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Surface modification of pine cone powder and its application for removal of Cu(II) from wastewater

A.E. Ofomaja*, E.B. Naidoo, S.J. Modise

Department of Chemistry Vaal University of Technology, Vanderbiljpark, South Africa
Tel. +27 768202689, +27 738126830, +234 80715034; email: aus_ofomaja@yahoo.com or augustine@vut.ac.za

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ABSTRACT

Pine cone powder is an agricultural waste material from the wood industry. In this investigation, chemical modification of pine cone powder using NaOH solution of different concentrations (0.01, 0.05, 0.10, and 0.15 mol dm^{-3}) was carried out. The changes in surface properties produced by modification and the ability of the modified products to remove copper(II) from aqueous solution was examined. Chemical characterization of the adsorbent surface by FTIR and Bohem titration showed that an increase in NaOH concentration in the wash solution was found to reduce the amounts of carboxyl and phenolic groups and increase the iodine number. The pH_{PZC} of the raw pine cone powder reduced with NaOH concentration in the wash solution from 7.49 to 2.55. Optimum NaOH concetration for pine cone powder surface modification was 0.15 mol dm^{-3}, while the optimum solution pH, contact time and biosorbent dose for copper(II) removal were pH 5.0, 5 min and 4.0 g dm^{-3} for all samples. Copper(II) removal capacity was higher for samples washed with higher concentrations of NaOH solution (PCP 6.8 mg g^{-1}, PCP 0.1 13.01 mg g^{-1}, PCP 0.05 15.03 mg g^{-1}, PCP 0.10 16.38 mg g^{-1} and PCP 0.15 17.22 mg g^{-1}). The equilibrium solution pH at the end of the biosorption experiments were higher than the initial solution pH when modified samples were used for biosorption but lower than the initial pH when the raw pine cone powder was applied. This may suggest a different mechanism of copper(II) uptake by raw pine cone powder as compared with the modified samples. The paseudo-second order kinetics for copper(II) biosorption gave the best fit with the experimental data for both the raw and NaOH modified pine cone powder.

Keywords: Pine cone powder; NaOH modification; Equilibrium solution pH; Copper(II) capacity

1. Introduction

Natural adsorbents for the removal of pollutants from wastewater have been sourced from different raw materials. The need for cheap, readilly available and efficient sources has become important because of increasing occurances for high levels of pollutants found in industrial wastewaters, the present and future cost of adsorption materials and the need to remove pollutants from waste streams even at low concentrations. In recent times adsorbents have been developed to remove heavy metals from wastewater, and the spendings on filtration are estimated to increase from $17 billion to $75 billion by 2020 [1,2]. Therefore the development and improvement of new, cheap and effective filter seperation technologies is needed to reduce cost of purifying industrial wastewaters before disposal.

Biosorption has been shown to be a cost effective and efficient option since the biosorbent materials are naturally available and cheap. Agricultural waste products are built up of lignocellulosic materials, i.e. consists mainly of cellulose, hemicellulose and lignin [3,4]. As

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* Corresponding author.

compared with activated carbon and other adsorbents, raw agricultural waste materials used as biosorbent have the following disadvantages: (1) the biosorption capacity of agricultural waste products are rather low, (2) after filtration with agricultural waste biosobents, 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 NaOH solution has been the most popular method of improving surface properties and removing soluble organic components of plant wastes applied as biosorbents [4,7–10].

Agricultural wastes are lignocellulosic in nature. Lignin in plant materials serve two major purposes: (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 carboxylic group content displayed by agricultural wastes with high lignin concentrations. Dilute NaOH solution treatment is known to solubulize a small fraction of the lignin and soluble organics in the plant waste [12]; improve the penetration of modifying agents such as citric acid into the biosorbent matrix and thereby increasing metal biosorption 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 tree 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 are sold as crafts, but consumer demand for these cones are small compared to by-products from other industries. This paper seeks to (1) modify the surface properties of pine cone powder for metal biosorption which has not ben attempted in litrature, except for a few citations on chemical oxidation of pine cone [14] and carbonization of pine cone [15] (2) optimize the concentration of sodium hydroxide used for modification and relate the change in NaOH concentration with surface properties of pine cone powder (3) model the kinetic up take of copper(II) by the raw and NaOH modified pine cone powder via four kinetic models.

2. Materials and methods

2.1. Materials

Pine tree cones were obtained from a plantation in Sasolburg, Free State South Africa. Pine tree cones were collected between August and September 2007. The cones were washed to remove impurities such as sand and leaves, and 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 300 μm were collected and used for analysis.

The stock solution of copper nitrate ($Cu(NO_3)_2$) 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 where necessary.

