



## Removal of copper(II) from aqueous solution by pine and base modified pine cone powder as biosorbent

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### ABSTRACT

Pine cone, a popular agricultural waste in South Africa has been studied for its potential application as a biosorbent in its raw and sodium hydroxide modified form. Surface modification were carried out using sodium hydroxide solution of concentration ranging from 0.01 to 0.15 mol L<sup>-1</sup> and the samples characterized. Batch kinetics were carried out on the biosorption of copper(II) from aqueous solution using the prepared samples and varying biosorption parameters such as solution pH, dose and biosorption temperature.

The results revealed that pine cone surface was modified by sodium hydroxide treatment, carboxylic and phenolic functional groups were mostly affected as seen from Boehm's titration and FTIR analysis. Surface modification reduced  $pH_{PZC}$  from 7.49 to 2.55 and also increased the internal surface of pine cone powder. Copper(II) biosorption studies revealed that optimum solution pH and biosorbent dose for copper(II) removal was pH 5 and 8.0 g L<sup>-1</sup>, for the untreated and treated samples. Copper(II) uptake followed the pseudo-second order kinetic model and the intraparticle diffusion model. Copper(II) removal increased with NaOH modification and higher NaOH concentration.

Biosorption temperature was found to increase copper(II) uptake for all samples indicating that copper(II) biosorption is endothermic in nature. Activation energy computed from the pseudo-second order rate constant increased with NaOH modification from 18.22 to 21.39 kJ mol<sup>-1</sup>. The thermodynamic parameters of activation ( $\Delta G^*$ ,  $\Delta H^*$  and  $\Delta S^*$ ) were computed using Eyring equation and the results show that the reorientation step is mostly entropy controlled at the activation state and the contribution of entropy to the reorientation step of activation tends to decrease with NaOH washing and with increase in NaOH concentration.

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### 1. Introduction

Industrial wastewater treatment for the removal of pollutants such as heavy metal ions, remains a challenge to both developed and developing countries of the world. Heavy metal ions discharged with industrial effluents usually find their way into receiving water bodies such as rivers, lakes and streams therefore increasing the amounts of these pollutants in such water bodies. In recent times filters have been developed to remove heavy metals from wastewater, and the spending on filtration is estimated to increase from \$17 billion to \$75 billion by 2020 [1,2]. Therefore the development and improvement of filter separation technologies is needed to reduce cost of purifying industrial wastewaters before disposal.

Among the new and developing technologies available is biosorption using agricultural waste products. Biosorption has been shown to be a cost effective and efficient option since the biosor-

bent materials are naturally available and cheap. Agricultural waste products are built up of lignocellulosic materials, i.e. contains mainly of cellulose, hemicellulose and lignin [3,4]. As compared to activated carbon and other adsorbents, raw agricultural waste materials used as biosorbent have the following disadvantages: (1) the sorption capacity of agricultural waste products are rather low and (2) after filtration with agricultural wastes biosorbents, the water is seen to have high chemical oxygen demand (COD) and biological oxygen demand (BOD) as well as total carbon (TOC) due to release of soluble organic compounds contained in the plant material [5,6]. Pretreatment with dilute sodium hydroxide solution has been the most popular method of improving surface properties and removing soluble organic components of plant wastes applied for biosorption [4,7–10]. Agricultural wastes are lignocellulosic in nature. Lignin in plant materials serve two major purpose: (1) to strengthen the cell walls and (2) to protect the microfibrils of the cell wall from chemical, physical, and biological attack [11]. Therefore, these properties of lignin may help to explain the low total negative charge and low carboxyl group content displayed by agricultural wastes with high lignin concentrations. Dilute sodium hydroxide

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solution treatment is known to solubilize a small fraction of the lignin and soluble organics in the plant waste [12]; improving the penetration of modifying agents such as citric acid into the biosorbent matrix and thereby increasing metal sorption capacity. It has been observed that most authors use the optimum NaOH concentration (0.1 M NaOH) obtained by Marshall et al. [13] for base washing plant materials without optimization.

Pine seeds are carried in cones. Large quantities of pine cones are produced annually throughout the world, especially in pine plantations grown for the pulp and paper industry. They are collected, dried to facilitate seed release, and generally discarded. Some nurseries grind the cones into mulch or they may be sold for crafts, but consumer demand for cones is small compared to by-products from other industries. This paper seeks (1) to modify the surface properties of pine cone powder for metal sorption which has not been attempted in the literature; (2) to determine the effect of temperature on the biosorption of copper(II) on to the modified samples; (3) to determine thermodynamic parameters of copper(II) removal by the modified biosorbents.

## 2. Materials and methods

### 2.1. Materials

Pine tree cones were obtained from a plantation in Sasolburg. Pine tree cones were collected between August and September 2007. The cones were washed to remove impurity such as sand and leaves, the washed cones were then dried at 90 °C for 48 h in an oven. The scales on the cones were then removed and blended in a food processing blender. The resultant powder was sieved and particles below 150 μm were collected and used for analysis.

The stock solution of copper nitrate ( $\text{Cu}(\text{NO}_3)_2$ ) was prepared by dissolving an accurately weighed amount of the salt in deionized water. The experimental solutions were prepared by diluting the stock solution with distilled water when necessary.

#### 2.1.1. Theory

The pseudo-second order chemisorption kinetics may be expressed as [14,15]:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2, \quad (1)$$

where  $k_2$  is the rate constant of sorption,  $q_e$  and  $q_t$  have the same definition as above. Separating the variables in Eq. (3) gives:

$$\frac{dq_t}{(q_e - q_t)^2} = k_2 dt. \quad (2)$$

Integrating this for the boundary conditions  $t=0$  to  $t=t$  and  $q_t=0$  to  $q_t=q_t$  gives:

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 t, \quad (3)$$

which is the integrated rate law for a pseudo-second order reaction. Eq. (3) can be rearranged to obtain:

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

which has a linear form of

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t. \quad (5)$$

If the initial sorption rate is

$$h = k_2 q_e^2, \quad (6)$$

then Eqs. (5) and (6) becomes

$$q_t = \frac{t}{(1/h) + (t/q_e)}, \quad (7)$$

and

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e} t. \quad (8)$$

The constants can be determined experimentally by plotting of  $t/q_t$  against  $t$ . The intercept =  $1/h$  and slope =  $1/q_e$ .

