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Abstract In this study, electrocoagulation (EC) with hybrid Fe-Al electrodes was used to remove antimony from contaminated surface water. Response surface methodology was applied to investigate the interactive effects of the operating parameters on antimony removal and optimize these variables. Results showed that the relationship between operating parameters and the response was well described by a second-order polynomial equation. Under the optimal conditions of current density 2.58 mA/cm², pH 5.24, initial concentration 521.3 µg/L, and time 89.17 min, more than 99 % antimony were removed. Besides, the antimony adsorption behavior in EC process was also investigated. Adsorption kinetics and isotherms studies suggested that the adsorption process followed well the pseudosecond-order kinetic model and the Langmuir adsorption model, respectively. Adsorption thermodynamics study revealed that the reaction was spontaneous, endothermic, and thermodynamically favorable. These

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e-mail: yzh@hnu.edu.cn results further proved that the main mechanism involved in antimony removal in EC process could be chemisorption.

Keywords Antimony \cdot Electrocoagulation \cdot Response surface methodology \cdot Kinetics \cdot Isotherms \cdot Thermodynamics

1 Introduction

Nowadays, antimony (Sb) and its compounds are widely consumed as alloys, flame retardants, catalyst in plastics, pigment in paints, addictive in glassware and ceramics, and so on (Filella et al. 2002; Guo et al. 2009). Owing to natural processes and human activities, large quantities of antimony and its compounds are released into the environment. Specifically in the "World Antimony Capital" Xikuangshan, located in Hunan province, China, the contaminated surface water contains antimony ranging from 385 to 934 μ g/L, which is higher than the corresponding rules (Song et al. 2014).

Antimony and its compounds have been listed as pollutants of priority interest by the Environmental [Protection Agency of the United States (USEPA) and the European Union a^COuncil of the European Communities) (USEPA 1979; CEC (Council of the European Communities 1976)]. They can irritate the nose, throat, eyes, and the skin of people. Long-term exposures often result in nausea and vomiting, heart and liver damage (Winship 1986). USEPA and EU have established the maximum permissible antimony concentration in drinking water of 6 and 10 μ g/L, respectively [USEPA 1984; CEC (Council of the European Communities) 1980]. In China, the maximum admissible value for antimony concentration in drinking water is set as 5 μ g/L [SAC (Standardization Administration of the People's Republic of China 2006)], which is identical to the guideline of the World Health Organizations (WHO 2006; Yousuf et al. 2001).

Recently, owing to high removal efficiency, no addition of chemicals, sludge reduction as well as ease of operation (Holt et al. 2005; Lai and Lin 2003), electrocoagulation (EC) as an efficient treatment technology has been applied successfully to treat various wastewaters (Lai and Lin 2003; Kobya et al. 2003; Chen et al. 2000; Bhatti et al. 2011). In EC process, when a direct current is applied, the sacrificial anodes usually aluminum or iron plates dissolve and the metallic cations such as Al^{3+} , Fe^{2+} , or Fe^{3+} generate, forming a range of coagulant species or metal hydroxide which would absorb or coprecipitate with dissolved pollutants (Qu and Liu 2007; Ville et al. 2013; Vasudevan and Oturan 2014). However, antimony removal from wastewaters by EC has been reported by only a few studies (Song et al. 2014; Zhu et al. 2011). In our previous study (Song et al. 2014), high antimony removal efficiency was obtained by EC using Fe-Al electrodes. We carried out single factor experiments and evaluated the influence of many factors such as current density, pH, aeration intensity, initial concentration and treatment time on antimony removal. However, the interactive effects of influencing factors on antimony removal were not investigated and the optimization of EC process is still needed a subject of further investigation. Of late, Response Surface Methodology (RSM), a collection of mathematical and statistical methodology, has been employed to understand and optimize the performance of complex systems (Myers and Montgomery 2002; Ahmadi et al. 2005; Ölmez 2009). With a limited number of planned experiments, RSM makes it possible to evaluate the interactive effects of operating parameters on antimony removal, reveal the optimum conditions of the EC process, and further build appropriate models. Additionally, the previous study also found out that adsorption onto iron and aluminum hydroxides/ oxyhydroxides was the main mechanism of antimony removal. However, the type of adsorption in EC process is still unclear and barely touched by the environmental researchers. Therefore, further studies in adsorption behavior of antimony in EC process are expected. The mechanism of adsorption and its potential ratecontrolling steps could be analyzed by adsorption kinetic models. The equilibrium adsorption behavior could be investigated by fitting the isotherm models of Langmuir and Freundlich, and the nature of adsorption could be evaluated by the thermodynamic analysis (Ganesan et al. 2013).