2.2. Methods

2.2.1. Percentage recovery after base washing

A weighed amount (50 g) of the powder was contacted with 0.5 dm^{-3} of NaOH solution of concentration ranging from 0.01 to 0.15 mol dm^{-3} and the slurry stirred overnight. The powder was then rinsed with distilled water to remove excess NaOH. This procedure was repeated two more times to ensure removal of NaOH from the powder. The residue was then dried overnight at 90°C and percentage recoveries were determined after one NaOH wash and three water washes to remove NaOH and the value calculated by the following equation [1]:

$$\%\ \text{Recovery} = \frac{\text{Weight of NaOH washed cones}}{\text{Initial weight of cones}} \times 100 \quad (1)$$

The pine cone powder samples were coded as PCP for raw sample; PCP 0.01 for sample treated with 0.01 mol dm^{-3} NaOH solution; PCP 0.05 for sample treated with 0.05 mol dm^{-3} NaOH solution; PCP 0.10 for sample treated with 0.10 mol dm^{-3} NaOH solution and PCP 0.15 for sample treated with 0.01 mol dm^{-3} NaOH solution.

2.2.2. FTIR analysis

For FTIR spectra, 5.00 mg of powdered pine cone was properly mixed with parafin oil and pasted on potassium bromide disks. Analysis was performed on a Perkin–Elmer infrared spectrophotometer.

2.2.3. Bulk density

Bulk density measurements were carried out in a density bottle of 25 ml. The dry pine cone powder was added to the density bottle with gentle tapping to ensure that the particles would settle to the bottom of the flask and all air spaces are filled. The mass of the density bottle containing the pine cone powder was then determined. The mass of pine cone powder that occupied 25 ml was then obtained from the mass of the bottle plus pine cone powder minus the mass of the empty bottle.

$$\text{Bulk density} = \frac{\text{Mass of PCP occupying 25 ml volume}}{\text{25 ml}} \quad (2)$$

2.2.4. pH at point zero charge (pH_{PZC}) determination

The pH at point zero charge (pH_{PZC}) of the pine cone powder was determined by the solid addition method [17]. To a series of 100 ml conical flasks, 45 ml of 0.01 mol dm^{-3} of KNO_3 solution was transferred. The initial solution pH values (pHi) were roughly adjusted from pH 2 to 12 by adding either 0.10 mol dm^{-3} HCl or NaOH using a pH meter (Crison Basic 20+). The total volume of the solution in each flask was then made up to 50 ml by adding KNO_3 solution of the same strength. The pH_i of the solution was accurately noted, and 0.10 g of pine cone powder was added to each of the flask, which was then securely capped immediately. The suspensions were then manually shaken and allowed to equilibrate for 48 h with intermittent manual shaking. The final pH values (pH_f) of the supernatant liquids were then noted. The difference between the initial and final pH values ($\Delta pH = pH_f - pH_i$) was plotted against the pH_i. The point of intersection of the resulting curve at which $\Delta pH = 0$ gives the pH_{PZC}.

2.2.5. Determination of active sites

Acidic and basic sites on both raw and modified pine cone powder surface 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 0.10 mol dm^{-3} of NaOH solution while the basic sites were neutralized with a 0.10 mol dm^{-3} HCl solution. The carboxylic and lactonic sites were titrated with a 0.05 mol dm^{-3} Na_2CO_3 solution and the carboxylic sites were determined with a 0.10 mol dm^{-3} $NaHCO_3$ solution, while the phenolic sites were estimated by difference [18].

The acidic and basic sites were determined by adding 50 ml of 0.1 mol dm^{-3} of the titrating solution and 1.00 g of pine cone powder to a 50 ml volumetric flask. The flasks were partially immersed in a constant temperature water bath set at 20°C and it was left for 5 days. The flasks was agitated manually twice a day. Afterward, a sample of 10 ml was titrated with 0.10 mol dm^{-3} HCl or NaOH solution. The titration was carried out in triplicates.

2.2.6. Iodine number determination

A 25 ml solution of 0.05 mol dm^{-3} iodine was added to a 5 250 ml beakers in which different amounts of pine cone powder ranging from 0.031 to 0.500 g have been added. The flasks were then shaken for 24 h to ensure equilibrium adsorption of iodine onto pine cone powder. The iodine number or iodine adsorption capacity (mg g^{-1}) was determined from the titration of 10 ml of the residual solution with 0.10 mol dm^{-3} sodium thiosulfate in the presence of 1 ml of 1 wt % starch solution as an indicator. The iodine adsorption capacity was then calculated from the adsorbed iodine/unit mass of the adsorbent at the residual iodine concentration.