Intraparticle diffusion model can be expressed as follows [16]:

$$q_t = k_i t^{0.5} + C, \quad (10)$$

where  $k_i$  is the intraparticle diffusion constant ( $\text{mg}/(\text{g min}^{0.5})$ ), and  $C$  is the intercept. In this model, due to the porous nature of the adsorbent, pore diffusion is expanded to be surface sorption. Therefore, the rate constant of intraparticle transport ( $k_i$ ) is estimated from the slope of the linear portion of the plot of amount sorbed ( $\text{mg g}^{-1}$ ) against square root of time.

### 2.2. Methods

#### 2.2.1. Surface modification with NaOH solution

A weighed amount (50 g) of pine cone powder was contacted with 0.5 L of sodium hydroxide solutions of concentration (0.01, 0.05, 0.10 and 0.15  $\text{mol L}^{-1}$ ) and the slurry stirred for 18 h at room temperature. The powder was rinsed with 0.5 L of distilled water. This procedure was repeated two more times to ensure removal of sodium hydroxide from the powder. The residue was then dried overnight at 90 °C. The samples were labelled PCP 0.01, PCP 0.05, PCP 0.10 and PCP 0.15, while the unwashed sample was labelled PCP.

#### 2.2.2. Point zero charge determination

The pH at point zero charge ( $\text{pH}_{\text{PZC}}$ ) of the pine cone powder was determined by the solid addition method [17]. To a series of 100 ml conical flasks, 45 ml 0.01  $\text{mol L}^{-1}$  of  $\text{KNO}_3$  solution of known concentration was transferred. The  $\text{pH}_i$  values of the solution were roughly adjusted from pH 2 to 12 by adding either 0.1  $\text{mol dm}^{-3}$  HCl or NaOH on a pH meter (Crison Basic 20+). The total volume of the solution in each flask was made up to 50 ml by adding the  $\text{KNO}_3$  solution of the same strength. The  $\text{pH}_i$  of the solution was accurately noted, and 0.1 g of pine cone powder was added to the flask, which was securely capped immediately. The suspensions were then manually shaken and allowed to equilibrate for 48 h with intermittent manual shaking. The pH values of the supernatant liquids were noted. The difference between the initial and final pH values ( $\Delta\text{pH} = \text{pH}_f - \text{pH}_i$ ) was plotted against the  $\text{pH}_i$ . The point of intersection of the resulting curve at which  $\Delta\text{pH} = 0$  gave the  $\text{pH}_{\text{PZC}}$ .

#### 2.2.3. Determination of active sites

Acidic and basic sites on both raw and modified pine cone powder were determined by the acid–base titration method proposed by Boehm [18]. The total acid sites matching the carboxylic, phenolic and lactonic sites [18] were neutralized using a 0.1  $\text{mol dm}^{-3}$  NaOH solution while the basic sites were neutralized with a 0.1  $\text{mol L}^{-1}$  HCl solution. The carboxylic and lactonic sites were titrated with a 0.05  $\text{mol L}^{-1}$   $\text{Na}_2\text{CO}_3$  solution and the carboxylic sites were determined with a 0.1  $\text{mol L}^{-1}$   $\text{NaHCO}_3$  solution, and the phenolic sites were estimated by difference [18].

The acidic and basic sites were determined by adding 50 ml of 0.1  $\text{mol dm}^{-3}$  titrating solution and 1 g of pine cone powder to a 50 ml volumetric flask. The flask was partially immersed in a constant temperature water bath set at 20 °C and it was left there for 5 days. The flask was agitated manually twice a day. Afterward, a

sample of 10 ml was titrated with 0.1 mol L<sup>-1</sup> HCl or NaOH solution. The titration was carried out in triplicates.

### 2.2.4. Iodine number determination

In principle, 25 ml of iodine solution of 0.05 mol dm<sup>-3</sup> was added to flasks, which contained different amount of pine cone powder ranging from 0.031 to 0.500 g. The flasks were then shaken for 24 h to assure equilibrium adsorption of iodine onto pine cone powder. The iodine number (mg g<sup>-1</sup>) (or adsorption capacity) was determined from the titration of the residual solution of 10 ml with 0.1 mol dm<sup>-3</sup> sodium thiosulfate in the presence of 1 ml of 1 wt% starch solution as an indicator. The iodine adsorption capacity was determined from the adsorbed iodine/unit mass of the adsorbent at the residual iodine concentration [19].

### 2.2.5. Effect of solution pH

The effect of solution pH on the equilibrium uptake of copper(II) was investigated between pH 2 and 6. The experiments were performed by adding a known weight pine cone powder in to eight 500 ml beakers containing 100 ml of 50 mg L<sup>-1</sup> copper(II) solution and the pH of the solution pH adjusted using 0.1 mol L<sup>-1</sup> HCl or NaOH. The flasks were shaken at 160 rpm and 291 K for 2 h and the amount of copper(II) adsorbed determined by Perkin-Elmer model 2100 atomic absorption spectrometer (AAS).

### 2.2.6. Effect of biosorbent dose

The effect of sorbent dose on the equilibrium uptake of copper(II) was investigated with sorbent masses of 0.05, 0.10, 0.15, 0.20, 0.25, 0.30, 0.35, and 0.40 g. The experiments were performed by adding the known weights of pine cone powder to five 250 ml beakers containing 100 ml of 100 mg L<sup>-1</sup> solution at pH 5.0. The flasks were shaken at 160 rpm and 291 K for 1 h and the equilibrium concentration of copper(II) remaining was determined by Perkin-Elmer model 2100 atomic absorption spectrometer.

### 2.2.7. Effect of temperature

A range of reaction temperatures (291, 297, 307, 317, 327, 337, and 347 K) was used and the flasks were agitated for 15 min. All contact investigations were performed in a 0.5 L flask. A 0.4 g sample of pine cone powder was added to 100 ml volume of copper(II) solution set at pH 5.0 and agitated at 160 rpm for all the experiments. The experiments were carried out at initial copper(II) concentration 120 mg L<sup>-1</sup> for all the studies. Samples were withdrawn at suitable time interval, filtered and the filtrate analyzed for the remaining copper(II) by Perkin-Elmer model 2100 atomic absorption spectrometer.