Thus, the main objectives of this study are: (1) to evaluate the interactive effects of influencing factors (current density, pH, initial concentration, and treatment time) on antimony removal and obtain the most suitable combination of variables resulting in the maximum antimony removal efficiency; (2) to further explore the antimony adsorption behavior in EC process based on adsorption kinetics, adsorption isotherm, and thermodynamics studies.

2 Experiment

2.1 Materials

All the chemicals used in this study were of guarantee reagent (GR). 1 g/L of Sb stock solution were prepared from antimony potassium tartrate (KSbC₄H₄O₇·1/2H₂O) dissolved in 20 % (ν/ν) HCl, and Sb presents as Sb(III). The stock solution was stored at 4 °C in the refrigerator. In laboratory experiments, antimony concentration was varied in the range of 300~600 µg/L. The pH of the solution was adjusted with 0.1 mol/L HCl and 0.1 mol/L NaOH. All solutions were prepared with ultrapure water and desired volumes of stock solutions. All glassware, polyethylene bottles, and sample vessels were immersed in 5 % (ν/ν) HNO₃ solution, and rinsed three times with distilled water.

2.2 Experimental setup and procedure

Each experiment was carried out in air environment using a 4-L plexiglas reactor (200 mm×160 mm× 125 mm). Electrodes (Fe, 99.5 % purity; Al, 99.3 % purity; 150 mm×150 mm×1 mm) were vertically positioned in the aqueous solution with 2 cm apart. Two Fe plates and two Al plates were in monopolar serial connection mode. The total submerged surface area of each electrode was 120 cm². Current density was adjusted to the desired value by a DC power supply.

Prior to each trial, the electrodes were abraded with sand paper to remove rust and then cleaned with 1 mol/L

HNO₃ and deionized water. For each experiment, 2.5 L Sb solution were added. 10 mL of samples were collected at 10, 30, 50, 70, and 90 min, and then filtered by 0.45-mm filter membrane for analysis. Concentrations of antimony were measured by the atomic fluorescence spectrophotometer (AFS) (AFS-9760, Beijing) (CEPA 2002). Fe and Al analysis were performed using the flame atomic absorption spectrometer (FAAS) (PerkinElmer AA700, USA) (CEPA 2002). Triplicate runs were carried out for each set of experimental conditions.

2.3 Experimental design

2.3.1 RSM experimental design

Experimental design of the EC process for antimony removal was performed by response surface methodology (RSM). RSM was applied to evaluate the relative significance of several affecting factors in the presence of complex interactions (Myers and Montgomery 2002; Ahmadi et al. 2005; Ölmez 2009). In this study, Central Composite Design (CCD), a widely used form of RSM, was selected for the optimization of the operating parameters which had great influence on antimony removal efficiency. It usually contains three steps: (1) design and experiments, (2) response surface modeling through regression, and (3) optimization (Myers and Montgomery 2002; Ahmadi et al. 2005; Ölmez 2009; Kobya et al. 2013). Aydin and Aksoy 2009. To ensure the adequacy of the employed model, analysis of variance (ANOVA) was used for graphical analysis of the data to obtain the interaction between the process variables and the response. The quality of the fit polynomial model was assessed by the determination of coefficient (R^2) , and its statistical significance was checked by the Fisher F test in the same program. Model terms were evaluated by the P value (probability) with 95 % confidence level. The response variable was fitted by a second-order model in the form of quadratic polynomial equation (Myers and Montgomery 2002):

$$y = \beta_0 + \sum_{i=1}^{m} \beta_i \chi_i + \sum_{i< j}^{m} \beta_{ij} \chi_i \chi_j + \sum_{i=1}^{m} \beta_{ii} \chi_i^2 \qquad (1)$$

where y is the response variable to be modeled, χ_i and χ_j are independent variables which determine y, β_0 , β_i and β_{ii} are the offset terms, i and j are linear coefficient and

the quadratic coefficient, respectively. β_{ij} is the term that reflects the interaction between χ_i and χ_j .

In this study, the important operating parameters were current density, pH, initial concentration and treatment time, and the response was antimony removal efficiency. Experimental runs were carried out in triplicates. The actual design ran by the statistic software, Design-expert V8.0.6 (Stat-Ease Inc., USA), was presented in Electronic supplementary material (ESM) Table S1.