2.2.7. Effect of solution pH

The effect of solution pH on the equilibrium uptake of copper(II) from aqueous solution by pine cone powder and NaOH modified pine cone powder was investigated between pH 2 and 6. The experiments were performed by adding a known weight of pine cone or NaOH modified pine cone powder into eight 500 ml beakers containing 50 ml of 70 mg dm^{-3} of copper(II) solution and the pH of the solution adjusted using 0.10 mol dm^{-3} HCl or NaOH. The flasks were shaken at 160 rpm and 291 K for 1 h and the amount of copper(II) remaining in solution was measured by a Perkin–Elmer model 2100 atomic absorption spectrometer (AAS).

2.2.8. Effect of biosorbent dose

The effect of biosorbent dose on the equilibrium uptake of copper(II) from aqueous solution by pine cone and NaOH modified pine cone powder was investigated with biosorbent 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 50 ml of 70 mg dm^{-3} 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 a Perkin–Elmer model 2100 atomic absorption spectrometer (AAS).

2.2.9. Kinetic experiment

The effect of contact time on the copper(II) removal from solution using pine cone and NaOH modified pine cone powder was investigated by contacting 0.40 g of pine cone or NaOH modified pine cone powder with 100 ml of 120 mg dm^{-3} of copper(II) solution at 291 K and an optimum pH of 5.0 with constant agitation of 160 rpm for 15 min. Samples (3 ml) were pipetted out at different time intervals, centrifuged and the concentration of copper(II) analyzed using A Perkin–Elmer model 2100 atomic absorption spectrometer (AAS).

3. Result and discussion

3.1. Percentage recovery after base washing

Table 1 shows the results of percentage recoveries of pine cone powder after NaOH washing with different concentrations of NaOH solutions. The results revealed that some fraction of the pine cone powder was leached out as can be seen in the reduction of the masses of pine cone powder after NaOH washing. It was observed that the percentage recovery decreased with increasing concentration of NaOH used for the washing (PCP 0.01

Table 1
Kinetic models and their linear forms

Kinetic model	Linear form	Plot	Parameters
First order	$\log [C] = \log [C_o] - k_1 t$	$\log [A]$ vs. t	Intercept = $\log [C]$ Slope = $-k$
Second order	$1/C_e = 1/C_o + k_2 t$	$1/C_e$ vs. t	Intercept = $1/Co$ Slope = k_2
Pseudo-first order	$\log (q_e - q_t) = \log q_e - kt$	$\log (q_e - q_t)$ vs. t	Intercept = $\log q_e$ Slope = $-2.303\ k$
Pseudo-second order	$t/q_t = 1/h + t/q_e$	t/q_t vs. t	Intercept= $1/h$ Slope= $1/q_e$

94.21%, PCP 0.05 93.42%, PCP 0.10 92.38% and PCP 0.15 88.53%). As NaOH concentration increased in solution from 0.01 to 0.15 mol dm^{-3}, percentage recovery decreased from 94.21 to 88.53 %. The colour of the wash solution was also observed to be darker as the concentration of NaOH solution increased. Base solutions are known to dissolve organic components of plant, extract plant pigments, and disrupt a fraction of the lignin structure [12,13,19]. The percentage recovery when 200 g of almond shell, almond hull, English walnut shells, black walnut shells, pecan shells were washed with 4 dm^{-3} of 0.10 M NaOH solutions were 82.5, 23.9, 87.3, 90.0 and 89.6% respectively [12]. Such results suggest that pine cone powder is more resistant to NaOH solution treatment as compared to these other agricultural wastes.

3.2. Bulk density

The results of the bulk density determination of pine cone and NaOH modified pine cone powder are shown in Fig. 1. The results revealed that the bulk densities of the various NaOH washed pine cone powders are different from the raw pine cone powder. This difference may be due to the extracted components from the pine cone powder during NaOH washing. Bulk density reduced from 0.4993 for the unwashed pine cone powder to 0.3947 for the 0.15 mol dm^{-3} NaOH washed pine cone powder. Wartelle and Marshall [12] attributed the decrease in bulk density of almond hulls from 0.63 to 0.25 to be largely due to the removal of soluble sugars, which comprises of 27% of the unextracted almond hull. Pine cone powder on analysis is known to contain 46.2% glucose, 24.6% mannose, and galactose 4.60%. Extraction of these sugars to different extents will cause the reduction in bulk density in each of the pine cone powder samples. Increasing concentration of NaOH in the wash solution will extract more of these sugars and reduce the bulk density further. The bulk density of a powder is inversely proportional to the amount of void spaces or volume in the material. Therefore, pine cone powder samples washed with higher concentrations of NaOH will have lower bulk density and consequently larger amounts of void volume and better filtration properties (the ease at which water flow through a packed column of the biosorbent).

