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ORIGINAL ARTICLE

**Equilibrium, kinetic and thermodynamic studies
on the removal of Aluminum by modified
Eucalyptus camaldulensis barks**



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Abstract In this study, a low-cost eco-friendly adsorbent was prepared from *Eucalyptus camaldulensis* barks through chemical activation. The effect of operating variables namely initial pH, sorbent dose, initial metal concentration, shaking speed and temperature on the aluminum removal percentage and uptake capacity has been studied. The optimal pH was found as 5.0 and the sorbent dosage 5.0 g/L. Temperature effect proved the process to be endothermic. The experimental observations were fitted to Langmuir and Freundlich isotherms where Langmuir proved to be a better fit. Pseudo-second order and intraparticle diffusion kinetic models were employed to the experimental data to verify the mechanism of sorption. The constants of isotherms and kinetic models were evaluated at different operating conditions. From the thermodynamic studies, the activation energy was evaluated as 43.23 kJ mol⁻¹.

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1. Introduction

Heavy metals are generally considered to be those whose density are more than 5.0 gram per cubic meter and have atomic weights in the range of 63.5 and 200.6 [1]. The industrial

effluents contaminated with heavy metals are categorized as the most hazardous among the chemical intensive industries because of the non-biodegradable nature of the metal pollutants and their tendency to get accumulated in living organisms leading to carcinogenic effects. Major industries that contribute to heavy metal pollution are electroplating industries, mining industries, tanneries, fertilizer industries, batteries and pesticide industries. Aluminum is identified as one of the major heavy metal pollutants released by industries which use aluminum and its alloys for example aircraft and motor vehicle industries. At acidic and basic conditions, aluminum is having dissolution property. Even in trace quantities, aluminum is reported to cause chronic (long term) effects on human health rather than short – term acute effects. Aluminum has

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been proved to have a neurotoxic effect when it enters the bloodstream. Defective brain disease, encephalopathy, is caused due to long time exposure aluminum contaminated water to dialysis patients. Aluminum is also reported to be a causing agent for Alzheimer's disease, senile dementia and Lou Gehring's disease. The Environmental Protection agency has set the secondary permissible levels of aluminum as 0.05–0.20 mg/L [2]. In this background, it is inevitable to treat aluminum contaminated waste water. Many methods like chemical precipitation, ion exchange, coagulation, membrane filtration and electrochemical techniques are practiced to remove these heavy metals. Unfortunately, these methods are proven to be inefficient and extremely expensive in handling heavy metal waste waters [3]. Also, these conventional methods lead to the production of large quantities of chemical sludge which caused disposal problems. Currently, the most popular and effective physical method employed for the treatment metal contaminated waste water is adsorption. The effectiveness and economic feasibility of this process lies largely on the cost of adsorbent [4]. Activated carbon, even though very effective, is not favoured because of its high cost [5]. Thus, the search of cheaper and readily available adsorbent material is initiated. A number of agricultural and waste by-products like leaf powder [6], rice husk ash [7], egg shell [8], *Lemna perpusilla* Torr. [9] etc. have been tried. The advantages of using plant based material as an adsorbent are simple technique, good adsorption capacity, little processing, low cost, high selectivity towards adsorbate and easy regeneration [10]. The most convenient method for designing the adsorption systems is through the application of adsorption isotherms [11]. The theoretical adsorption capacity of the adsorbent for a particular contaminant can be determined by calculating its adsorption isotherm [12]. In this research work, *Eucalyptus camaldulensis*, a common tree species, is identified as a potential adsorbent for the removal of aluminum. The mature trees grow laterally to increase the thickness of stem leading to the production of huge amount of tree barks. The outermost layer dies and is deciduous in long strips annually. Eucalyptus bark has successfully used for the removal of chromium [13] and mercury [4]. Till date, no published literature is available on the removal of aluminum using *E. Camaldulensis* barks. The objectives of this study are to evaluate the sorption potential of aluminum ions by the *E. Camaldulensis* barks under batch conditions. The effect of operating variables like initial pH, sorbent dose, initial metal concentration, temperature and shaking speed were investigated. The determination of metal sorption capacity of *E. Camaldulensis* barks adds a valuable input to the adsorption system design approach to systems for metal removal from waste water. Kinetic studies were conducted to analyze the rates of metal adsorption.