2.3.2 Adsorption behavior studied

The amount of antimony adsorbed at equilibrium (q_e) was calculated using the following equations:

$$q_e = (C_0 - C_e)V/W \tag{2}$$

$$W = ItM/(zF) \tag{3}$$

where C_0 is initial concentration (in microgram per liter), C_e is equilibrium concentration (in microgram per liter), V is the volume of solutions (in liter), W is the mass of adsorbent (in gram), I is current (in ampere), t is time (in second), M is molar mass of electrode, Z is number of electrons involved in the redox reaction, and F is Faraday's constant (in coulomb per mole) (Isa et al 2014). The suitability of both pseudo-first-order and pseudo-second-order kinetic models were further evaluated using the chi-square (χ^2) represented as follows (Isa et al. 2014; Sundaram et al. 2008):

$$\chi^2 = \left(q_e^{\exp} - q_e^{\operatorname{cal}}\right)^2 / q_e^{\operatorname{cal}} \tag{4}$$

where q_e^{\exp} is experimental equilibrium adsorption capacity (in microgram per gram), and q_e^{cal} is the calculated equilibrium adsorption capacity (in microgram per gram). χ^2 measures the goodness of fit between the experimental and calculated equilibrium adsorption capacity. The value of χ^2 for the suitable model should be lowest. A good correlation coefficient and a low χ^2 indicate that the model is applicable.

3 Results and discussion

3.1 Response surface methodology

3.1.1 Data analysis of antimony removal efficiency

In order to determine the optimum conditions of antimony removal, the parameters that had greatest influence on the response were identified. A full factorial design for four independent variables along with responses was given in ESM Table S2.

Figure 1a, b, c displayed that antimony removal efficiency were enhanced with the increase of current density. From Faraday's law, at higher current density, the increased anodic metals dissolution caused an accumulation of hydroxide cationic complexes, leading to higher antimony removal efficiency (Kobya et al. 2011; Wan et al. 2011). From Fig. 1a, d, e, antimony removal efficiency decreased with the increase of initial pH from 5 to 9. The pH may affect antimony species distribution and the surface charge of the metal oxides formed in EC process (ESM Fig. S1). When pH was 5, the dominate ion for Sb was Sb(OH)₆⁻ and the zeta potential of metal oxides was positive. The negatively charged Sb species were more likely to be adsorbed and were generally

more easily removed, hence higher antimony removal efficiency was obtained (Song et al. 2014; Gomes et al. 2007). With the increase of pH, the surface charge of the metal oxides changed from positive to negative, and Sb species were negatively or neutrally charged. So the adsorption was less favorable. As a result, the removal efficiencies of Sb decreased (Song et al. 2014; Gomes et al. 2007).

From Fig. 1b, d, f, increase in initial concentration was found to cause a decline in removal efficiency. This can be attributed to the fact that at higher initial concentration, more metallic hydroxide were needed to decrease the dissolved antimony. As a result, antimony removal efficiency was limited by the production rate of metallic hydroxide. Due to prolonged interaction between metallic hydroxides and antimony, increase in treatment time resulted in increase in antimony removal efficiency as shown in Fig. 1c, e, f.

RSM was aimed to investigate the combined effects of four variables on removal efficiency and determine regress model of antimony removal in EC process. According to experimental data, the combined effects and final regression model was expressed by the second-order polynomial equation as follows:

Y = 63.35 + 7.66A - 5.83B + 1.04C + 18.39D - 0.89AB + 0.39AC - 1.27AD-0.93BC + 1.05BD - 0.73CD - 1.58A² + 3.32B² - 2.25C² - 2.70D²

(5)

where *Y* is the predicted response, and *A*, *B*, *C*, *D* are the coded values of current density, pH, initial concentration, and treatment time, respectively.

In order to ensure the adequacy of employed model, an adequate fit of the model should be given to avoid poor or ambiguous results. The significance of quadratic regression model was tested by the value of F and P, correlation coefficient, and so on. ESM Table S3 displayed the ANOVA results for the response surface quadratic model. The Model *F* value of 38.29 and *p* value<0.0001 implied that the model was significant. Values of "Prob > F" less than 0.05 indicated that model terms were significant. Figure 2 indicated that the terms of *D*, *A*, *B*, and *B*² extended behind the reference line. In this case, the variables of treatment time, current density, and pH were significant and remarkably affected the antimony removal efficiency (*y*) (Yang et al. 2015). The value of lack of fit was not significant, indicating that the model for antimony removal in EC process was valid. Adequate Precision ratio was 23.613, which was an adequate signal for the model. Additionally, a high coefficient of determination value (R^2 =0.9728) demonstrated a satisfactory adjustment of the quardratic regression with experimental data (Myers and Montgomery 2002; Ahmadi et al. 2005; Ölmez 2009).