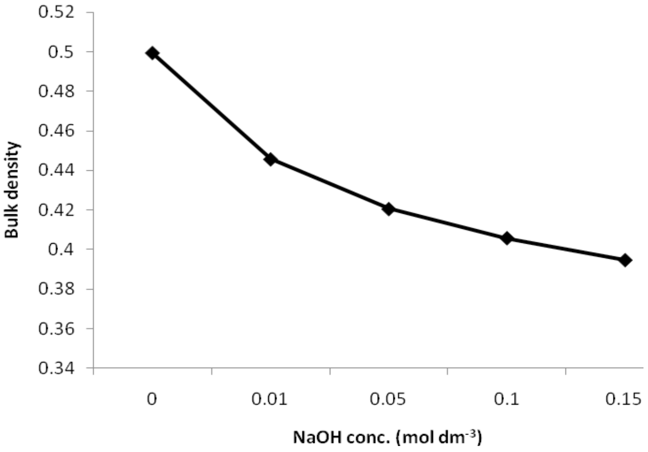

Fig. 1. Variation of bulk density of pine cone powder with increasing NaOH concentration for surface modification.

3.3. Determination of surface active sites

Pine cone is composed of epidermal and sclerenchyma cells which contain cellulose, hemicellulose, lignin, rosin, and tannins in the cell walls. These plants components contain polar functional groups such as alcohols, aldehydes, ketones, carboxylic, phenolic and ether [19,20]. These groups can form active sites for biosorption on the biosorbent surface. Results of surface active sites determination on pine cone powder show that the biosorbent contains 0.80 mmol g^{-1} of carboxylic group, 1.33 mmol g^{-1} of lactone group, 1.07 mmol g^{-1} of phenolic group. The total acidity and basicity were 3.20 and 4.27 mmol g^{-1}, respectively. The predominant acidic group on pine cone powder is the lactone group. Generally, the total acidity of pine cone powder is lower than those of corncob (total acidity: 4.33 mmol g^{-1} and basicity: 3.40 mmol g^{-1}) [21], and untreated coffee husks (total acidity: 3.35 mmol g^{-1} and basicity: 0.49) [22] but higher than that of orange peels (total acidity: 2.47 mmol g^{-1} and basicity:

0.50 mmol g^{-1}) [9]. However, the amount of carboxylic groups on pine cone powder (0.80 mmol g^{-1}) is more than those in corncob (0.62 mmol g^{-1}) and untreated coffee husks (0.60 mmol g^{-1}).

Treatment of pine cone powder with different concentrations of NaOH solutions altered the carboxylic, lactonic and phenolic content of pine cone powder to different extents. Fig. 2 shows 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 is increased. Reduction in carboxylic and phenolic content may be attributed to the extraction of resin acids which are converted to their sodium salt and the reduction in phenolic content may be due to the slight solubility of lignin which contains phenolic compounds. The extraction of these compounds increases with NaOH concentration in the wash solution. The lactone content on the other hand, was found to increase with concentration of NaOH in the wash solution. It is likely that the reduction in other components during NaOH wash lead to the increase in lactone content.

3.4. FTIR analysis

Fig. 3 shows the FTIR spectra's of pine cone and NaOH modified 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 cm^{-1} represents –OH and aliphatic

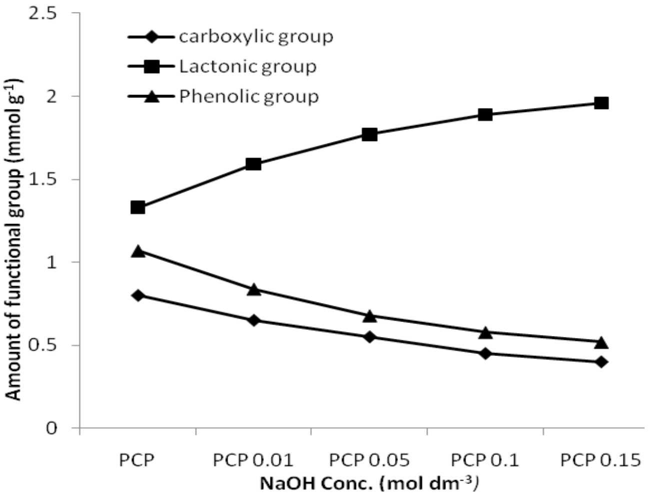

Fig. 2. Variation of carboxylic, lactonic and phenolic functional groups on pine cone powder surface with NaOH treatment.

C–H groups, respectively. The peak at 1647.08 cm^{-1} corresponds to the C=O stretch. The peaks between 1058.81 and 559.32 cm^{-1} may be assigned to the –C–C– and –CN stretching, respectively [23].