## 3. Result and discussion

### 3.1. Determination of surface active sites

Pine cone is composed of epidermal and sclerenchyma cells which contain cellulose, hemicellulose, lignin, rosin, and tannins in their cell walls which contains polar functional groups such as alcohols, aldehydes, ketones, carboxylic, phenolic and ether groups [20,21]. These groups will form active sites for sorption on the material surface. Acidic groups of importance include carboxylic, phenolic and lactonic groups. Results of surface active sites determination on pine cone powder reveals that it contains 0.80 mmol g<sup>-1</sup> of carboxylic group, 1.33 mmol g<sup>-1</sup> of lactone group, 1.07 mmol g<sup>-1</sup> of phenolic group and a total acidity and total basicity of 3.20 and 4.27 mmol g<sup>-1</sup> respectively. The predominant acid group in pine cone is the lactone group. Generally, the total acidity of pine cone powder is lower than those of corncob (total acidity: 4.33 mmol g<sup>-1</sup> and basicity: 3.40 mmol g<sup>-1</sup>) [22], and untreated coffee husks (total

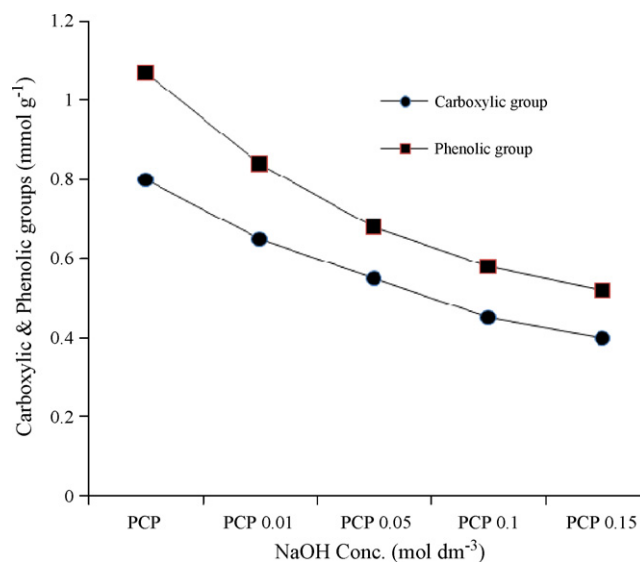


Fig. 1. Variation of carboxylic and phenolic functional groups on pine cone powder surface with NaOH treatment.

acidity: 3.35 mmol g<sup>-1</sup> and basicity: 0.49) [23] but higher than that of orange peels (total acidity: 2.47 mmol g<sup>-1</sup> and basicity: 0.50 mmol g<sup>-1</sup>) [24]. Although the amount of carboxylic groups on pine cone powder (0.80 mmol g<sup>-1</sup>) is more than those in corncob (0.62 mmol g<sup>-1</sup>) and untreated coffee husks (0.60 mmol g<sup>-1</sup>).

Treatment of pine cone powder with different concentrations of NaOH varies the carboxylic, lactonic and phenolic content of pine cone powder. Figs. 1 and 2 show the variation in surface functional groups with concentration of NaOH treatment. It can be observed that the carboxylic and phenolic content of the pine cone powder reduced as the concentration of NaOH in the wash solution increased. Reduction in carboxylic and phenolic content may be attributed to the extraction of resin acids as they are converted to their sodium salt and phenolic content may decrease due to the slight solubility of lignin that contains phenolic compounds. The higher the base concentration, the more the extraction of these compounds. The lactone content on the other hand, was found to increase with concentration of NaOH in the wash solution. It is likely that some sort of conversion takes place during NaOH wash leading to an increase in lactone content.

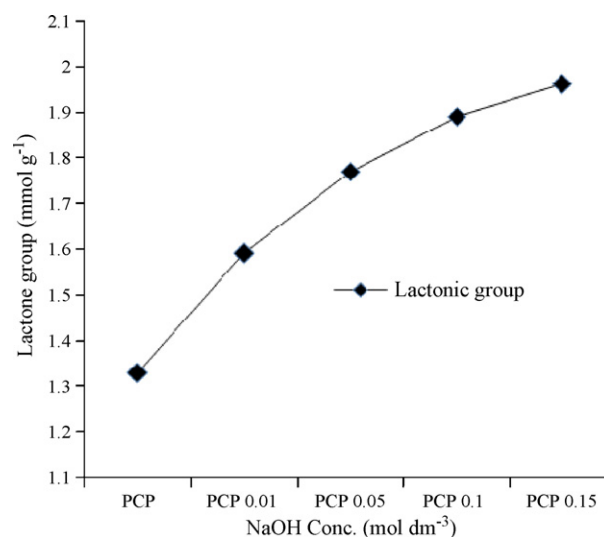


Fig. 2. Variation of lactonic functional groups on pine cone powder surface with NaOH treatment.

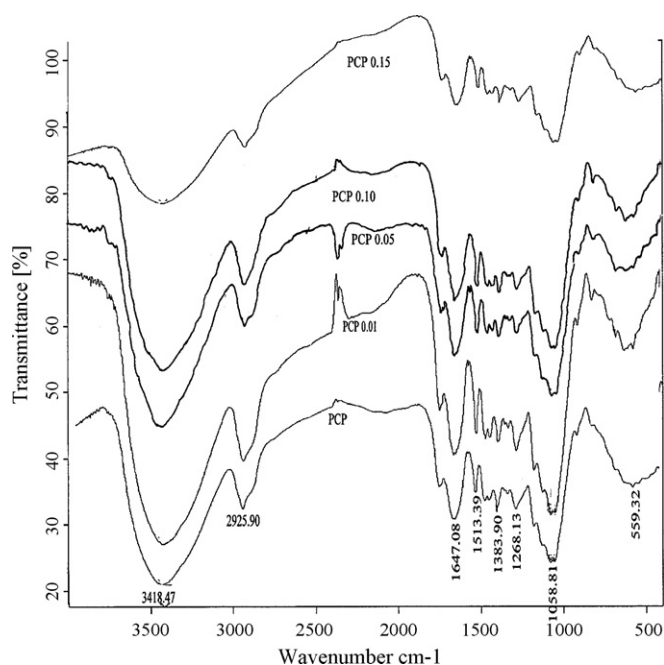


Fig. 3. FTIR spectra of pine and NaOH treated pine cone powder.

### 3.2. FTIR analysis

Fig. 3 shows the FTIR spectra of pine cone and NaOH pine cone powder. Several peaks were observed from the spectra indicating that pine cone is composed of various functional groups. Spectra bands observed at 3418.47 and 2925.90  $\text{cm}^{-1}$  represent  $-\text{OH}$  and aliphatic  $\text{C}-\text{H}$  group. The peak at 1647.08  $\text{cm}^{-1}$  corresponds to the  $\text{C}=\text{O}$  stretch. The peaks between 1058.81 and 559.32  $\text{cm}^{-1}$  may be assigned to the  $-\text{C}-\text{C}-$  and  $-\text{CN}$  stretching, respectively [25].