3.1.2 Optimization of the EC process for antimony removal

The main objective of the optimization was to determine the optimum values of variables for antimony removal from the model obtained using experimental data. The desired goal for each operational condition (current density, pH, initial concentration, and treatment time) was chosen within the range while the response Author's personal copy



Fig. 1 3D response surface graphs of combined effects on antimony removal efficiency

(antimony removal efficiency) was defined as the maximum value.

The optimum predicted value of the maximum antimony removal efficiency was 99.62 %. The corresponding optimal parameters were current density 2.58 mA/cm^2 , pH 5.24, initial concentration

521.3 μ g/L and time 89.17 min. To confirm the validity of the optimization procedure, actual experiments were performed under the predicted optimal conditions. Results showed that 99.36 % antimony removal efficiency was achieved. Therefore, it can be concluded that RSM developed in this study was

Fig. 2 Pareto chart of standardized effects for the model. The *line* indicates the 95 % confidence level, and factors with standardized effect values to the right of this line are statistically significant



a powerful tool for optimization and prediction of antimony removal in EC process.

3.2 Adsorption kinetics studies

To investigate the adsorption kinetics and its potential rate-controlling steps including mass transport and chemical reaction processes, kinetic models were used to analyze the experimental data. In this study, pseudofirst-order model, pseudo-second-order model, intraparticle diffusion model, and Elovich model were applied.

3.2.1 Pseudo-first-order model

The linearized form of the pseudo first order rate equation was given as (Boparai et al. 2011; Mall et al. 2007):

$$\log(q_e - q_t) = \log q_e - k_1 t / 2.303 \tag{6}$$

where q_e and q_t are the amount of antimony adsorbed on EC products at equilibrium (in milligram per gram) and at any time (t), respectively, and k_I (in per minute) is the calculated pseudo-first-order rate constant of adsorption.

Experimental data were analyzed with the pseudo first order model as shown in Fig. 3a and Table 1. From the plot of log $(q_e - q_i)$ versus *t*, k_I , and q_e can be determined by the slope and intercept, respectively. The results showed that experimental data did not completely conform to a liner plot, and the correlation coefficient was low. Hence, the reaction could not be classified as the pseudo-first-order, further experimental data were fitted with pseudo-second-order model.

3.2.2 Pseudo-second-order model

The linearized form of the pseudo-second-order equation was represented below (Allen 1996; Ho and McKay 1998):

$$t/q_t = 1/(k_2 q_e^2) + t/q_e$$
(7)

where k_2 is the second-order adsorption rate constant (in gram per microgram minute), and q_e is the adsorption capacity calculated by the pseudo-second-order kinetic model (in microgram per gram).

The linearized form of the pseudo-second-order model for antimony removal by EC with different initial concentrations was shown in Fig. 3b. The q_e and k_2 can be calculated from the slope and intercept of plot of t/q_t versus t. From Fig. 2b and Table 1, the plots were found to be linear with extremely high correlation coefficients. Besides, the theoretical values $q_e^{\text{ cal}}$ were in good agreement with the experimental values q_e^{\exp} at all initial concentrations studied. It suggested that the pseudosecond-order model could be applied suitably to explain the adsorption of antimony in EC process. These results supported the assumption that the rate limiting step was chemisorption involving valence forces through the sharing or exchange of electrons between adsorbent and metal ions (Aydin et al.), which was consistent with some previous studies (Dou et al. 2015; Guo et al. 2014; Vithanage et al. 2013).

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Fig. 3 Adsorption kinetic models of antimony removal by electrocoagulation at different concentrations: a pseudo-first-order model; b pseudo-second-order model; c intra-particle diffusion model and d Elovich model

3.2.3 Intra-particle diffusion model

The linearized form of intra-particle diffusion equation was represented below (Isa et al. 2014; Weber and Morris 1963):

$$q_t = K_{id}t^{0.5} + C_i \tag{8}$$

where K_{id} (in milligram per gram minute^{0.5}) is a measure of the diffusion coefficient and C_i is the intraparticle diffusion constant (in milligram per gram).

Experimental data were fitted to the intra-particle diffusion model using Eq. (8) as shown in Fig. 3c. K_{id} and C_i in Table 2 were obtained from the slope and intercept of the plot of q_t versus $t^{0.5}$, respectively. The

C ₀ (μg/L)	$q_{\rm e}^{\rm exp}$ (mg/g)	Pseudo-first order				Pseudo-second order			
		$k_1 (\min^{-1})$	$q_{\rm e}^{\rm cal} ({\rm mg/g})$	R^2	χ^2	k_2 (g/mg min)	$q_{\rm e}^{\rm cal} ({\rm mg/g})$	R^2	χ^2
400	1.984	0.0037	1.760	0.9802	0.029	0.0078	1.806	0.9996	0.018
500	2.794	0.1059	2.336	0.9837	0.090	0.0177	2.499	0.9995	0.035
600	3.482	0.2256	2.986	0.9716	0.082	0.0086	3.058	0.9992	0.059