There were observed decreases in the bands at 3418.47 and 2925.90 cm^{-1} with the increase in the concentration of NaOH in the wash solution. The decreases observed are smaller for PCP washed with lower concentration of NaOH but increases with NaOH concentrations. The

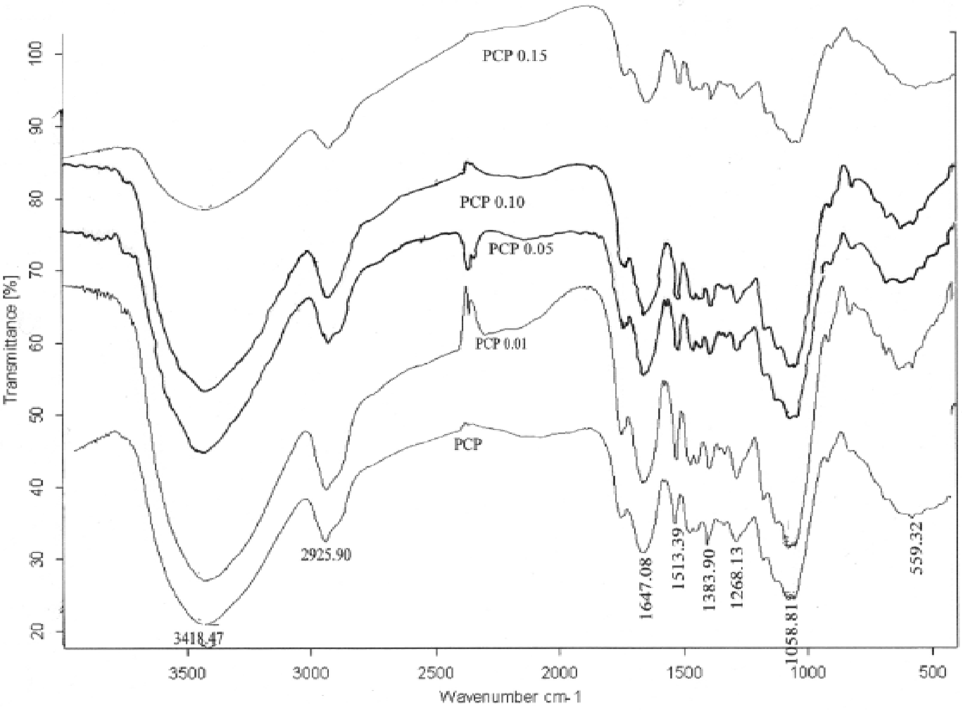

Fig. 3. FTIR spectra of pine cone and various NaOH modified pine cone powder samples.

decrease is maximum for PCP 0.15. These results are in support of the reported reduction in carboxylic acid function as observed in the results from Boehm titration.

3.5. Point of zero charge

The pH at point zero charge (pH_{PZC}) 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 p*K*a of acidic groups, the sites are mainly in dissociated form and acquire a negative charge, while at pH values lower than p*K*a of these groups; the functional groups will be associated with a proton to become positively charged. The pH_{PZC} for pine cone powder was determined to be 7.49. This pH_{PZC} value is high in comparison to Corncob (6.2) [21], untreated coffee waste (4.4) [22] mustard husk (6.0) [24] and yellow passion fruit wastes (3.7) [25]. The high value of pH_{PZC} may be attributed to the higher amount of basic groups present on the pine cone powder (4.27 mmol g^{-1}).

Treatment of pine cone powder with different concentrations of NaOH solution lead to the reduction in pH_{PZC} from 7.49 to 2.62 for 0.01 mol dm^{-3} treated, 2.58 for 0.05 mol dm^{-3} treated, 2.56 for 0.10 mol dm^{-3} and 2.55 for 0.15 mol dm^{-3} treated pine cone powder. The fall in pH_{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.

3.6. 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 [26]. 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 numbers were found to be PCP 15.5 mg g^{-1}, PCP 0.01 16.7 mg g^{-1}, PCP 0.05 17.0 mg g-1, PCP 0.10 17.4 mg g^{-1} and PCP 0.15 17.6 mg g^{-1}. Iodine number for pine cone powder was obtained to be 15.46 mg g^{-1}. This value is quite low compared to iodine number obtained for some agricultural wastes in literature. For example Iodine number for HCl treated rice husks is 68.00 mg g^{-1} [26], sugarcane baggase is 75 mg g^{-1} [27], and tendu leaf refuse is 128 mg g^{-1} [28]. The low iodine number can be attributed to high lignin and other plant cell wall contents of pine cone. The lignin contents of pine cone, rice husk, and sugarcane baggase and tendu leaf are 37.4, 23, 21.23 and 19.4 % respectively and their iodine numbers are 15.46, 68.00, 75.00 and 128.00 mg g^{-1}. It will be observed that the higher the iodine number the lower lignin content .

