Q_o b C_e}{1 + bC_e} \tag{8}$$

where Q_o is the maximum amount of the dye molecule per unit weight of the coagulant to form a complete monolayer on the surface C_e (mg g^{-1}) is the concentration of the dye remaining in solution at equilibrium and b is equilibrium constant (dm^3 mg^{-1}). The essential features of the Langmuir isotherm can be expressed in terms of a dimensionless constant, R_L called separation factor [27] represented by equation 9.:

$$R_L = \frac{1}{1 + bC_0} \tag{9}$$

where C_o is the initial concentration (mg L^{-1}) and b is the Langmuir equilibrium constant (L mg^{-1}). The value of R_L indicated the type of Langmuir isotherm to be either irreversible if $R_L = 0$, favourable when $0 < R_L < 1$, linear when $R_L = 1$ and unfavourable when $R_L > 1$. However, it can be explained apparently that when $b > 0$, sorption system is favorable [28].

Freundlich Isotherm

The Freundlich isotherm is an empirical equation based on sorption on a heterogeneous surface. It is commonly presented as:

$$Q_{eq} = K_F C_e^{1/n} \tag{10}$$

where K_F and n are the Freundlich constants related to the adsorption capacity and intensity of the sorbent, respectively [29, 30].

Tempkin Isotherm Model:

Temkin isotherm model (equation 12) was also used to fit the experimental data. Unlike the Langmuir and Freundlich equations, the interactions between sorbent and adsorbent were taken into account in Temkin isotherm with the assumption that the free energy of sorption is a function of the surface coverage [24].

$$Q_e = \frac{RT}{b_T} \ln a_T C_e \tag{12}$$

where C_e is concentration of dye in solution at equilibrium (mg L^{-1}), Q_e is the amount of dye molecule coagulated at equilibrium (mg g^{-1}), T is the temperature (K), and R is the ideal gas constant (8.314 J mol^{-1} K^{-1}) and 'a_T' and 'b_T' are constants relating to binding constant (L mg^{-1}) equilibrium corresponding to the maximum bonding energy and the heat of adsorption respectively.

The Dubinin–Radushkevich isotherm

The Dubinin–Radushkevich model represented by equation 13 [24] was chosen to estimate the heterogeneity of the surface energies and also to determine the nature of adsorption processes as physical or chemical. This isotherm is more general than the Langmuir isotherm as its derivation is based on ideal assumptions such as equipotent of the sorption sites, absence of stoic hindrance between sorbed, incoming particles and surface homogeneity on microscopic level [31, 32].

$$Q_e = Q_m e^{-\beta \varepsilon^2} \tag{13}$$

where Q_m is the theoretical saturation capacity (mol g^{-1}), β is a constant related to the mean free energy of adsorption per mole of the adsorbate (mol^2 J^{-2}), and ε is the Polanyi potential given by the relation; $\varepsilon = RT\ln(1+ {1}/{C_e})$. Ce is the equilibrium concentration of dye in solution (mg L^{-1}), R (J mol^{-1} K^{-1}) is the gas constant and T (K) is the absolute temperature. The constant β is related to the mean free energy, E (kJ mol^{-1}) of adsorption per molecule of the adsorbate according to equation 14 [33]. The magnitude of E determines whether the adsorption process is chemisorption (i.e. 8<E<16) or physiorption (i.e. E < 8)

$$E = -(2\beta)^{-0.5} \tag{14}$$

KINETIC DATA ANALYSIS

The pseudo - first order kinetics model

A simple kinetics analysis of the process under the pseudo-first order assumption is given by equation 17 below [8, 30]:

$$\frac{dQ}{dt} = k_1(Q_e - Q_t) \tag{17}$$

where Q_e and Q_t are the dye concentrations (mg g^{-1}) at equilibrium and at time t (min), respectively, and k_1 the adsorption rate constant (min^{-1}), and t is the contact time (min). The integration of equation 17 with initial concentrations, Q_t = 0 at t = 0, and Q_t = Q_t at t = t, yields equation 18 below:

$$\ln(Q_e - Q_t) = \ln Q_e - k_1 t \tag{18}$$

Upon rearrangement, equation 18 becomes:

$$Q_t = Q_e(1 - e^{-k_1 t}) \tag{19}$$

The values of Q_e and k_1 were calculated from the least square fit of Q_t versus t at different dye concentrations.

The pseudo-second order kinetics model

A pseudo-second order kinetics model is based on equilibrium adsorption [26, 30] and it is expressed as shown equation 20 below:

$$t/Q_t = 1/k_2 Q_e^2 + (1/Q_t)t \tag{20}$$

The expression above can also be rearranged to give equation 21 below:

$$Q_t = \frac{k_2 Q_e^2 t}{1 + k_2 Q_e t} \tag{21}$$

where k_2 (g mg^{-1} min^{-1}) is the rates constant of pseudo-second order adsorption, The values of Q_e and k_2 were calculated from the least square fit of Q_t versus t at different dye concentrations.