2. Materials and methods

2.1. Biosorbent preparation

The *E. camaldulensis* tree barks used in this study was obtained from Nilgiris, Tamilnadu, India. This tree usually is 24–40 m high and has short and stout trunk. This tree is a native of Australia. The dry basis chemical composition of Eucalyptus bark is a presented in Table 1 [14]. The collected biomaterial was extensively washed with distilled water to remove soil and dust and sliced into small pieces. The sliced material was

Table 1 Chemical composition of tree bark.

Component	%(w/w)
Cellulose	37.4
Hemicellulose	19.2
Total carbohydrates	62.2
Free sugars	5.5
Lignin	28.0
Total nitrogen	1.1

sun dried by exposure to the sunlight for 3 days and subsequently in a hot air convection oven at 60 °C for 48 h. The dried material was milled into a powder using blender and sieved to obtain constant size particles (0.85–1.70 mm).

2.2. Characteristics of the adsorbent

The surface area of the *E. camaldulensis* powder was determined by a three-point N₂ gas adsorption method using a Smart Sorb Surface Area Analyzer (model 92/93; Smart Instruments, India). The bulk density of the sorbent was determined by densitometer. Porosity of the biosorbent was determined by porosimeter (model H; M7 V, Ngri, India). The physicochemical properties of the sorbent are given in Table 2.

2.3. Acid activation of the sorbent

The sieved powder of the raw biosorbent (100 g) was soaked in 1.0 L of 4 N C₄H₆O₆ (tartaric acid) in a mechanical shaker at 300 rpm for 24 h. The samples were filtered and rinsed with distilled water, until the pH was neutral. The acid activated biosorbent material was sealed in plastic bags and stored in desiccators for further use.

2.4. Preparation of adsorbate

Aluminum solutions of desired concentrations have been prepared by dissolving calculated quantity of Al (NO₃)₂·9H₂O, supplied by Merck, Germany. All other chemicals used in this study were AR Grade supplied by Sigma, USA.

2.5. Effect of operating parameters and equilibrium studies

The adsorption experiments were conducted by mixing various amounts of *E. camaldulensis* powder (1.0–6.0 g L⁻¹) in conical flasks containing 100 mg L⁻¹ metal concentration. The effect of pH was studied in the range of 2.0–10.0 at a fixed metal

Table 2 Physicochemical properties of the biomass.

Property	Value
Bulk density (g/cc)	0.62
Specific gravity	0.72
Particle size (mm)	0.85–0.170
Porosity (%)	69
Surface area (m ² /g)	70.9
Moisture content (%)	63
Loss on ignition (w/w,%)	95.4

concentration of 100 mg L^{-1} and a sorbent dosage of 3.0 g L^{-1} . The effect of initial metal concentration on the metal uptake was studied in the range of $0\text{--}200 \text{ mg L}^{-1}$ at optimal conditions of pH and sorbent dosage. The effect of temperature was studied in the range of $30\text{--}40^\circ \text{C}$ by shaking the flasks in a thermostatic water bath shaker operating at 400 rpm for 120 min to ensure the attainment of equilibrium. The effect of shaking speed was studied in the range of $0\text{--}800 \text{ rpm}$ at optimal conditions of pH and sorbent dosage at a fixed metal concentration of 100 mg L^{-1} . All the experiments were conducted at room temperature of 30°C unless or otherwise specified. The results of these equilibrium studies were verified with Langmuir and Freundlich isotherms.

2.6. Kinetic studies

The kinetic studies were conducted to estimate the contact time required for the attainment of equilibrium between the dissolved and solid bound adsorbate. For aluminum removal kinetic experiments, a metal solution containing 50 mg L^{-1} aluminum was agitated with 6.0 g of sorbent in a 500 mL sealed flask at optimal pH placed in a shaker operating at 400 rpm and 30°C . Similar experiments were carried out by agitating with 500 mL of metal solutions whose concentrations were 100, 150 and 200 mg L^{-1} at the optimum conditions as given above.