Table 1 Adsorption constants for first and second order kinetic model

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C ₀ (μg/L)	Intra-particle diffusion		Elovich model			
	$K_{\rm id} ({\rm mg/g}{\rm min}^{0.5})$	$C_{\rm i} ({\rm mg/g})$	R^2	α (mg/g min)	β (g/mg)	R^2
400	0.1446	0.0382	0.9903	0.1091	2.4546	0.9988
500	0.2844	0.0826	0.9965	0.2346	1.3238	0.9722
600	0.3382	0.1296	0.9935	0.2679	1.0551	0.9913

Table 2 Adsorption constants for intra-particle diffusion and Elovich model

plots of q_t versus $t^{0.5}$ seemed to be linear but did not pass through the origin, which may be due to the boundary layer effect. Besides, with the increase of initial concentration, K_{id} , and C_i were also found to increase. These results implied that intra particle diffusion may not be the only transport mechanism involved in adsorption of antimony in EC process.

3.2.4 Elovich model

The modified form of Elovich equation was represented below (Chien and Clayton 1980; Mall et al. 2005):

$$q_t = 1/\beta \ln(\alpha\beta) + 1/\beta \ln(t) \tag{9}$$

where α is the initial adsorption rate (in milligram per gram minute) and β is the desorption constant (gram per milligram) during the experiment.

The linearized form of the Elovich model for antimony removal by EC at various initial concentrations was given in Fig. 3d. The adsorption rate α

and desorption constant β were calculated from the slope and intercept of the plot of q vs $\ln(t)$ in Table 2. Elovich model was helpful in explaining predominantly, chemical adsorption on highly heterogeneous adsorbents (Gupta and Bhattacharyya 2006). Results suggested that experimental data were fitted into the Elovich equation and the plots of q_t vs $\ln(t)$ seemed to be linear. Additionally, with the increase of initial concentration, the initial adsorption rate α increased and desorption constant β decreased. These results further suggested that the process of adsorption of antimony by EC was chemisorption (Isa et al. 2014).

3.3 Adsorption isotherms studies

In order to identify the efficacy and mechanism of antimony adsorption in EC process, it was important to establish the most appropriate correlation for the equilibrium curves. Langmuir and Freundlich models were employed in this study.



Fig. 4 Adsorption isotherm models of antimony removal by electrocoagulation at different temeprature: a Langmuir isotherm model and b Freundlich isotherm model





3.3.1 Langmuir isotherm model

The Langmuir isotherm model assumed monolayer deposition of adsorbate on homogenous adsorbent surface. The linearised form of Langmuir isotherm model was given as (Balasubramanian et al. 2009; Feng et al. 2013):

$$C_e/q_e = 1/(k_l q_{\max}) + C_e/q_{\max}$$
 (10)

where C_e (in milligram per liter) is the equilibrium concentration of antimony. q_e (in milligram per gram) is the amount of antimony adsorbed at equilibrium. k_l (in liter per milligram) is the equilibrium adsorption constant which is related to the affinity of the binding sites and q_{max} (in milligram per gram) is the Langmuir constant representing maximum monolayer adsorption capacity.

The essential feature of the Langmuir isotherm could be expressed by means of a separation factor or equilibrium parameter R_l , which was calculated by the following equation:

$$R_l = 1/(1 + k_l C_0) \tag{11}$$

where k_l (in liter per milligram) is the Langmuir constant

 Table 3
 Parameters for Langmuir and Freundlich isotherm model

and C_o (in milligram per liter) is the initial concentration. R_l values between 0 and 1 indicate that the adsorption process was favourable.

Experimental data were plotted as C_e/q_e versus C_e and shown in Fig. 4a. The values of q_{max} , R_{l} , k_{l} , and R^2 were listed in Table 3.

3.3.2 Freundlich isotherm model

Considering the surface heterogeneity and exponential distribution of the active adsorption and thus the possibility of multilayer formation, the mathematical expression of the Freundlich model was given by (Balasubramanian et al. 2009; Feng et al. 2013):

$$\log q_e = \log k_f + 1/n \log C_e \tag{12}$$

where k_f (in milligram per gram) and n are the constants that account for adsorption capacity of the adsorbent and the adsorption intensity.

Experimental data were plotted as log q_e versus log C_e and shown in Fig. 4b. The Freundlich constants k_f and n values were listed in Table 3.