Elovich Model

Elovich model is a kinetic equation describing a chemisorption process [31], it describes the rate of adsorption which decreases exponentially with an increase in the adsorbed. It is generally expressed as SHOWN BY EQN. 22 [32]:

$$Q_t = \frac{1}{\beta}\ln(\alpha\beta * t) \tag{22}$$

where α is the initial adsorption rate (mg g-1 min-1), β is the desorption constant (g mg-1). The value of reciprocal of β reflects the number of sites available for adsorption whereas the value of adsorbed quantity when ln t is equal to zero is given by $\frac{1}{\beta}\ln(\alpha\beta)$.

Intra-particulate Diffusion Model

Due to the fact that the diffusion mechanism cannot be obtained from the kinetics model, the intraparticlate diffusion model [8] was also tested. The initial rate of the intraparticle diffusion is given by the following expression:

$$Q_t = K_{id}t^{0.5} + Ci \tag{24}$$

where K_{id} is the intraparticle diffusion rate constant (mg g^{-1} $min^{-0.5}$) and C_i is intercept and a measure of surface thickness.

Statistical Test for the kinetics data

The acceptability and hence the best fit of the kinetic data were based on the square of the correlation coefficients R^2 and the percentage error function which measures the differences (% SSE) in the amount of the dye concentration coagulated at equlibrium predicted by the models, (Q_{cal}) and the actual, (i.e. Q_{exp}) measured experimentally. The validity of each model was determined by the sum of error squares (SSE, %) given by:

$$\%SSE = \sqrt{\frac{((Q_{(\exp)} - Q_{(cal)})/Q_{\exp})^2}{N-1}} \times 100 \tag{23}$$

N is the number of data points. The higher is the value of R^2 and the lower the value of SSE; the better fitted the data.

Thermodynamics of electrocoagulation process

Arrhenius equation is applied to estimate the activation energy of adsorption according to the relationship:

$$\ln k = \ln A - \frac{E_a}{RT} \tag{25}$$

where k is the rate constant obtained from the kinetic model, Ea is the Arrhenius activation energy of adsorption, (kJ/mol), A is the Arrhenius factor, R is the universal gas constant (8.314 J mol^{-1} K^{-1}) and T is the absolute temperature. The thermodynamics parameters i.e. $\Delta G°$, $\Delta H°$ and $\Delta S°$ were estimated using the following relation:

$$\Delta G^o = -RT\ln K_d \tag{26}$$

$$\ln K_d = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \tag{27}$$

The equilibrium constant, $K_{d,}$ is obtained from the value of Q_e/C_e at different temperature equilibrium study. Van't Hoff plot of ln K_d against the reciprocal of temperature (1/T), should give a straight line with intercept as $\frac{\Delta S^0}{R}$ and slope as $\frac{\Delta H^0}{R}$.

RESULT AND DISCUSSION

Batch Equilibrium Studies

Effect of current density

Current density determines the coagulant production rate, and adjusts the rate and size of the bubble production, and hence affects the growth of flocs [33, 34]. Figure 3 shows the plot of current density versus the percentage colour removal by the electrocoagulation process. This figure showed that increased in current density led to significant increase in the colour removal, the percentage colour removal increases from 60 to 99.31 % as the current density increases from 0.12 to 0.59 Am^2. Increasing current density results in a corresponding increase in the production of coagulant in the solution leading to high efficiency. The optimum current density was used throughout the study.

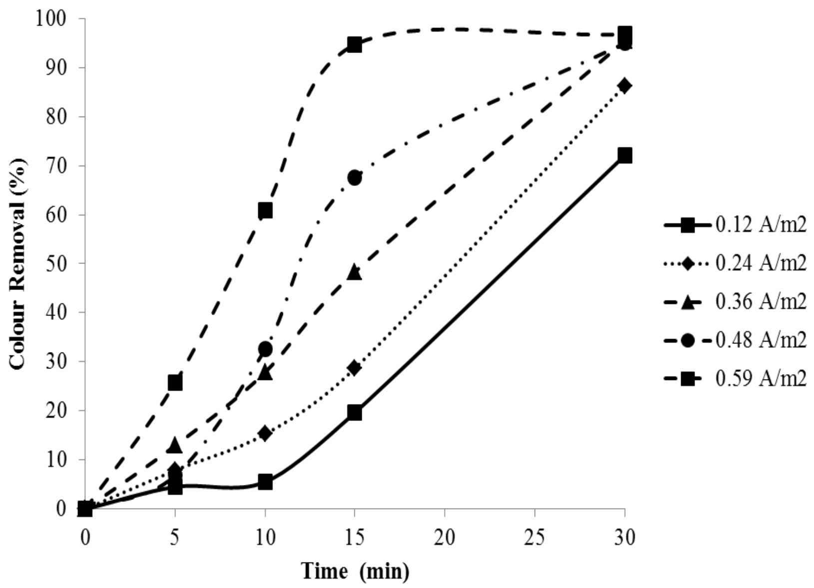

Fig. 3. Effect of current density on % Colour Removal, Dye concentration 50 mg L^{-1}, at 30 ^{o}C, pH 7.0 and NaCl; 2 g L^{-1}