There were clear decreases of the bands at 3418.47 and 2925.90  $\text{cm}^{-1}$  with increase in the concentration of sodium hydroxide wash solution. This decrease was maximum for PCP 0.15. The result supports the reported reduction in carboxylic acid function as observed in the results from Boehm titration.

### 3.3. Point zero charge

The pH at point zero charge is the pH at which the amount of negative charges on the biosorbent surface just equals the amount of positive charges. The organic functional groups on the biosorbent surface may acquire a negative or positive charge depending on the solution pH. For pH values greater than the  $\text{pK}_a$  of acidic groups, the sites are mainly in dissociated form and acquire a negative charge, while at pH values lower than  $\text{pK}_a$  of these groups will be associated with a proton to become positively charged. The  $\text{pH}_{\text{PZC}}$  for pine cone powder was determined to be 7.49. This  $\text{pH}_{\text{PZC}}$  value is much higher than for corncob (6.2) [22], untreated coffee waste (4.4) [23] modified orange peel cellulose (3.4) [24], cone biomass of *Thuja orientalis* (4.5) [25] mustard husk (6.0) [26] and yellow passion fruit (3.7) [27]. The high value of  $\text{pH}_{\text{PZC}}$  may be attributed to the higher amount of basic groups present on the pine cone powder (4.27  $\text{mmol g}^{-1}$ ).

Treatment of pine cone powder with different concentrations of NaOH led to the reduction in  $\text{pH}_{\text{PZC}}$  from 7.49 to 2.62 for 0.01  $\text{mol dm}^{-3}$  treated, 2.58 for 0.05  $\text{mol dm}^{-3}$  treated, 2.56 for 0.10  $\text{mol dm}^{-3}$  and 2.55 for 0.15  $\text{mol dm}^{-3}$  treated pine cone powder. The fall in  $\text{pH}_{\text{PZC}}$  can be attributed to the sharp reduction in basic functional groups due to NaOH washing of the pine cone powder making the amount of negative charges much higher than the positive charges.

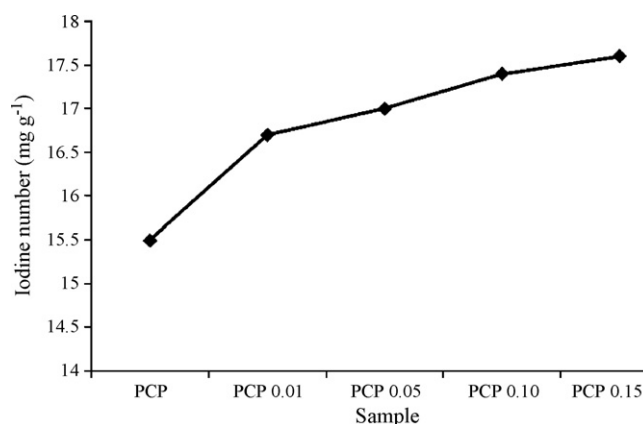


Fig. 4. Iodine number of pine and NaOH treated pine cone powder.

### 3.4. Iodine number

The total surface area of an adsorbent is made up of both external and internal surface. The iodine number gives information on the internal surface of an adsorbent [28]. The iodine number for the pine cone powder and NaOH treated pine cone powder were obtained from the isotherm plot of the amount of iodine biosorbed versus that remaining in solution and the values for iodine number are shown in Fig. 4. Iodine number for pine cone powder was obtained to be 15.46  $\text{mg g}^{-1}$ . This value is quite low compared to iodine values obtained of some agricultural wastes in the literature. For example, iodine number for HCl treated rice husks is 68.00  $\text{mg g}^{-1}$  [28], sugarcane baggase is 75  $\text{mg g}^{-1}$  [29], and tendu leaf refuse is 128  $\text{mg g}^{-1}$  [30]. The low iodine number can be attributed to high lignin and other plant cell wall content in pine cone.

Treatment of pine cone powder with NaOH solution increased the iodine number. The iodine number is found to increase with increasing NaOH concentration in the wash solution. The trend was found to be in line with the trend in bulk density, suggesting that the extraction of plant components would have opened up pore spaces and increased internal surface area of the pine cone.

### 3.5. Effect of solution pH on copper sorption

The pH of the aqueous solution in which sorption is being conducted is an important controlling parameter in the sorption process [31–33]. The magnitude of electrostatic charges imparted by the ionized metal ions and the functional groups on the adsorbent surface are primarily controlled by pH of the medium [33]. The effect of solution pH on the sorption of copper(II) ions from aqueous solution using pine cone and sodium hydroxide treated (0.01, 0.05, 0.10 and 0.125  $\text{mol dm}^{-3}$ ) pine cone powder is shown in Fig. 5. Fig. 5 shows the relationship between amounts of copper(II) adsorbed and initial solution pH. At solution pH 2, the amount of copper(II) removed from solution is smaller than for any other initial solution pH tested, this is can be attributed to the competition between copper(II) ions and  $\text{H}^+$  for biosorption sites. The NaOH treated samples had higher copper(II) sorption capacities than the untreated. PCP 0.15 adsorbed more copper(II) than any of the samples (6.30  $\text{mg g}^{-1}$ ) and adsorption capacity increased for samples treated with increasing concentration of NaOH solution. As solution pH increases, the copper(II) capacities of the samples increase up to solution pH 5. This can be attributed to the increase in negative charge on the biosorbents surface with increasing solution pH, as solution pH rises towards and above  $\text{pH}_{\text{PZC}}$  and the reduction of  $\text{H}^+$  ions in solution which competes with copper(II) for sorption sites. The increase in capacity with initial solution pH was more

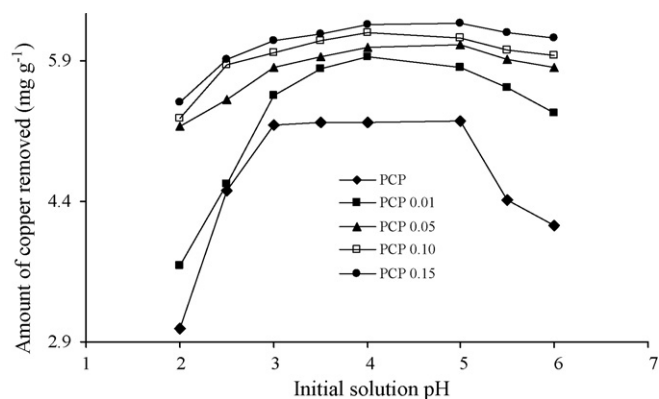


Fig. 5. Effect of initial solution pH on copper(II) uptake by pine and NaOH treated pine cone powder.

rapid with PCP than any other sample, since the initial solution pH dose not rise above the  $pH_{PZC}$  for PCP but for other samples the  $pH_{PZC}$  is reached and passed after pH 3. After initial solution pH 5.0 the sorption capacities for all samples was found to decrease, due to the decreasing concentration of  $Cu^{2+}$  and  $Cu(OH)^+$  at higher pH and the appearance of  $Cu(OH)_2$  species in solution. Higher initial solution pH were not tested because of the possibility copper(II) precipitation as  $Cu(OH)_2$ .