T (K)	Langmuir isotherm				Freundlich iso	Freundlich isotherm		
	$q_{\rm max}({\rm mg/g})$	k_l (L/g)	R_l	R^2	$\overline{k_{\mathrm{f}}(\mathrm{mg/g})}$	п	R^2	
298	2.004	0.185	0.049	0.9997	1.573	4.697	0.9959	
308	2.439	0.267	0.034	0.9996	2.110	5.949	0.9973	
318	2.703	0.336	0.028	0.9994	2.623	6.752	0.9934	

Temperature (K)	lnK _D	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (J/mol [·] K)
298 308	8.833 9.199	-21.885 -23.556	24.1264	154.516
318	9.430	-24.932		
328	9.745	-26.576		

 Table 4
 Thermodynamics constants for antimony adsorption

The applicability of the two isotherm equations was compared by the correlation coefficient (R^2) . From Table 3, the values of correlation coefficient (R^2) of the Langmuir model were higher than that of the Freundlich model. Namely, the Langmuir model provided a better fit than Freundlich model within the studied temperature range. From Langmuir model, q_{max} and k_l increased with the increase of experimental temperature, indicating that adsorption of antimony would be stronger at higher temperature and the adsorption process was endothermic. All R_l values obtained were between 0 and 1 indicating that the adsorption of antimony on the adsorbent was favorable. Results showed that Langmuir model could well describe the equilibrium isotherms. It could be concluded that the adsorption of antimony in EC process followed monolayer adsorption (Ganesan et al. 2013; Balasubramanian et al. 2009).

3.4 Adsorption thermodynamics studies

The thermodynamic parameters (ΔG° , ΔH° , ΔS°) were calculated from the following equations (Ganesan et al. 2013; Isa et al. 2014; Feng et al. 2013):

$$\Delta G^{\rm o} = -RT \ln K_D \tag{13}$$

where ΔG° (in kilojoule per moler) is the free energy, K_D is the distribution coefficient, R is the universal gas constant (8.314 J/(mol·k) and T is the temperature (in kelvin).

The relationship between ΔG° , ΔH° , and ΔS° could be expressed as:

$$\Delta G^{\rm o} = \Delta H^{\rm o} - T \Delta S^{\rm o} \tag{14}$$

Combining Eq. (13) and (14),

$$\ln K_D = \Delta S^o / R - \Delta H^o / (RT)$$
(15)

The enthalpy change (ΔH°) and entropy (ΔS°) were calculated from the slope and intercept of the plot of ln $K_{\rm D}$ versus 1/T as shown in Fig. 5. The thermodynamics constants obtained from the plot were given in Table 4.

As shown in Table 4, the values of ΔG° were negative, indicating that the adsorption of antimony in EC process was spontaneous and thermodynamically favorable. The degree of spontaneity of the reaction increased with increasing temperature which may be attributed to the enlargement of pore size or activation of the adsorbent surface. The positive values of ΔH° implied that the adsorption process was endothermic at 298–328 K. The positive values of ΔS° confirmed the increased randomness of the solution interface during the adsorption of antimony (Ganesan et al. 2013; Feng et al. 2013).

4 Conclusions

In this study, response surface methodology was verified to be a powerful tool for investigation of the interactive effects of influencing factors on antimony removal efficiency and optimization of the EC process. Analysis of variance showed a high coefficient of determination value, ensuring a satisfactory adjustment of the second order polynomial equation with experimental data. More than 99 % antimony were removed and the corresponding optimum parameters were current density 2.58 mA/cm², pH 5.24, initial concentration 521.3 µg/L, and time 89.17 min. Additionally, the adsorption of antimony in EC process followed well the pseudo-second-order model, and the Langmuir isotherm model best fitted with experimental data. The thermodynamics study revealed that the adsorption of antimony in EC process was spontaneous, endothermic, and thermodynamically favorable. These results further proved that the main mechanism involved in antimony removal by EC with hybrid Fe-Al electrodes could be chemisorption.