2.7. Analysis of the metal

Samples of solutions were filtered through filter paper and then the filtrates were collected and analyzed for metal concentration using atomic absorption spectrometry (PerkinElmer A 310). The amount of metal adsorbed during the contact time with activated *E. camaldulensis* powder was estimated using the Eq. (1):

$$q_e = \frac{V(C_0 - C_e)}{M} \quad (1)$$

where q_e (mg of metal removed/g of adsorbent) is the amount of metal adsorbed on the selected adsorbent, C_e and C_0 (mg L^{-1}) are and concentration of the dye at initial and equilibrium conditions, respectively, V is the volume of the sample solution and M is the mass of the adsorbent. All experiments were conducted in triplicate and the mean values were reported.

3. Results and discussion

3.1. Effect of pH

The pH of the aqueous metal solution is an important operating variable in the adsorption process because it affects the solubility of metal ions, concentration of the counter ions on the functional groups of the adsorbent and the degree of ionization of the adsorbate during reaction [15]. The effect of pH on the sorption of aluminum by *E. camaldulensis* was studied by varying the initial pH in the range of $2.0\text{--}10.0$ under constant process parameters at equilibrium conditions and was presented in Fig. 1. The maximum metal uptake takes place at pH 5.0 (27.1 mg/g) and increased from 5.0 mg/g (at pH 2.0) to 27.1 mg/g (at pH 5.0). With further increase in pH from 5.0 to 10.0, the uptake decreased. Reduced uptake at acidic pH

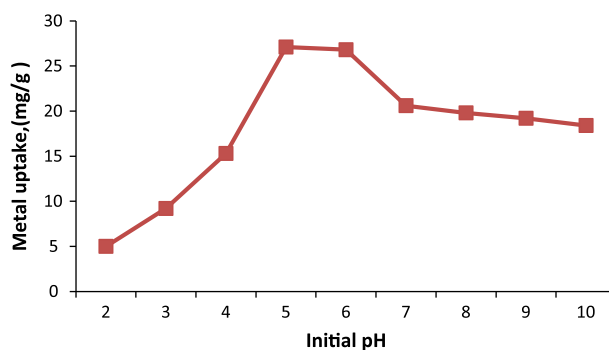


Figure 1 Effect of initial pH on the uptake of Al (III) by activated *Eucalyptus camaldulensis* powder (metal concentration = 100 mg L^{-1} ; sorbent dose = 6.0 g L^{-1} ; contact time = 90 min; shaking speed = 400 rpm; $T = 30^\circ \text{C}$).

is attributed to the presence of excess hydrogen ions which compete with the metal cations for the adsorption sites. In addition, at lower pH values of (2.0–4.0) the adsorbent surface is covered with more number of positively charged sites which is unfavorable for the sorption of metal cations (Al^{3+} , AlOH^{2+}). At a higher pH, more Aluminum appears in a neutral or negatively charged form ($\text{Al}(\text{OH})_3$, $\text{Al}(\text{OH})_4^-$) and these cannot be adsorbed on a negatively charged sorbent surface [16]. Similar investigation is reported on the sorption of aluminum in different adsorbents [17].

3.2. Effect of sorbent dosage

The surface area made available for the contact with the sorbate is decided by the amount of sorbent used. Therefore, the effect of *E. camaldulensis* dosage on aluminum removal was studied in the range of $1.0\text{--}6.0 \text{ g/L}$ at an optimal pH of 5.0 and initial metal concentration 100 mg/L . As illustrated in Fig. 2, the percentage metal removal was 42.0% (at 1.0 g/L of sorbent dose) and increased to 82.0% (at 6.0 g/L of sorbent dose). The increase in adsorption removal percentages with increasing *E. camaldulensis* dosage is related to the increase in surface area and by extension the increased number of ion exchangeable sites available for interaction with aluminum ions. Similar observations were reported on the