Treatment of pine cone powder with NaOH solution increased the iodine number. The iodine number was found to increase with increasing NaOH concentration in the wash solution. The trend was found to be in agreement 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 powder.

3.7. Effect of solution pH on copper sorption

The pH of the aqueous solution in which biosorption is conducted is an important controlling parameter in the biosorption process [29–31]. 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 [31]. The effect of solution pH on the biosorption of copper(II) ions from aqueous solution using pine cone powder and NaOH treated pine cone powder are shown in Fig. 4. 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 H^+ for biosorption sites. The NaOH treated samples had higher copper(II) biosorption capacities than the untreated sample. PCP 0.15 biosorbed more copper(II) (6.30 mg g^{-1}) than any of the sample. The copper(II) biosorption capacity increased with increasing concentration of NaOH in solution used for treatment at a particular initial solution pH.

As solution pH increases, the copper(II) capacities of the samples increase up to solution pH 5. This can be attributed to three reasons (i) the increase in negative charge on the biosorbent surface with increasing solution pH, (ii) the solution pH rises towards and above pH_{PZC} and (iii) the reduction of H^+ ions in solution which competes with copper(II) for sorption sites. The increase in copper(II)

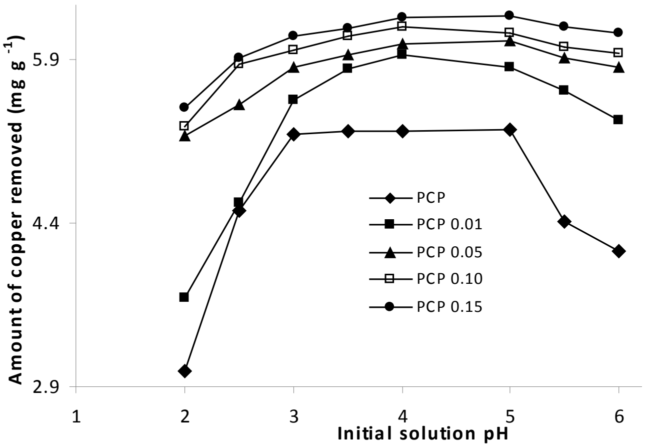

Fig. 4. Effect of initial solution pH on copper(II) uptake by pine and NaOH treated pine cone powder (biosorbent mass: 0.4 g; temperature: 291 K; agitation speed: 160 rpm; initial Cu(II) concentration: 70 mg dm^{-3}).

capacity with initial solution pH was more 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} was reached and passed after pH 3. After initial solution pH 5.0, the biosorption capacities for all samples were found to decrease, due to the decreasing concentration of Cu^{2+} and $Cu(OH)^+$ at higher solution pH and the appearance of $Cu(OH)_2$ species in the solution. Higher initial solution pHs were not tested because of the possibility copper(II) precipitation as $Cu(OH)_2$.

3.8. *Effect of biosorbent dose*

The effect of varying adsorbent dose, ms, for a fixed volume (500 ml) of copper(II) solution at constant concentration (50 mg dm^{-3}) is shown in Figs. 5 and 6. It is observed from Fig. 5 that increasing the pine cone powder dose, m_s, increased the percentage of copper(II) removal from aqueous solution. On the other hand, the amount of copper(II) biosorbed per unit mass of pine cone powder was found to decrease with biosorbent dose, m_s (Fig. 6). It is apparent that by increasing the dose of the pine cone powder, the number of biosorption 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 literature [32,33].

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

Mathematical equations were derived to predict the relationship between the dose, m_s, the copper(II) biosorption capacity and the percentage copper(II) ion removal for each sample within the biosorbent dose range of 1–8 g dm^{-3}. These relationships have correlation coefficients as high as 0.999 and are shown below:

$$\text{PCP: } q_e = 8.301 m_s^{-0.363} \quad \left(r^2 = 0.997\right) \tag{3}$$

$$\%\,\text{Re} = 18.539\, m_s^{1.261} \quad \left(r^2 = 0.997\right) \tag{4}$$

$$\text{PCP 0.01: } q_e = 9.311\, m_s^{-0.231} \quad \left(r^2 = 0.999\right) \tag{5}$$

$$\%\,\text{Re} = 18.621\, m_s^{1.270} \quad \left(r^2 = 0.999\right) \tag{6}$$

$$\text{PCP 0.05: } q_e = 18.994\, m_s^{-0.567} \quad \left(r^2 = 0.999\right) \tag{7}$$