Effect of pH on electrocoagulation process

pH is an important parameter influencing the performance of the EC process [33], it affects the chemistry of both the coagulants, dye molecules and that of electrochemical process in the solution. The percentages colour removal for dye solutions with various initial pH values were shown in Fig. 4a, while the final pH of the solution is shown in Fig. 4b. The colour removal efficiency is optimum at pH 7 with roughly 100 % colour removal efficiency. The decrease in removal efficiency at more acidic and alkaline pH had been attributed to amphoteric behaviour of $Al(OH)_3$ which leads to soluble Al^{3+} cations (at acidic pH) and formation of monomeric anions (at alkaline pH). These ions transform finally into solid $Al(OH)_3$ according to complex precipitation kinetics thereby affecting the removal efficiency [35, 36].

Effect of electrolyte concentration

Solution conductivity influences the current efficiency, cell voltage and consumption of electrical energy in electrolytic cells. The use of NaCl to increase solution conductivity is also accompanied by the production of chloride ions that reduce the effects of other anions, such as bicarbonate and sulphate which may lead to precipitation of Ca^{2+} leading to ohmic resistance of the electrochemical cell [36]. Figure 5 shows that the maximum removal efficiency was obtained at 1 gL^{-1} a further increase in electrolyte concentration beyond this value do not significantly affect the removal efficiency of the dye from the solution. The results also suggest that high color removal percentage with low cell voltages and low energy consumption can be obtained at NaCl concentration of 1 g L^{-1}.

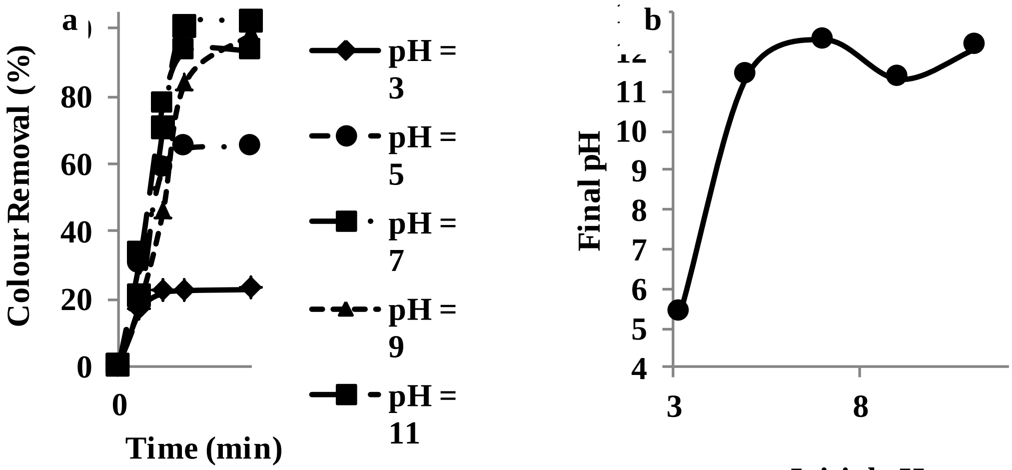

Fig. 4. (a) Effect of initial pH on % Colour Removal (b) Initial and final pH of the dye solution. Dye concentration 50 mg L^{-1}, at 30 °C, Current Density: 0.59 Am^{-2} and NaCl; 2 g L^{-1}

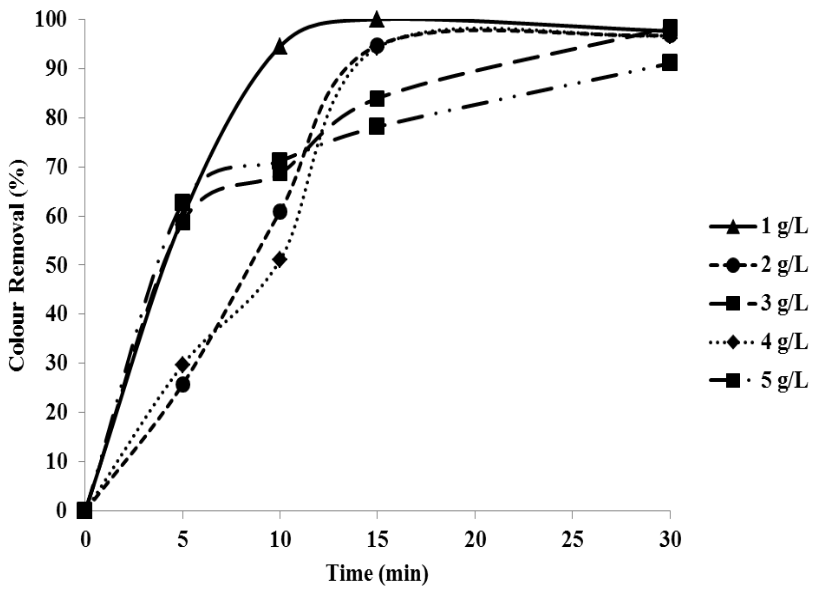

Fig. 5. Effect of electrolyte concentration on % Colour Removal. Dye concentration 50 mg L^{-1}, at 30 °C, Current Density: 0.59 Am^{-2} and pH 7.