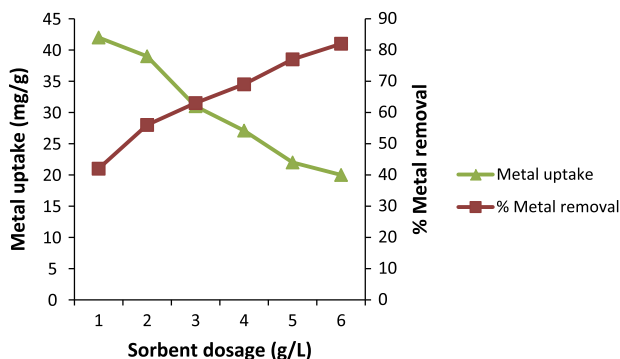


Figure 2 Effect of sorbent dosage on the % metal removal and uptake of Al (III) by activated *Eucalyptus camaldulensis* powder (metal concentration = 100 mg L^{-1} ; pH = 5.0; contact time = 90 min; shaking speed = 400 rpm; $T = 30^\circ \text{C}$).

application of date palm tree powder for the removal of dye [18]. A superficial sorption onto the sorbent surface that produces a lower metal concentration in the solution is reported to occur at high ratios of sorbent to sorbate concentrations. The decrease in metal uptake with increase in dosage is due to the split in flux between the aluminum concentrations in the solution and the sorbent surface [3]. Thus, the optimal sorbent dosage was identified as 5.0 g/L.

3.3. Effect of contact time and initial metal concentration

In order to establish time dependence of adsorption systems under various conditions, it is required to study the influence of contact time. The experimental runs measuring the effect of contact time and initial metal concentration on the batch sorption of metal solution containing 100 mg/L of aluminum at 30 °C and initial pH 5.0 is shown in Fig. 3. It was observed that the general uptake rate was fast during the initial phase of 30 min after which a steady state adsorption was achieved. The initial rapid uptake rate within the first 30 min may be due to physical adsorption or ion exchange at the sorbent surface and due to complexation and micro-precipitation of the binding sites during the later phase resulted in reduced uptake [19]. Moreover, the concentration gradient is more during the initial stages of the adsorption process. The equilibrium time increased with increase in metal concentrations. At low metal concentrations, the sorbent sites took the metal ions quickly whereas at high concentrations, the metal ions need to diffuse to the inner sites of the sorbent. Saturation of sites was reported to occur at high metal/sorbent ratios leading to reduced metal removal efficiency.

3.4. Effect of shaking speed

The sorption of aluminum on *E. camaldulensis* at different shaking speed was studied on the range 0–700 rpm using a metal concentration of 100 mg/L and time of 90 min. The metal uptake increased from 8.4 to 29.6 mg/g when the shaking speed increased from 0 (static condition) to 600 rpm, as shown in Fig. 4. Increased speed leads to better external mass transfer through the film by reducing the boundary layer thickness at the film. More collisions between the sorption sites and metal ions are also reported to be a reason for his behavior. At speeds greater than 600 rpm, there was no effect on uptake

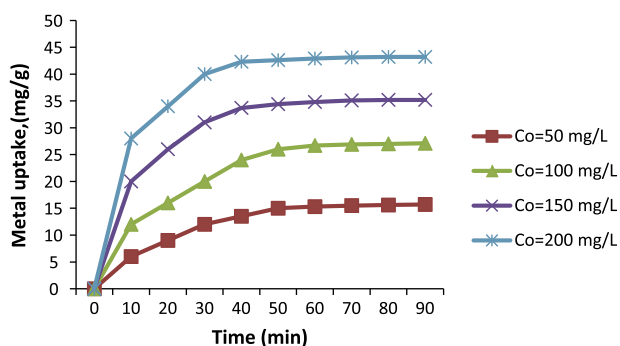


Figure 3 Effect of contact time and initial metal concentration on the uptake of Al (III) by activated *Eucalyptus camaldulensis* powder (pH = 5.0; contact time = 90 min; shaking speed = 400 rpm; $T = 30^\circ\text{C}$).