$$\%\,\text{Re} = 37.991\, m_s^{0.432} \quad \left(r^2 = 0.999\right) \tag{8}$$

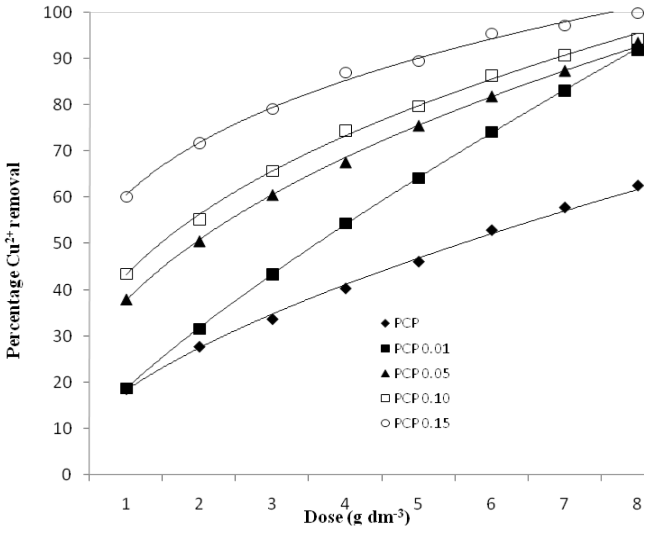

Fig. 5. Percentage removal of copper(II) with increasing dose of pine and NaOH treated pine cone powder (biosorbent mass: 0.4 g; solution pH 5.0; temperature: 291 K; agitation speed: 160 rpm; initial Cu(II) concentration: 70 mg dm^{-3}).

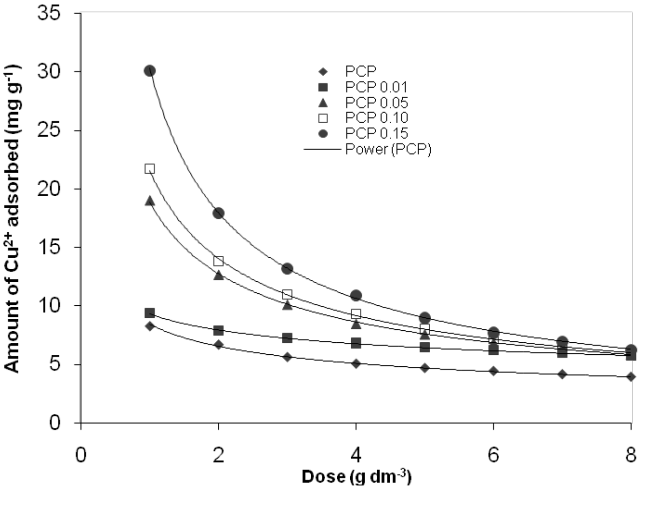

Fig. 6. Effect of dose on copper(II) removal by pine and NaOH treated pine cone powder (biosorbent mass: 0.4 g; solution pH 5.0; temperature: 291 K; agitation speed: 160 rpm; initial Cu(II) concentration 70 mg dm^{-3}).

$$\text{PCP 0.10: } q_e = 21.317\, m_s^{-0.618} \quad \left(r^2 = 0.999\right) \tag{9}$$

$$\%\,\text{Re} = 42.632\, m_s^{0.381} \quad \left(r^2 = 0.998\right) \tag{10}$$

$$\text{PCP 0.15: } q_e = 30.269\, m_s^{-0.757} \quad \left(r^2 = 0.999\right) \tag{11}$$

$$\%\,\text{Re} = 59.695\, m_s^{0.247} \quad \left(r^2 = 0.995\right) \tag{12}$$

The solution pH before and after these experiments were measured to study the effect of biosorbent dose on change in H^+ ion concentration. Fig. 7 shows the plots of equilibrium pH with biosorbent dose. The results revealed that the equilibrium pH's for the PCP sample with different biosorbent doses were all lower than the initial solution pH of the experiment (pH 5.0) and the equilibrium pH increased with increasing the biosorbent dose. Mathematical equations can be derived to show the relationships between the biosorbent dose and the equilibrium solution pH so as to predict the equilibrium pH at any biosorbent dose within the range of pine cone powder dose 1–8 g dm^{-3} having high correlation coefficients, r^2, below:

$$\text{PCP: pH}_{ea} = m_s / \left(0.200\, m_s + 0.103\right) \quad \left(r^2 = 0.997\right) \tag{13}$$

$$\text{PCP 0.01: pH}_{ea} = m_s / \left(0.174\, m_s + 0.037\right) \quad \left(r^2 = 0.999\right) \tag{14}$$

$$\text{PCP 0.05: pH}_{ea} = m_s / \left(0.140\, m_s + 0.059\right) \quad \left(r^2 = 0.999\right) \tag{15}$$

$$\text{PCP 0.10: pH}_{ea} = m_s / \left(0.131\, m_s + 0.068\right) \quad \left(r^2 = 0.998\right) \tag{16}$$

$$\text{PCP 0.15: pH}_{ea} = m_s / \left(0.112\, m_s + 0.069\right) \quad \left(r^2 = 0.998\right) \tag{17}$$