Effect of initial dye concentrations

The effect of initial dye concentration on the electrocoagulation removal of BPB is shown in Figure 6 for dye concentrations increasing from 25 to 100 mg L^{-1}. The process showed rapid removal in the first

10 minutes for all the concentrations studied. The efficiency of the process increases from 9.5 to 50.3 mg g^{-1} as the initial concentration increase from 10 to 50 mg L^{-1}. There is no significant difference in the amount coagulated after 15 minutes of the process, a steady-state approximation was assumed and a quasi-equilibrium situation was suggested. The electrocoagulation curves were single, smooth, and continuous, leading to saturation. This is an indication of possible monolayer coverage on the surface of electrochemically generated coagulant [17, 37].

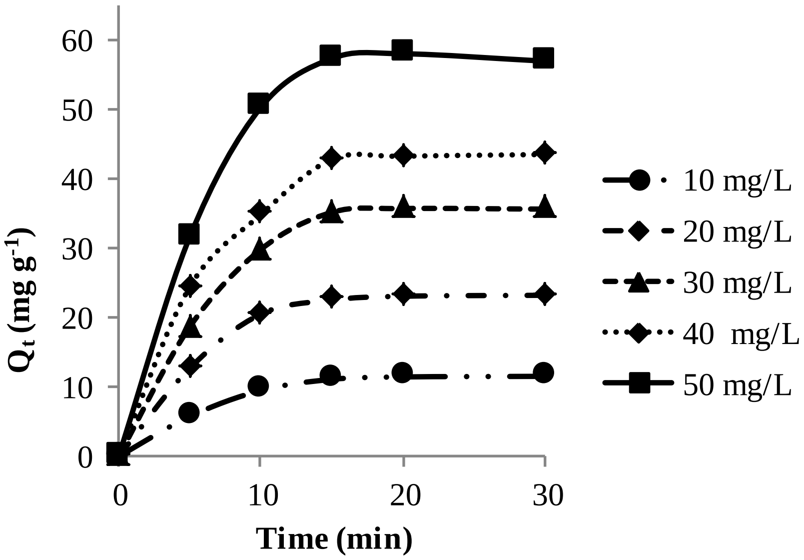

Fig. 6. Effect of initial concentration on the electrocoagulation removal of Bromophenol Blue Dye. Temp 30 °C, Current Density: 0.59 Am^{-2} and pH 7.

ADSORPTION STUDY

Adsorption Isotherms

The adsorption data obtained at different initial dye concentrations were fitted into six different isotherm models as shown in Figure 7. The adsorption data fitted well with all the isotherms with Redlich-Peterson having the highest R^2 (Table 1). The Q_m value of 166.50 mg g^{-1} was obtained for the Langmuir isotherm model (Table 1). The slope of Freudlinch isotherm is 0.85 which is an indication of adsorption becoming more heterogeneous. The mean adsorption energy E obtained from Dubinin–Radushkevich was 0.592 kJ/mol which is an indication of physisorption dominated processes.

Table 1. Langmuir, Freudlinch, Tempkin, and Dubinin–Radushkevich the removal of Bromophenol Blue

Langmuir		**Freudlinch**		**Temkin**		**Dubinin–Radushkevich**	
Q_{max} (mg g^{-1})	166.50	K_f (mg g^{-1} $min^{-1/n}$)	7.47	a_T (L g^{-1})	0.83	Q (mg g^{-1})	46.29
b (L mg^{-1})	0.044	1/n	0.85	b_T	112.45	β (mol $J^{-1})^2$	1.43x 10^{-6}
R_L	0.47	R^2	0.963	R^2	0.965	E (kJ mol^{-1})	0.592
R^2	0.964					R^2	0.965

Temperature; 30 °C, Current Density: 0.59 Am^{-2} and pH 7.