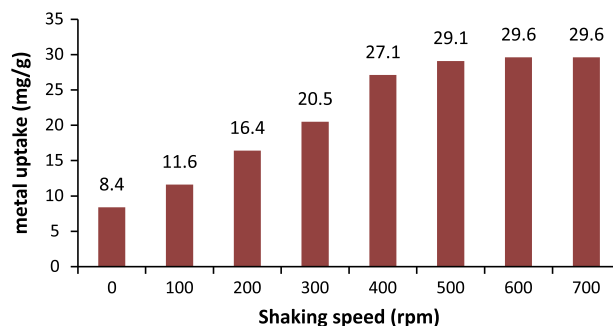


Figure 4 Effect of shaking speed on the uptake of Al (III) by activated *Eucalyptus camaldulensis* powder (metal concentration = 100 mg L⁻¹; pH = 5.0; contact time = 90 min; $T = 30^\circ\text{C}$).

as reported in other literature [4]. Also, the suspension loses homogeneity at rapid speeds [20].

3.5. Effect of operating temperature

The uptake of alumina by *E. camaldulensis* at different temperatures (25, 30 and 35 °C) was shown in Fig. 5. The result demonstrated that the uptake capacity increases with increase in temperature and thus confirms the endothermic nature of sorption process. The enhancement in uptake is attributed to better interaction between metal ions and sorbent, creation of new sorption sites and increased intraparticle diffusion at higher temperatures [4]. The uptake increased from 24.2 to 29.8 mg/g when the temperature increased from 25 to 35 °C. Other studies have reported similar observations regarding the effect of temperature on sorption capacity [9,21].

3.6. Biosorption isotherm models

Biosorption isotherms are used to represent the equilibrium relationship between the mass of the solute adsorbed per unit mass of the adsorbent and the equilibrium concentration of the solute. In this study, Langmuir and Freundlich models [Eqs. (2) and (3) respectively] were employed to fit the experimental data. Langmuir considered adsorption of an ideal gas on ideal surface. Langmuir isotherm is based on the assumption that the sorption takes place at specific homogeneous sites on the adsorbent. Freundlich isotherm is based

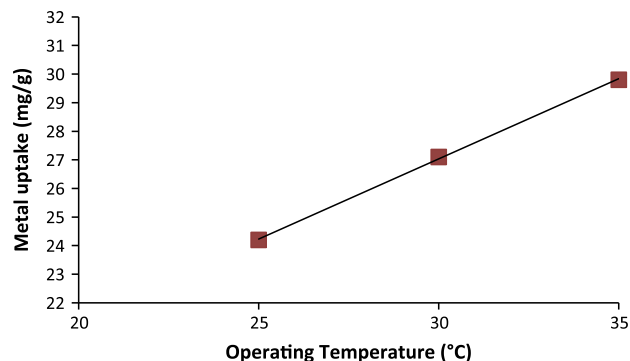


Figure 5 Effect of operating temperature on the uptake of Al (III) by activated *Eucalyptus camaldulensis* powder (metal concentration = 100 mg L⁻¹; pH = 5.0; contact time = 90 min; shaking speed = 400 rpm).

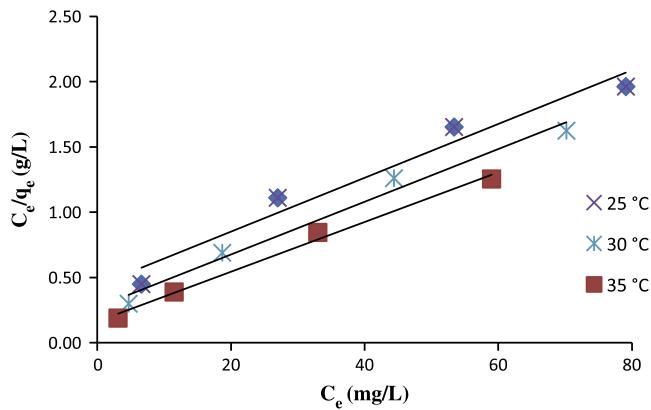


Figure 6 Langmuir plot for the removal of Al onto *Eucalyptus camaldulensis*.