### 3.6. Effect of biosorbents dose

The effect of varying the pine cone and NaOH treated pine cone powder dose,  $m_s$ , for a fixed volume ( $0.05 \text{ dm}^3$ ) of dye solution at constant concentration ( $50 \text{ mg dm}^{-3}$ ) is shown in Figs. 6 and 7. It is observed from Fig. 6 that increasing the pine cone dose,  $m_s$ , increased the percentage of copper(II) removal from aqueous solution from 18.54 to 62.56% for PCP, 18.70 to 91.84% for PCP 0.01, 37.98 to 93.44% for PCP 0.05, 43.42 to 94.24% for PCP 0.10 and from 60.2 to 99.84% for PCP 0.15. On the other hand, the amount of copper(II) adsorbed per unit mass of pine cone powder was found to decrease with biosorbents dose,  $m_s$  (Fig. 7). It is apparent that by increasing the dose of the pine cone powder, the number of sorption sites available for sorbent–solute interaction is increased, thereby resulting in the increased percentage copper(II) removal from solution. Similar observation has been reported in the literature [34,35].

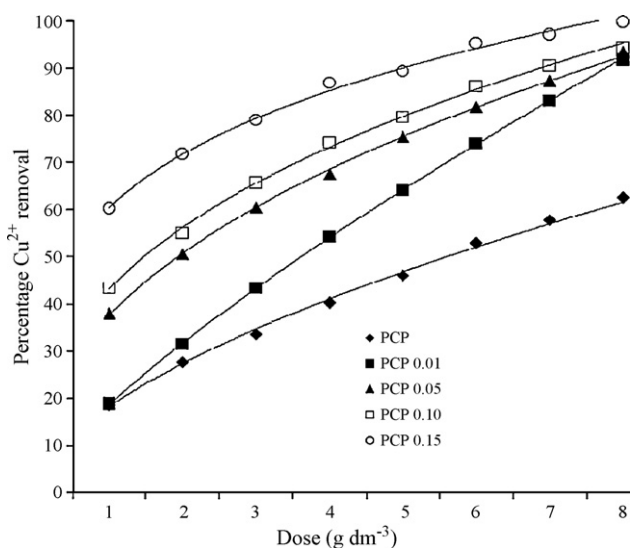


Fig. 6. Percentage removal of copper(II) with increasing dose of pine and NaOH treated pine cone powder.

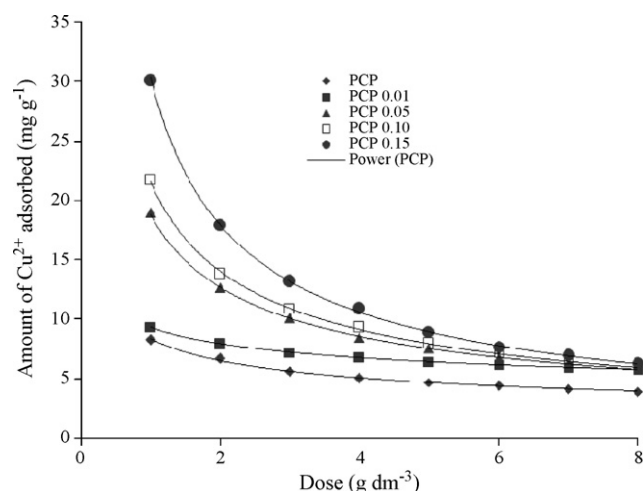


Fig. 7. Effect of dose on copper(II) removal by pine and NaOH treated pine cone powder.

The pattern in the results shows that the copper(II) capacity for all samples versus biosorbent dose,  $m_s$ , was lower for PCP and higher PCP 0.15 (copper(II) capacity increasing with concentration of NaOH wash). Increasing dose also increases the surface area of contact with sorbate ions. For PCP, when dose,  $m_s$ , is increased from 1 to  $8 \text{ g dm}^{-3}$ , percentage copper(II) removal increased from 18.54 to 62.56% and biosorption capacity decreased from  $8.27$  to  $3.91 \text{ mg g}^{-1}$ . For PCP 0.15, the change in dose from 1 to  $8 \text{ g dm}^{-3}$ , produced a percentage increase from 60.2 to 99.84% and capacity reduced from  $30.10$  to  $6.24 \text{ g dm}^{-3}$ . The interpretation to this will be that the PCP 0.15 had a higher surface for contact with adsorbate ions than the PCP which on increase in the dose (increase in surface area for contact) removed more of the copper(II) ions from solution. This result is in line with the results obtained from iodine capacity measurements (Table 1).

Mathematic equations of the form

$$q_e = A m_s^B, \quad (11)$$

$$\%Re = A m_s^B, \quad (12)$$

were derived to predict the relationship between the dose,  $m_s$ , the copper sorption capacity, and the percentage copper(II) ion removal for each sample within the sorbent dose range of  $1\text{--}8 \text{ g dm}^{-3}$ . These relationships have correlation coefficient as high as 0.999 and the values of A and B for each sample are shown in Table 3.

### 3.7. Effect of temperature

The temperature dependence of copper(II) sorption onto pine and NaOH washed pine cone powder was studied with a constant initial copper(II) concentration of  $120 \text{ mg L}^{-1}$  at 160 rpm and pine cone powder dose  $8 \text{ g L}^{-1}$  at various temperature of biosorption reaction. Table 2 shows the kinetic data for the biosorption of copper using the pine cone samples at different temperatures, while Fig. 8 shows the effect of contact time on the amount of copper(II) removed from aqueous solution at 347 K for pine cone

Table 1  
Iodine number ( $\text{mg g}^{-1}$ ) for raw and base treated pine cone powder (PCP).

Sample	Iodine number ( $\text{mg g}^{-1}$ )
PCP	15.5
PCP 0.01	16.7
PCP 0.05	17.0
PCP 0.10	17.4
PCP 0.15	17.6

**Table 2**  
Pseudo-second order parameters for the sorption of copper(II) on to pine and NaOH treated pine cone powder.