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References

- Ahmadi, M., Vahabzadeh, F., Bonakdarpour, B., Mofarrah, E., & Mehranian, M. (2005). Application of the central composite design and response surface methodology to the advanced treatment of olive oil processing wastewater using Fenton's peroxidation. J Hazard Mater, 123(1-3), 187–195.
- Allen, S. J. (1996). Types of adsorbent materials-use of adsorbents for removal of pollutants from wastewaters (p. 59). Boca Raton, FL, USA: CRC.
- Aydin, Y. A., & Aksoy, N. D. (2009). Adsorption of chromium on chitosan: optimization, kinetics and thermodynamics. *Chem Eng J*, 151(1-3), 188–194.
- Balasubramanian, N., Kojima, T., & Srinivasakannan, C. (2009). Arsenic removal through electrocoagulation: kinetic and statistical modeling. *Chem Eng J*, 155(1-2), 76–82.
- Bhatti, M. S., Reddy, A. S., Kalia, R. K., & Thukral, A. K. (2011). Modeling and optimization of voltage and treatment time for electrocoagulation removal of hexavalent chromium. *Desalination*, 269(1-3), 157–162.
- Boparai, H. K., Joseph, M., & O'Carroll, D. M. (2011). Kinetics and thermodynamics of cadmium ion removal by adsorption onto nano zerovalent iron particles. *J Hazard Mater*, 186(1), 458–465.
- CEC (Council of the European Communities). (1976). Council Directive 76/substances discharged into aquatic environment of the community. *Off J L, 129*, 23–29.
- CEC (Council of the European Communities). (1980). Council Directive relating to the quality of water intended for human consumption. 80/778/EEC.
- CEPA. (2002). Water and wastewater monitoring analysis methods (4th ed.). China Environmental Science: Beijing.
- Chen, X. M., Chen, G. H., & Yue, P. L. (2000). Separation of pollutants from restaurant wastewater by electrocoagulation. *Sep Purif Technol*, 19(1-2), 65–76.
- Chien, S. H., & Clayton, W. R. (1980). Application of Elovich equation to the kinetics of phosphate release and sorption in soils. *Soil Sci Soc Am J*, 44(2), 265–268.
- Dou, X. M., Mohan, D., Zhao, X. Q., & Pittman, C. U. (2015). Antimonate removal from water using hierarchical macro-/ mesoporous amorphous alumina. *Chem Eng J*, 264, 617– 624.
- Feng, J., Yang, Z. H., Zeng, G. M., Huang, J., Xu, H. Y., Zhang, Y. Y., Wei, S. H., & Wang, L. K. (2013). The adsorption behavior and mechanism investigation of Pb(II) removal by flocculation using microbial flocculant GA1. *Bioresource Technol, 148*, 414–421.
- Filella, M., Belzile, N., & Chen, Y. W. (2002). Antimony in the environment: a review focused on natural waters. I. Occurrence. *Earth Sci Rev*, 57(1-2), 125–176.
- Ganesan, P., Lakshmi, J., Sozhan, G., & Vasudevan, S. (2013). Removal of manganese from water by electrocoagulation: adsorption, kinetics and thermodynamic studies. *Can J Chem Eng*, 91(3), 448–458.

- Gomes, J. A. G., Daida, P., & Kesmez, M. (2007). Arsenic removal by electrocoagulation using combined Al-Fe electrode system and characterization of products. *J Hazard Mater*, 139(10), 220–231.
- Guo, X. J., Wu, Z. J., & He, M. C. (2009). Removal of antimony(V) and antimony(III) from drinking water by coagulation-flocculation-sedimentation (CFS). *Water Res*, 43(17), 4327–4335.
- Guo, X. J., Wu, Z. J., He, M. C., Meng, X. G., Jin, X., Qiu, N., & Zhang, J. (2014). Adsorption of antimony onto iron oxyhydroxides: adsorption behavior and surface structure. J Hazard Mater, 276, 339–345.
- Gupta, S. S., & Bhattacharyya, K. G. (2006). Adsorption of Ni(II) on clays. J Colloid Interface Sci, 295(1), 21–32.
- Ho, Y. S., & McKay, G. (1998). A comparison of chemisorption kinetic models applied to pollutant removal on various sorbents. *Proc Saf Environ Prot*, 76(4), 332–340.
- Holt, P. K., Barton, G. W., & Mitchell, C. A. (2005). The future for electrocoagulation as a localised water treatment technology. *Chemosphere*, 59(3), 355–367.
- Isa, M. H., Ezechi, E. H., Ahmed, Z., Magram, S. F., & Kutty, S. R. M. (2014). Boron removal by electrocoagulation and recovery. *Water Res*, 51, 113–123.
- Kobya, M., Can, O. T., & Bayramoglu, M. (2003). Treatment of textile wastewaters by electrocoagulation using iron and aluminum electrodes. J Hazard Mater, 100(1-3), 163–178.
- Kobya, M., Gebologlu, U., Ulu, F., & Oncel, S. (2011). Removal of arsenic from drinking water by the electrocoagulation using Fe and Al electrodes. *Electrochim Acta*, 56(14), 5060–5070.
- Kobya, M., Demirbas, E., Gebologlu, U., Oncel, M. S., & Yildirim, Y. (2013). Optimization of arsenic removal from drinking water by electrocoagulation batch process using response surface methodology. *Desalin Water Treat*, 51(34-36), 1–10.
- Lai, C. L., & Lin, S. H. (2003). Electrocoagulation of chemical mechanical polishing (CMP) wastewater from semiconductor fabrication. *Chem Eng J*, 95(1-3), 205–211.
- Mall, I. D., Srivastava, V. C., Agarwal, N. K., & Mishra, I. M. (2005). Removal of Congo Red from aqueous solution by bagasse fly ash and activate d carbon: kinetic study and equilibrium isotherm analysis. *Chemosphere*, 61(4), 492– 501.
- Mall, I. D., Srivastava, V. C., Agarwal, N. K., & Mishra, I. M. (2007). Removal of Congo Red on coal-based mesoporous activated carbon. *Dyes Pigm*, 74(1), 34–40.
- Myers, R. H., & Montgomery, D. C. (2002). Response surface methodology: process and product optimization using designed experiments (2nd ed.). New York: John Wiley and Sons.
- Ölmez, T. (2009). The optimization of Cr(VI) reduction and removal by electrocoagulation using response surface methodology. *J Hazard Mater*, 162(2-3), 1371–1378.
- Qu, J. H., & Liu, H. J. (2007). Electrochemical principles and techniques in water treatment (pp. 205–209). Beijing: Science Press.
- SAC (Standardization Administration of the People's Republic of China). (2006). Standards for drinking water quality. Beijing: SAC (Standardization Administration of the People's Republic of China). GB-5749-2006.