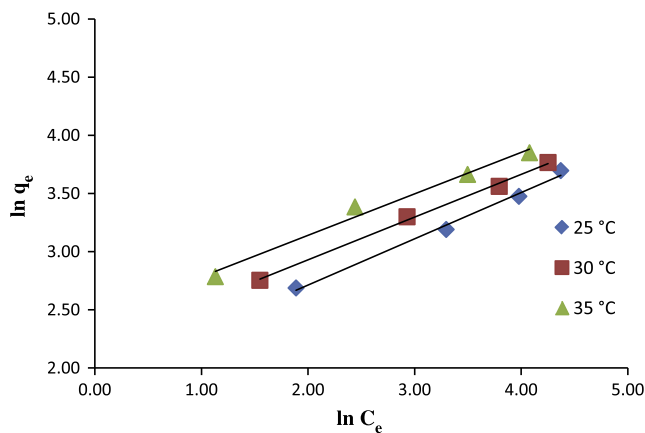


Figure 7 Freundlich plot for the removal of Al onto *Eucalyptus camaldulensis*.

on the assumption of heterogeneous adsorption surface and active sites with different energy.

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{q_{max}K_L} \quad (2)$$

$$\ln q_e = \ln K_f + \frac{1}{n} \ln c_e \quad (3)$$

where q_{max} (mg g^{-1}) is the maximum adsorption capacity and K_L (L mg^{-1}) is the Langmuir constant related to the free energy of adsorption, K_f (mg g^{-1}) is the Freundlich constant which is an estimate of relative adsorption capacity of the

sorbent and $\frac{1}{n}$ is the adsorption intensity. The experimental data were applied to the equation above and a plot of $\frac{C_e}{q_e}$ vs C_e was drawn to verify the applicability of Langmuir isotherm and was shown in Fig. 6. A linear plot of q_e vs c_e was tried to verify the suitability of Freundlich isotherm, as shown in Fig. 7. The constants in the isotherm equations were evaluated and reported in Table 3. From the table, it was observed that Langmuir isotherm represented the equilibrium sorption of aluminum and the value of regression coefficient (R^2) was comparatively higher for Langmuir isotherm than Freundlich isotherm. This result suggests monolayer coverage of the surface of *E. camaldulensis* by aluminum ions since the Langmuir isotherm assumes that the surface is homogeneous. Similar isotherm fit for sorption of aluminum has been reported [2]. As expected for an endothermic process, the values of q_{max} and K_L increased with increase in temperature.

3.7. Kinetic studies

The studies on the rate of removal are essential for the proper design of waste water treatment facilities. In this study, the pseudo-second-order equation [Eq. (4)] and intraparticle diffusion model [Eq. (5)] have been applied to the experimental data to analyze the adsorption kinetics of aluminum ions:

$$\frac{t}{q_t} = \frac{1}{k_2 q_1^2} + \frac{1}{q_1} t \quad (4)$$

where q_1 (mg g^{-1}) is the maximum adsorption capacity and q_t (mg g^{-1}) is the amount of dye adsorbed at time, t , and k_2 ($\text{g (mg min}^{-1/2})^{-1}$) is the equilibrium rate constant for pseudo-second order adsorption. The intraparticle diffusion model is represented as

$$q_t = k_t t^{1/2} + I \quad (5)$$

where q_1 (mg g^{-1}) is the maximum adsorption capacity and q_t (mg g^{-1}) is the amount of dye adsorbed at time, t , and k_t ($\text{mg (g min}^{1/2})^{-1}$) is the intraparticle diffusion rate constant and I (mg g^{-1}) is a constant that is related to boundary layer thickness. Results of the kinetic data modeling indicated that the pseudo-second order model (Fig. 8) describes the sorption of aluminum better than the other model. The pseudo second order model assumes that two surface sites will be occupied by one sorbate ion [22]. The pseudo-second order model could not identify the diffusion mechanism. Due to this, intra-particle diffusion model was employed and was presented in Fig. 9 as q vs $t^{1/2}$. If the plot passes through the origin, then intra-particle diffusion is the rate controlling step. But, a larger intercept was observed in this experiment which confirmed that

Table 3 Comparison of constants in the isotherms at different temperatures.