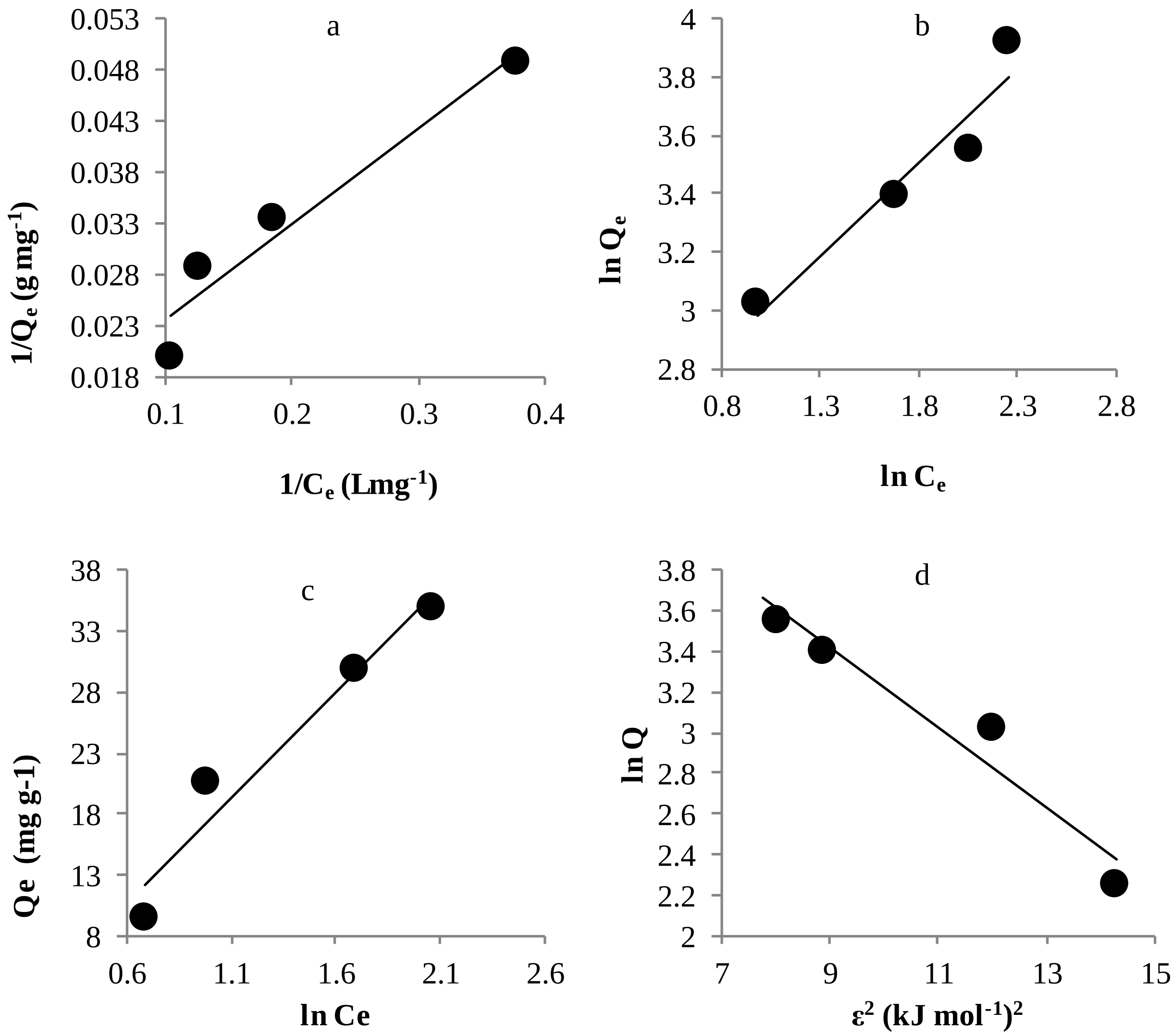

Fig. 7. Isothermal fits for electrocoagulation removal of Bromophenol Blue: (a) Langmuir (b) Freudlinch (c) Temkin, (d) Dubinin – Radushkevich.

Electrocoagulation kinetics

The plots of three different kinetic models used to explain the adsorption data are shown in Figure 8, the pseudo-first-order kinetic models fit well with experimental data when compared with other models (Table 2). The rate constant from all the models increases with initial dye concentration up to 10 mg L^{-1} before decreasing at 30 mg L^{-1}. This shows that at higher initial concentration the electrostatic interaction decreases at the site, thereby lowering the adsorption rate. The behaviour of Elovich constant shows that the process of adsorption is more than one mechanism.

Adsorption Mechanism

The mechanism of adsorption was investigated by subjecting the data to intraparticulate diffusion model. The plots are shown in Figure 9. The linearity of the plot is not over the whole time range rather they exhibit multi-linearity revealing the existence of two successive adsorption steps. The first stage is faster than the second, and it is attributed to the external surface adsorption referred to as the boundary layer diffusion. Thereafter, the second linear part is attributed to the intraparticle diffusion stage; this stage is the rate controlling step.