Sample	Temperature (K)	$q_e$ (mg g <sup>-1</sup> )	$h$ (mg g <sup>-1</sup> min <sup>-1</sup> )	$k_2$ (g mg <sup>-1</sup> min <sup>-1</sup> )
PCP	291	6.80	4.21	0.0910
	297	7.03	5.14	0.1040
	307	7.45	6.53	0.1177
	317	7.82	7.92	0.1295
	327	8.23	9.85	0.1454
	337	8.65	12.03	0.1608
	347	9.22	14.94	0.1757
PCP 0.01	291	13.01	9.38	0.0554
	297	13.43	11.74	0.0651
	307	14.15	17.04	0.0851
	317	14.83	23.92	0.1088
	327	15.65	33.83	0.1381
	337	16.41	47.31	0.1757
	347	17.43	59.22	0.1949
PCP 0.05	291	15.03	11.09	0.0491
	297	15.43	12.16	0.0511
	307	16.11	18.54	0.0714
	317	16.73	25.81	0.0922
	327	17.42	36.43	0.1201
	337	18.13	49.34	0.1501
	347	19.02	61.21	0.1692
PCP 0.10	291	16.38	23.87	0.0890
	297	16.74	28.34	0.1011
	307	17.37	41.56	0.1377
	317	18.12	55.32	0.1685
	327	18.86	78.62	0.2210
	337	19.53	106.44	0.2791
	347	20.23	133.88	0.3271
PCP 0.15	291	17.22	45.51	0.1535
	297	17.74	55.76	0.1772
	307	18.62	73.73	0.2127
	317	19.43	91.11	0.2413
	327	20.20	120.86	0.2950
	337	21.12	150.35	0.3371
	347	21.87	181.92	0.3804

powder samples. The results show that with increase in reaction temperature from 291 to 347 K, the maximum percentage copper(II) removal after 5 min of contact increased for all samples and the NaOH washed samples had a higher percentage removal than the unwashed sample. Among the NaOH washed samples, PCP 0.15 gave a higher percentage copper(II) removal than the PCP 0.01. The fact that the percentage copper removal is favored by temperature indicates that the mobility of the copper(II) ions increases with a rise in the temperature. It can also be said that reaction of copper(II) and surface functional groups is enhanced by increased temperature of reaction.

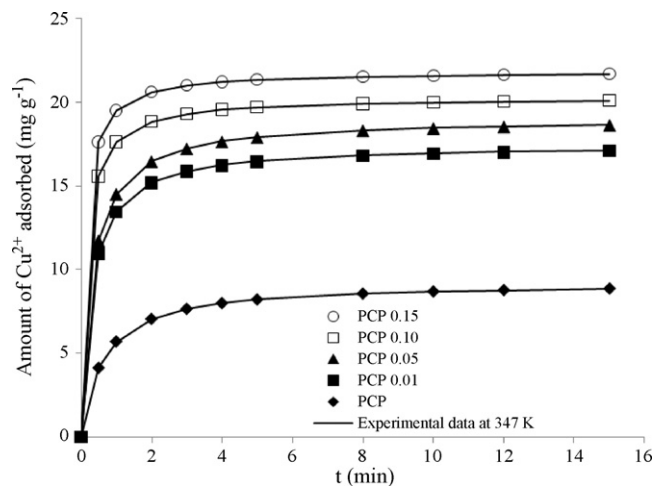
### 3.7.1. Pseudo-second order kinetics

Analysis of the experimental data with the pseudo-second order kinetic model shows a good agreement of the sets of data, which is reflected in the extremely high correlation coefficient of determination, obtained (Table 2). Table 2 shows the sorption rate constant,  $k_2$ , initial sorption rate,  $h$ , and equilibrium sorption capacity,  $q_e$ , as a function of solution temperature. Thus on increasing the temper-

**Table 3**  
Relationship between sorption capacity, percentage removal and dose for pine and NaOH treated pine cone powder.

Sample	Capacity		Percentage removal	
	A	B	A	B
PCP	8.301	-0.363	18.539	1.261
PCP 0.01	9.311	-0.232	18.621	1.270
PCP 0.05	18.994	-0.567	37.991	0.432
PCP 0.10	21.317	-0.618	42.632	0.381
PCP 0.15	30.269	-0.757	59.695	0.247

ature from 291 to 374 K, the sorption capacity at equilibrium,  $q_e$ , is increased from 5.62 to 8.86 mg g<sup>-1</sup> for PCP, 11.91 to 17.09 mg g<sup>-1</sup> for PCP 0.01, 13.78 to 18.63 mg g<sup>-1</sup> for PCP 0.05, 15.66 to 20.08 mg g<sup>-1</sup> for PCP 0.10 and 16.53 to 21.70 mg g<sup>-1</sup> for PCP 0.15. The initial sorption rate,  $h$ , and the pseudo-second order rate constant,  $k_2$ , were also found to increase with temperature variation from 291 to 347 K. This trend suggests that a chemisorption reaction or an activated sorption between copper(II) ions and functional groups on pine cone powder surface involving valency forces through sharing



**Fig. 8.** Effect of temperature on copper(II) sorption on to pine and NaOH modified pine cone powder at 347 K.

**Table 4**  
Relationship between  $q_e$ ,  $h$ , and  $k_2$  with temperature for pine and NaOH treated pine cone powder.

Sample	$q_e$		$h$		$k_2$	
	A	B	A	B	A	B
PCP	$4.61 \times 10^{-4}$	1.6916	$1.1376 \times 10^{-25}$	10.2900	$5.3580 \times 10^{-19}$	6.9065
PCP 0.01	$1.2196 \times 10^{-3}$	1.6343	$4.9659 \times 10^{-26}$	10.6670	$3.3420 \times 10^{-20}$	7.3988
PCP 0.05	$8.7963 \times 10^{-3}$	1.3117	$7.1121 \times 10^{-25}$	10.2180	$9.1833 \times 10^{-21}$	7.5944
PCP 0.10	$7.6278 \times 10^{-3}$	1.3616	$5.6624 \times 10^{-26}$	10.8360	$9.7499 \times 10^{-22}$	8.1125
PCP 0.15	$7.6380 \times 10^{-3}$	1.3610	$5.7544 \times 10^{-26}$	18.8300	$9.7724 \times 10^{-22}$	8.1120