	Temperature:25 °C				Temperature:30 °C				Temperature:35 °C			
	50	100	150	200	50	100	150	200	50	100	150	200
<i>Pseudo second order model</i>												
k_2 ($\text{g mg}^{-1} \text{min}^{-1}$) $\times 10^3$	5.46	3.22	2.50	1.92	6.80	4.74	3.82	2.67	8.02	5.39	4.50	3.59
q_1 (mg g^{-1})	59.52	14.72	36.50	45.04	17.40	29.7	38.31	47.60	19.70	32.05	40.81	50.50
R^2	0.992	0.991	0.997	0.996	0.995	0.993	0.994	0.993	0.990	0.990	0.994	0.998
<i>Intraparticle diffusion model</i>												
k_p ($\text{mg g min}^{-1/2}$)	1.570	1.923	1.526	1.270	1.740	1.587	1.139	1.095	1.650	1.112	0.897	0.7536
C	4.71	9.25	12.23	16.71	6.74	12.31	16.77	19.43	9.26	13.04	17.24	20.17
R^2	0.810	0.750	0.820	0.940	0.724	0.730	0.722	0.826	0.780	0.781	0.860	0.910

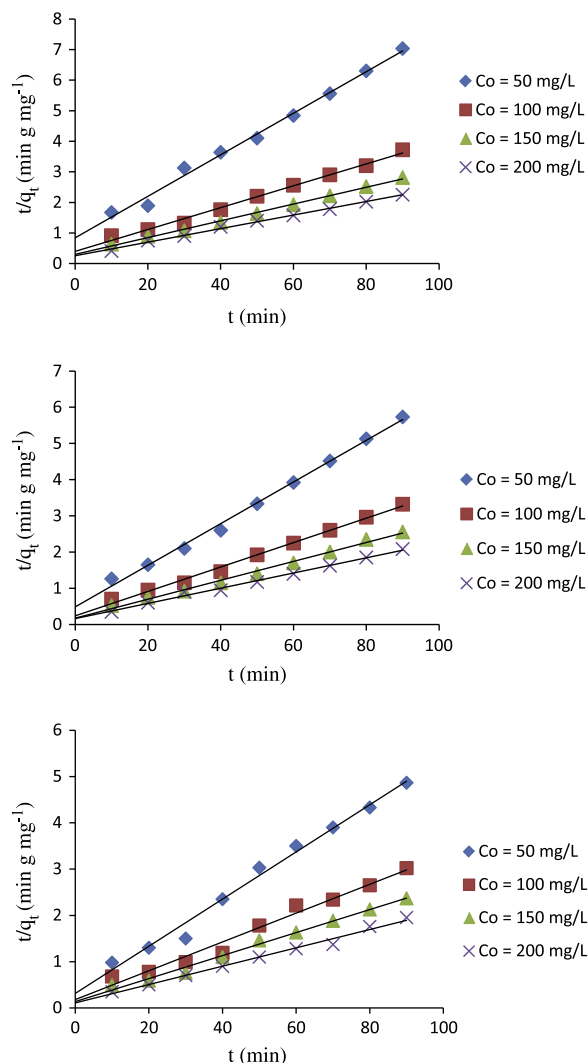


Figure 8 Pseudo-second-order kinetic plots for the sorption of Al at 25 °C, 30 °C and 35 °C.

the boundary layer effect is greater. The correlation coefficients of pseudo-second order model is greater than that of intra particle diffusion model. The constants in the kinetic models were presented in Table 4.

3.8. Thermodynamic studies – Activation energy determination

Thermodynamic analysis of the adsorption process is essential to conclude whether the process is spontaneous or not. The feasibility and spontaneous nature of the adsorption process