Table 2. The pseudo first, second-order and Elovich adsorption rate constants parameters and Q_e values for different initial dye concentration

C_o (mg/L)	First Order					Second order				Elovich		
	$Q_{e\,exp}$ (mg g^{-1})	$Q_{e\,cal}$ (mg/g)	k_1 (min^{-1})	R^2	% SSE	$Q_{e\,cal}$ (mg/g)	$k_2 \times 10^{-3}$ (g mg^{-1} min^{-1})	R^2	% SSE	β (g mg^{-1})	α (mg g^{-1} min^{-1})	R^2
10	9.51	13.34	0.09	0.97	0.64	18.86	3.76	0.97	1.56	2.18	0.19	0.97
20	20.52	24.98	0.13	0.91	0.74	32.03	3.86	0.99	1.92	6.88	0.13	0.98
30	29.85	39.36	0.11	0.99	1.56	52.10	1.95	0.98	3.71	8.79	0.07	0.98
40	34.87	49.51	0.10	0.98	2.44	68.46	1.16	0.98	5.60	8.90	0.05	0.98
50	50.34	62.71	0.12	0.99	2.06	81.44	1.41	0.98	5.18	15.65	0.05	0.98

. Temperature; 30 °C, Current Density: 0.59 Am^{-2} and pH 7.

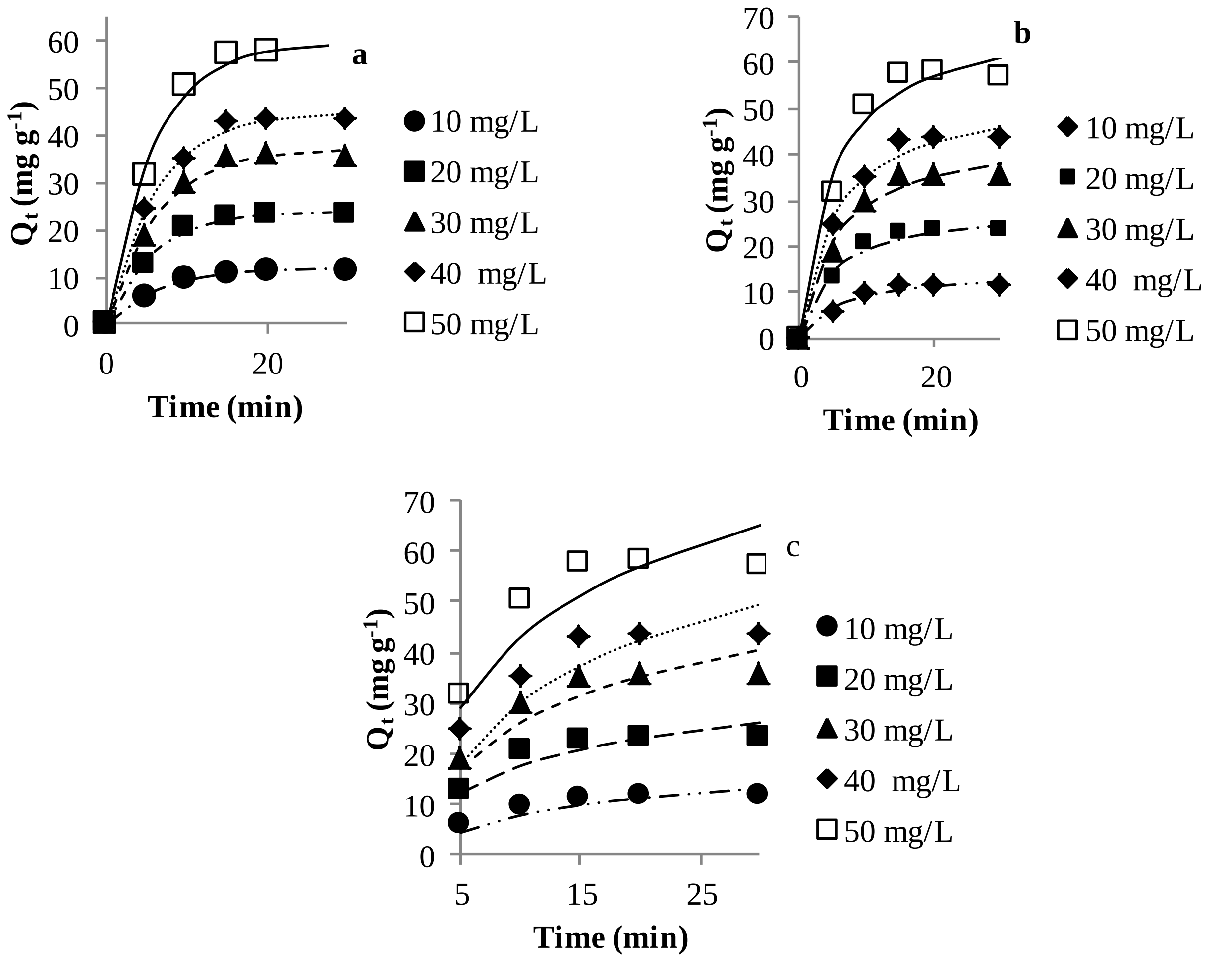

Fig. 8. Kinetic of electrocoagulation removal of Bromophenol Blue (a) Pseudo first-order kinetic (b) Pseudo second-order kinetic and (c) Elovich kinetic model fit. Temp 30 °C, Current Density: 0.59 Am^{-2} and pH 7.