or exchange of electrons between pine cone powder and copper(II) ion occurs. Similar results of copper and other adsorbents have also been reported in the literatures, for example copper on palm kernel fibre [36] and copper on to seeds of *Capsicum annuum* [37]. According to Ho et al. [38], if the copper(II) uptake is chemically rate controlled, the pseudo-second order constants will be independent of particle diameter and flow rate and will depend on temperature of the dye in solution. Increase in temperature will also lead to increase in the amount adsorbed at equilibrium for a chemisorption-controlled reaction. The logarithmic plots of initial sorption,  $h$ , pseudo-second order rate constant,  $k_2$ , and  $q_e$  versus temperature were made and the plots were found to give straight lines whose linear regression,  $r^2$ , are extremely high, indicating that dye uptake is chemically rate controlled. Mathematical expressions of the forms

$$q_e = AT^B, \quad (13)$$

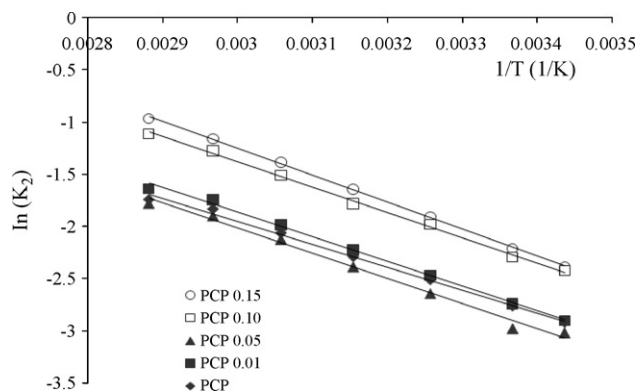
$$h = AT^B, \quad (14)$$

$$k_2 = AT^B, \quad (15)$$

were therefore drawn relating the initial sorption rate,  $h$ , the pseudo-second order rate constant,  $k_2$ , and equilibrium capacity,  $q_e$  and reaction temperature with the values of A and B shown in Table 4.

The values of rate constant,  $k_2$ , were found to increase from 0.0543 to 0.1757  $\text{g mg}^{-1} \text{min}^{-1}$  for PCP, 0.0554 to 0.1949  $\text{g mg}^{-1} \text{min}^{-1}$  for PCP 0.01, 0.0491 to 0.1692 for PCP 0.05, 0.0890 to 0.3271  $\text{g mg}^{-1} \text{min}^{-1}$  for PCP 0.10 and from 0.0928 to 0.3804  $\text{g mg}^{-1} \text{min}^{-1}$  for PCP 0.15, for an increase in the solution temperature of 291–347 K. There is a linear relationship between the pseudo-second order rate constant and temperature with coefficient of determination greater than 0.99 for all samples (Fig. 9). The sorption rate constant is usually expressed as a function of solution temperature by the relationship:

$$\ln k_2 = \ln k_0 - \frac{E_a}{RT}, \quad (16)$$



**Fig. 9.** Plot of linear relationship between pseudo-second order rate constant and reciprocal of sorption temperature.

where  $k_2$  is the pseudo-second order rate constant of sorption ( $\text{g mg}^{-1} \text{min}^{-1}$ ),  $k_0$  is the temperature-independent factor ( $\text{g mg}^{-1} \text{min}^{-1}$ ),  $E$  is the activation energy of sorption ( $\text{kJ mol}^{-1}$ ),  $R$  is the gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ) and  $T$  is the solution temperature (K). Therefore, the relationship between  $k_2$  and  $T$  can be represented in an Arrhenius form in Table 5.

From these equation, the rate constant for sorption,  $k_0$ , is  $1.02 \times 10^2 \text{ g mg}^{-1} \text{min}^{-1}$  for PCP,  $1.78 \times 10^2 \text{ g mg}^{-1} \text{min}^{-1}$  for PCP 0.01,  $1.83 \times 10^2 \text{ g mg}^{-1} \text{min}^{-1}$  for PCP 0.05,  $3.46 \times 10^2 \text{ g mg}^{-1} \text{min}^{-1}$  for PCP 0.10 and  $6.46 \times 10^2 \text{ g mg}^{-1} \text{min}^{-1}$  for PCP 0.15 and the activation energy for sorption,  $E_a$ , 18.22  $\text{kJ mol}^{-1}$  for PCP, 19.52  $\text{kJ mol}^{-1}$  for PCP 0.01, 20.02  $\text{kJ mol}^{-1}$  for PCP 0.05, 20.04  $\text{kJ mol}^{-1}$  for PCP 0.10 and 21.39  $\text{kJ mol}^{-1}$  for PCP 0.15 which are close to or higher than 20  $\text{kJ mol}^{-1}$ , except for PCP. The increase in activation energy with concentration of NaOH solution for treatment indicates that stronger bonds are formed between copper(II) and pine cone powder surface with NaOH treatment and the strength of such bonds increase with NaOH concentration. It can also be said that the surface of the pine cone sample increased with NaOH treatment and concentration of NaOH for treatment.

Diffusion controlled processes are known to activation energies much lower than 20  $\text{kJ mol}^{-1}$  [39]. The rate-controlling step in the process can be characterized in part by its activation energy. Therefore, since the sorption increased with temperature, which implies the uptake is endothermic in nature and activation energy is close to or higher than 20  $\text{kJ mol}^{-1}$ , then one can say that chemisorption process significant and rate controlling in the sorption of copper(II) ions onto NaOH modified pine cone powder but the untreated pine cone powder may follow a slightly different mechanism.

To investigate possibility of copper(II) being transported within pores of pine cone powder, the experimental data was fitted in an intraparticle diffusion plot of the amount of copper(II) sorbed per unit mass of sorbent against the square root of contact time. Fig. 10 shows the plot of amount sorbed,  $qt$  ( $\text{mg g}^{-1}$ ) versus  $t^{0.5}$  ( $\text{min}^{0.5}$ ), which shows that the sorption process tends to be followed by two phases. The initial curved portion of the plot indicates a boundary layer effect, while the second portion is due to intraparticle diffusion [34]. The slope of the second portion of the plot is defined as the intraparticle diffusion parameter,  $k_i$  ( $\text{mg}/(\text{g min}^{0.5})$ ) [40–42]. On the other hand, the intercept of the plot reflects the boundary layer effect. The larger the intercept, the greater the contribution of the surface sorption in the rate limiting step.

The boundary layer diffusion is found to increase with NaOH treatment and NaOH concentration. The values increased from 7.384 for PCP to 20.920 for PCP 0.15. The calculated intraparticle

**Table 5**  
Relationship between rate constant,  $k_2$ , temperature,  $T$  and activation energy,  $E_a$ , for pine and NaOH treated pine cone powder.