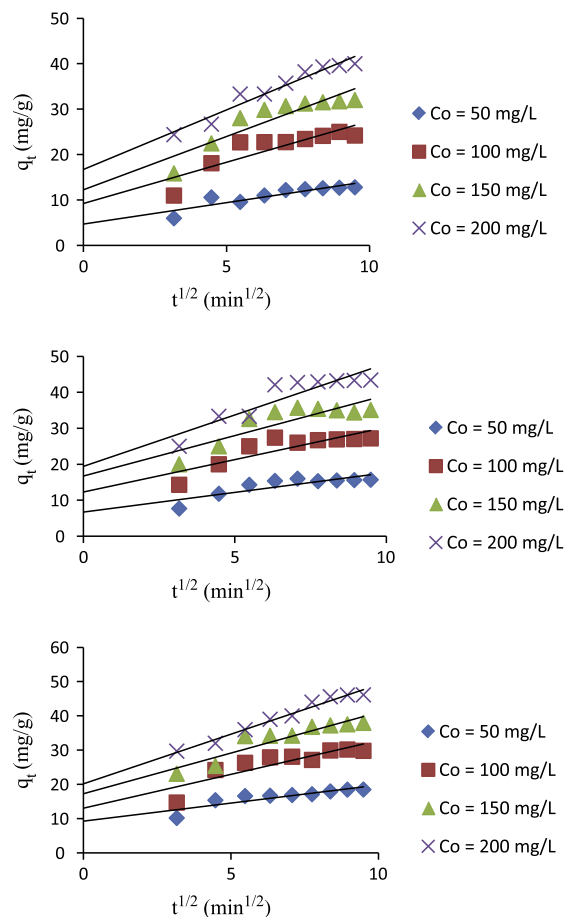


Figure 9 Intra-particle diffusion kinetic plots for the sorption of Al at 25 °C, 30 °C and 35 °C.

is reflected by the thermodynamic parameters. The relationship between rate constant and temperature is represented by Arrhenius equation [Eq. (6)] and is given as:

$$\ln k = \ln A - \frac{E_a}{RT} \quad (6)$$

where k is the rate constant obtained at different temperatures with the best fit kinetic model, E_a , (kJ mol^{-1}) is the activation energy, A ($\text{g (mg min}^{-1})$), is the Arrhenius factor, R , is the gas constant and T (K) is the solution temperature. In this study, the rate constant, k_2 , of the pseudo second order model (the best fit model) was used in Fig. 10. The activation energy estimated for this process from the slope of Fig. 10 was 43.23 kJ/mol.

Table 4 Constants in the Pseudo-second order and intraparticle diffusion models.

Temp °C	Langmuir isotherm constants			Freundlich isotherm constants		
	q_{max} (mg/g)	K_L (L/mg)	R^2	n	K_F (L/g)	R^2
25	48.54	0.047	0.982	2.51	6.81	0.98
30	49.50	0.074	0.982	2.72	8.97	0.97
35	52.63	0.116	0.992	2.81	11.34	0.97

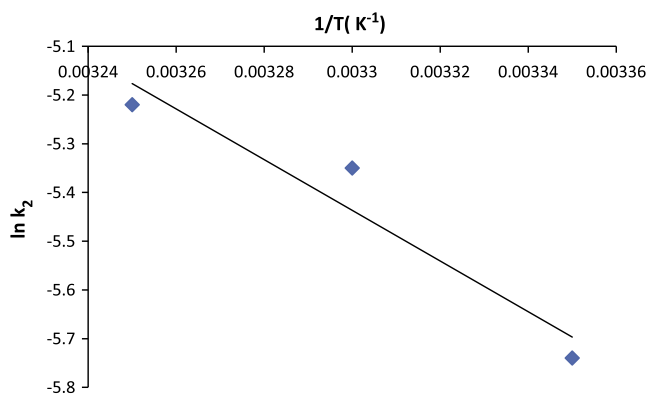


Figure 10 Arrhenius plot for determination of activation energy.

4. Conclusion

The study successfully demonstrated the application of *E. camaldulensis* powder as an adsorbent for the removal of Al (III) ions. An increase in pH was favorable up to 5.0 where as increase in sorbent dose resulted in increased removal efficiencies and decreased uptake capacities. Higher temperature was favoured confirming the endothermic nature of sorption process. The Langmuir isotherm was demonstrated to provide the best fit for the equilibrium sorption data confirming a monolayer sorption pattern. The pseudo-second order model fitted well (with $R^2 > 0.99$) for the kinetic data. Activation energy for this sorption process was evaluated using the Arrhenius theory model. From this study, we conclude that activated *E. camaldulensis* bark powder merits further exploration in large-scale continuous systems to evaluate the practical applicability of its use in effluent treatment plants.

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