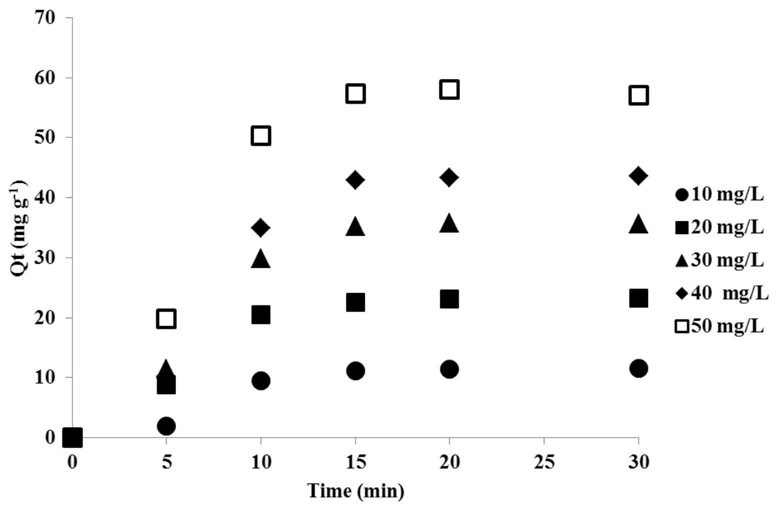

Fig. 9. Intraparticulate diffusion fit for electrocoagulation removal of Bromophenol Blue dye. Temp 30 ^oC, Current Density: 0.59 Am^{-2} and pH 7.

Table 3 shows the intraparticle model constants for the electrocoagulation removal of BPB dye The K_{di} values were found to be decreasing from first stage of adsorption toward the second stage. The increase in dye concentration results in an increase collision of dye molecules thereby affecting the dye diffusion rate.

Table 3. Intra-particle diffusion model's parameters for the removal of Bromophenol Blue

Co (mg/L)	Intraparticulate					
	k_{1d} (mg g^{-1} min $^{-0.5}$)	C_1 (mg g^{-1})	R^2	k_{2d} (mg g^{-1} min $^{-0.5}$)	C_2 (mg g^{-1})	R^2
10	2.956	-1.203	0.824	1.514	4.887	0.908
20	6.073	-1.1117	0.938	1.997	14.4	0.929
30	9.285	-2.382	0.92	4.601	15.96	0.855
40	11.19	-3.943	0.872	6.575	15.12	0.828
50	15.292	-3.575	0.924	6.031	32.14	0.853

Temperature; 30 ^oC, Current Density: 0.59 Am^{-2} and pH 7.

THERMODYNAMIC PARAMETERS

Figure 10 shows that the rate constants vary with temperature according to Equation (25). The activation energy (33.02 kJ mol^{-1}) was obtained from the slope of the fitted equation. The free energy change, ΔG is obtained from Equations (26 and 27) according to the van't Hoff linear plots of ln K_d versus 1/T plot in Figure 11.

The thermodynamic parameters are presented in Table 4. From the Table, it is found that the negative value of ΔG indicates the spontaneous nature of adsorption. Positive value of enthalpy change indicates that the adsorption process is endothermic in nature, and the negative value of change in internal energy (ΔG) show the spontaneous adsorption of BPB on the coagulant. Positive values of entropy change show the increased randomness of the solution interface during the adsorption process (Table 4).

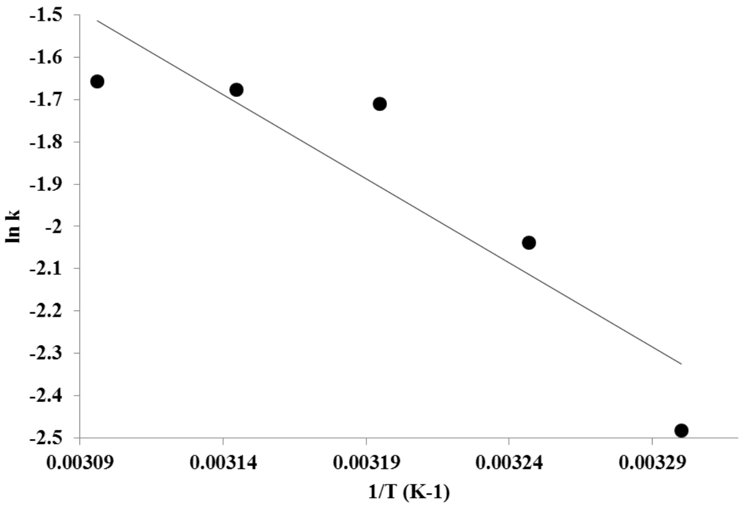

Fig.10. Plot of ln k vs. 1/T for estimation of Arrhenius parameters for the electrocoagulation removal of Bromophenol blue dye from aqueous solution.