Sample	$k_0$	Activation energy, $E_a$
PCP	$1.02 \times 10^2$	$-18.22 \times 10^3$
PCP 0.01	$1.78 \times 10^2$	$-19.52 \times 10^3$
PCP 0.05	$1.83 \times 10^2$	$-20.02 \times 10^3$
PCP	$3.46 \times 10^2$	$-20.04 \times 10^3$
PCP	$6.46 \times 10^2$	$-21.39 \times 10^3$

**Table 6**  
Activation energy parameters for copper(II) biosorption on to pine and NaOH modified pine cone powder.

Sample	$E_a$ (kJ mol <sup>-1</sup> )	$k_0$ (g mg <sup>-1</sup> min <sup>-1</sup> )	$\Delta S^*$ (kJ mol <sup>-1</sup> )	$\Delta H^*$ (kJ mol <sup>-1</sup> )	$\Delta G^*$ (kJ mol <sup>-1</sup> )
PCP	18.22	$1.02 \times 10^2$	-215.26	15.58	74.71
PCP 0.01	19.52	$1.78 \times 10^2$	-210.65	16.89	74.70
PCP 0.05	20.02	$1.83 \times 10^2$	-210.41	17.39	73.03
PCP 0.10	20.04	$3.64 \times 10^2$	-205.12	17.40	71.19
PCP 0.15	21.39	$6.46 \times 10^2$	-199.94	18.78	69.39

diffusion coefficient,  $k_i$ , values were given as 0.395 mg/(g min<sup>0.5</sup>) for PCP, 0.385 mg/(g min<sup>0.5</sup>) for PCP 0.01, 0.342 mg/(g min<sup>0.5</sup>) for PCP 0.05, 0.239 mg/(g min<sup>0.5</sup>) for PCP 0.10 and 0.206 mg/(g min<sup>0.5</sup>) for PCP 0.15. This indicates decrease in  $k_i$  with NaOH treatment and increasing concentration of NaOH 0.01–0.15 mol L<sup>-1</sup>. The rate constants were found to decrease with increasing NaOH concentration, perhaps due to the increased external surface for sorption indicated by iodine number of the sample, leading to a rapid fall in copper(II) concentration in solution and consequent reduction in the concentration difference driving force for the mass transfer.

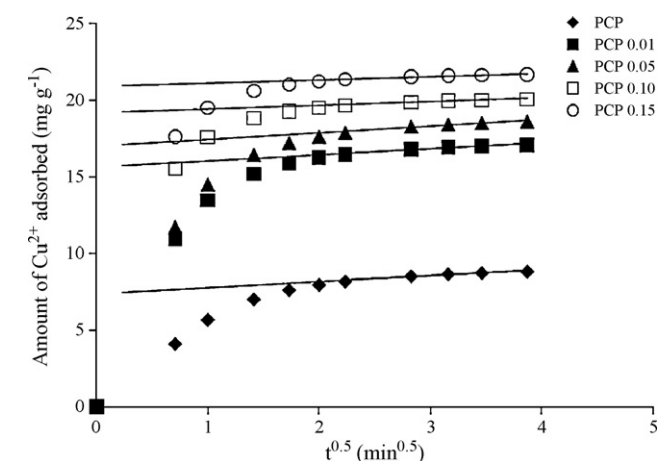
The change in enthalpy ( $\Delta H^*$ ) and entropy ( $\Delta S^*$ ) of activation for the treated and untreated pine cone powder was calculated by Eyring equation [38] below:

$$\ln\left(\frac{k_2}{T}\right) = \ln\left(\frac{k}{h}\right) + \frac{\Delta S^*}{R} - \frac{\Delta H^*}{RT}, \quad (17)$$

where  $k_2$  is the pseudo-second order rate constant,  $T$  is the Kelvin temperature,  $k$  and  $h$  are the Boltzmann's and Planck's constants respectively. The change in entropy of activation ( $\Delta S^*$ ) and enthalpy of activation ( $\Delta H^*$ ), for this step have been evaluated from the intercept and slope of each linear plot. The free energies of activation ( $\Delta G^*$ ) for the treated and untreated pine cone powder were computed from the equation:

$$\Delta G^* = \Delta H^* - T\Delta S^*. \quad (18)$$

The corresponding values for change in enthalpy of activation ( $\Delta H^*$ ), enthalpy of activation ( $\Delta S^*$ ) and free energy of activation ( $\Delta G^*$ ) has been calculated and the values for treated and untreated pine cone powder are given in Table 6. The entropy of activation ( $\Delta S^*$ ), for all pine cone powder samples were found to be smaller than zero, and the values tend to move towards zero with NaOH treatment and with increase in concentration of NaOH treatment. The enthalpy of activation ( $\Delta H^*$ ) obtained from Eyring equation is lower than  $T\Delta S^*$ , for all samples, indicating that the reorientation step is mostly entropy controlled at the activation state. The contribution of the reorientation step to activation tends to decrease with NaOH washing and with increase in NaOH concentration as



**Fig. 10.** Intraparticle diffusion plots of copper(II) removal by pine and NaOH treated pine cone powder.

seen from the increasing value of enthalpy ( $\Delta H^*$ ), compared with  $T\Delta S^*$ . The free energy of activated ( $\Delta G^*$ ), was found to decrease with NaOH treatment and with NaOH concentration, indicating that activation becomes more spontaneous with NaOH treatment and with increasing NaOH concentration.

#### 4. Conclusion

Pine cone and NaOH modified pine cone powder has been examined as biosorbent for copper(II) from aqueous solution. Modification of pine cone powder surface with NaOH solution was found to modified the surface by affecting the quantities of carboxylic and phenolic groups, reducing the  $pH_{PZC}$  and increasing internal surface.

The optimum solution pH and biosorbent dose were pH 5 and 8 g L<sup>-1</sup> for all samples. The pseudo-second order kinetics well described the batch kinetic data at different temperatures for all samples prepared. Biosorption of copper(II) increased with temperature. The modified pine cone powder removed more copper(II) from solution at all biosorption temperatures studied with all prepared samples. Activation energies calculated from the pseudo-second order rate constant showed that the activation energy increased with NaOH treatment and NaOH concentration. The thermodynamic parameters of activation ( $\Delta G^*$ ,  $\Delta H^*$  and  $\Delta S^*$ ) were computed using Eyring equation and the results show that the reorientation step is mostly entropy controlled at the activation state and the contribution of entropy to the reorientation step of activation tends to decrease with NaOH washing and with increase in NaOH concentration.

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