- Song, P. P., Yang, Z. H., Xu, H. Y., Huang, J., Yang, X., & Wang, L. K. (2014). Investigation of influencing factors and mechanism of antimony and arsenic removal by electrocoagulation using Fe–Al electrodes. *Ind Eng Chem Res*, 53(33), 12911– 12919.
- Sundaram, C. S., Viswanathan, N., & Meenakshi, S. (2008). Defluoridation chemistry of synthetic hydroxyapatite at nanoscale: equilibrium and kinetic studies. *J Hazard Mater*, 155(1-2), 206–215.
- USEPA. (1979). Water related fate of the 129 priority pollutants. Washington, DC: USEPA. Doc., 745-R-00-007.
- USEPA. (1984). Antimony: an environmental and health effects assessment. Washington, DC: US Environmental Protection Agency. Office of drinking water.
- Vasudevan, S., & Oturan, M. A. (2014). Electrochemistry: as cause and cure in water pollution—an overview. *Environ Chem Lett*, 12(1), 97–108.
- Ville, K., Toivo, K., Jaakko, R., & Ulla, L. (2013). Recent applications of electrocoagulation in treatment of water and wastewater-a review. *Green and Sus Chem*, 3, 89–121.
- Vithanage, M., Rajapaksha, A. U., Dou, X. M., Bolan, N. S., Yang, J. E., & Ok, Y. S. (2013). Surface complexation modeling and spectroscopic evidence of antimony adsorption on ironoxide-rich red earth soils. *J Colloid Interf Sci*, 406, 217–224.

- Wan, W., Pepping, T. J., Banerji, T., Chaudhari, S., & Giammar, D. E. (2011). Effects of water chemistry on arsenic removal from drinking water by electrocoagulation. *Water Res*, 45(1), 384–392.
- Weber, W. J., & Morris, J. C. (1963). Kinetics of adsorption on carbon from solution. *Journal of Sanitary Engineering Division (Proceeding of the asce)*, 89, 31–59.
- WHO. (2006). Health criteria and other supporting information in: Guidelines for Drinking-water Quality (Secondth ed.). Geneva: World Health Organization.
- Winship, K. A. (1986). Toxicity of antimony and its compounds. Adverse Drug React Acute Poisoning Rev, 6(2), 67–90.
- Yang, Z. H., Xu, H. Y., Zeng, G. M., Luo, Y. L., Yang, X., Huang, J., Wang, L. K., & Song, P. P. (2015). The behavior of dissolution/passivation and the transformation of passive films during electrocoagulation: influences of initial pH, Cr(VI) concentration, and alternating pulsed current. *Electrochim Acta*, 153(2), 149–158.
- Yousuf, M., Mollah, A., Schennach, R., & Parga, J. R. (2001). Electrocoagulation (EC) science and applications. *J Hazard Mater*, 84(1), 29–41.
- Zhu, J., Wu, F. C., Pan, X. L., Guo, J. Y., & Wen, D. S. (2011). Removal of antimony from antimony mine flotation wastewater by electrocoagulation with aluminum electrodes. J Environ Sci, 23(7), 1066–1071.