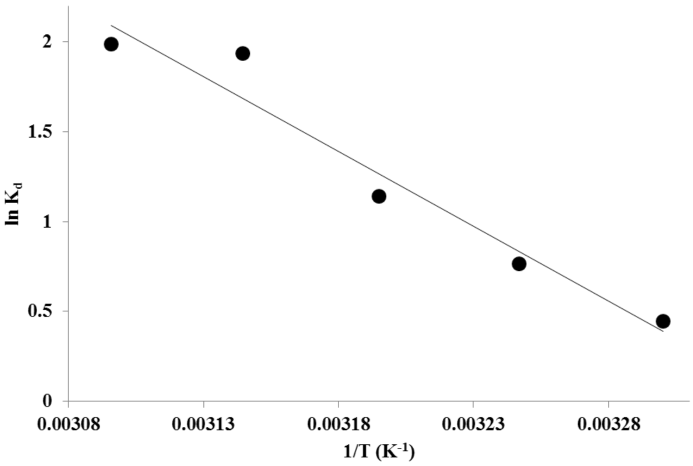

Fig. 11. van't Hoff linear plots of ln K_d versus 1/T for the electrocoagulation removal of Bromophenol blue dye from aqueous solution.

Table 4. Thermodynamic parameters for the removal of Bromophenol Blue

Temp (K)	K	ΔG ($J\ mol^{-1}$)	Ea ($kJ\ mol^{-1}$)	ΔS ($J\ mol^{-1}K^{-1}$)	ΔH ($kJ\ mol^{-1}$)	R^2
303	1.561	-982.07	33.03	231.74	69.24	0.949
308	2.147	-2140.78				
313	3.129	-3299.51				
318	6.927	-4458.23				
323	7.289	-5616.95				

Dye concentration 50 mg L^{-1}; pH 7.0 and NaCl; 2 g L^{-1}

FT-IR Studies of the dye solution before and after electrocoagulation

Figure 12 presents the FT-IR spectrum of the dye solution before and after the process. Before the electrocoagulation the spectrum show the following; sharp and strong peak at 3440.8 cm^{-1} could be assigned to –OH stretch on the dye molecule while, that at 2821 cm^{-1} is due to –CH–. Those at 1593 and 1350 cm^{-1} are due to the aromatic C=C stretching. After electrocoagulation, the extra structure noted such as that at 3840 cm^{-1} may be assigned to the (O–H) stretching vibration in the $Al(OH)_3$ structures.

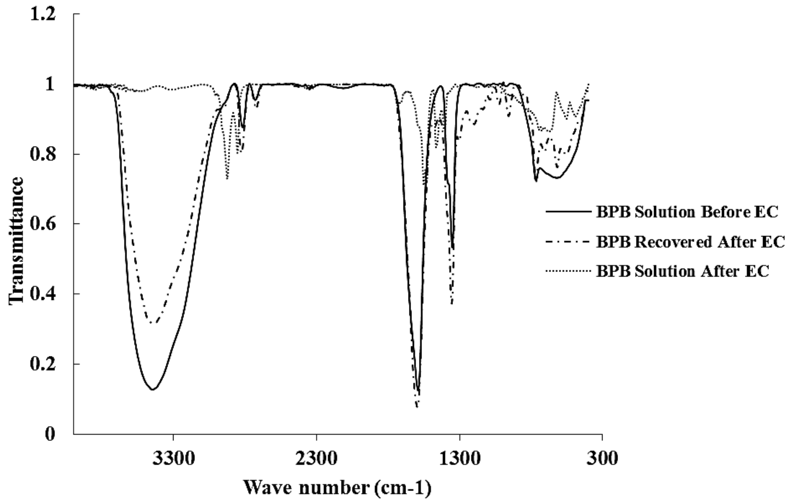

Fig.12. FTIR of the solution of BPB dye solution before and after removal.

CONCLUSION

This study revealed the feasibility of the use of electrocoagulation techniques for the removal of Bromophenol Blue from its aqueous solution. The process depends on numerous factors such as: current density, solution pH, temperature, initial dye concentration and contact time. The percentage removal of the dye increased with pH up to pH 7, also contact time and current density increase influence the removal positively. The maximum adsorption capacity of 166 Q_m value of 166.50 mg g^{-1} from Langmuir isotherm. The kinetics of the process is best explained using a pseudo first order kinetics model, with higher R^2 (Table 2). Intra-particle diffusion was not the sole rate controlling factor. The thermodynamics parameters obtained indicates that the process is spontaneous endothermic nature of the process. Therefore, the present findings suggested a better performance of electrocoagulation with Fe - Al electrode as an inexpensive method for the removal of BPB from aqueous solutions.

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