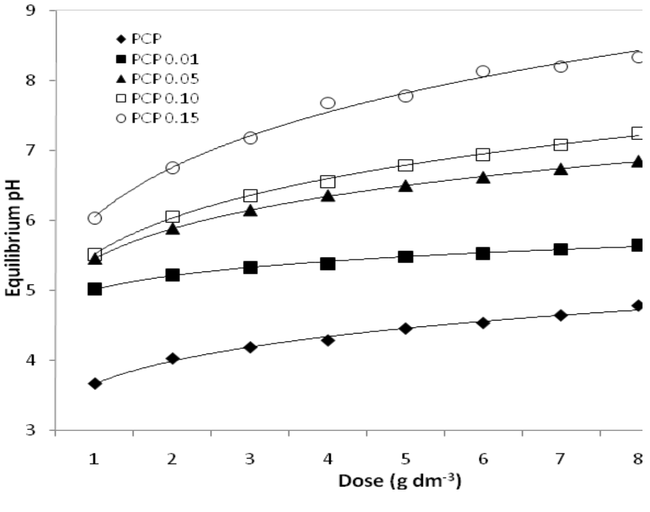

Fig. 7. Variation of equilibrium pH with dose (biosorbent mass: 0.4 g; solution pH 5.0; temperature 291 K; agitation speed: 160 rpm; initial Cu(II) concentration 70 mg dm^{-3}).

Fig. 8 also shows that as the equilibrium pHs for PCP increased, the percentage copper(II) removal for PCP also increased from 18.54 to 62.56%. On the other hand, the equilibrium pHs for the NaOH treated samples were all higher than the initial solution pH of the copper(II) ion solution and the percentage copper(II) removal increased with increasing equilibrium pH. PCP 0.15 having the highest values for equilibrium pH had a higher percentage copper(II) removal and the equilibrium pHs were observed to be higher as the concentration NaOH in the wash solution increases.

The above observation may indicate that the biosorption mechanism for the removal of copper(II) ions by NaOH modified pine cone powder and the unmodified pine cone powder may not be the same. Ho [34], and Ofomaja and Ho [35] showed that ion exchange biosorption is followed by a lowering of solution pH due to the replacement of H^+ ions by metal ions of the polar functional groups on the biosorbent surface. Han et al. [36] demonstrated that there was an increase in equilibrium pH when *Chlorella miniata*, a biosorbent, was used in the removal of chromium(III) from solution and the pattern is typical of complexation mechanism.

The change in equilibrium pH was also determined at various time intervals (1, 2, 3, 5, 10, 15, 20 min) during the biosorption of copper(II) from aqueous solution using pine cone powder dose of 8 g dm^{-3}. Fig. 9 shows the variation of equilibrium pH with time and reveals that, for PCP, the equilibrium pH reduces as the contact time increases from 0 to 20 min and this is accompanied by an increase in copper(II) biosorption capacity. After 5 min of biosorption, there was only a small change in copper(II) capacity.

For the NaOH treated pine cone powders, the equilibrium pHs were found to increase with time and PCP 0.15 had the highest equilibrium pH after 20 min. Mathemati-

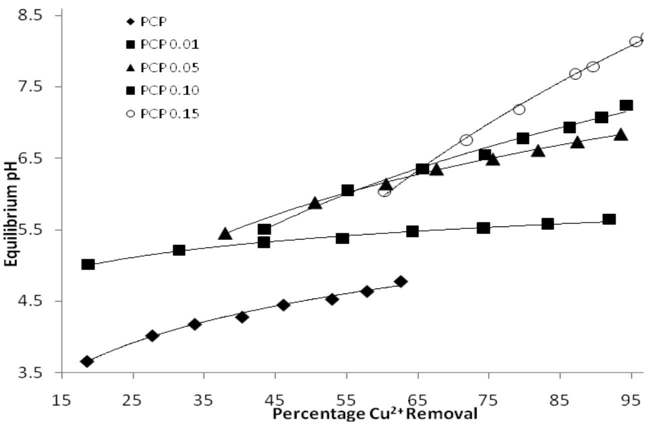

Fig. 8. Variation of equilibrium pH with percentage copper(II) removal (biosorbent mass: 0.4 g; solution pH 5.0; temperature: 291 K; agitation speed: 160 rpm; initial Cu(II) concentration: 70 mg dm^{-3}).

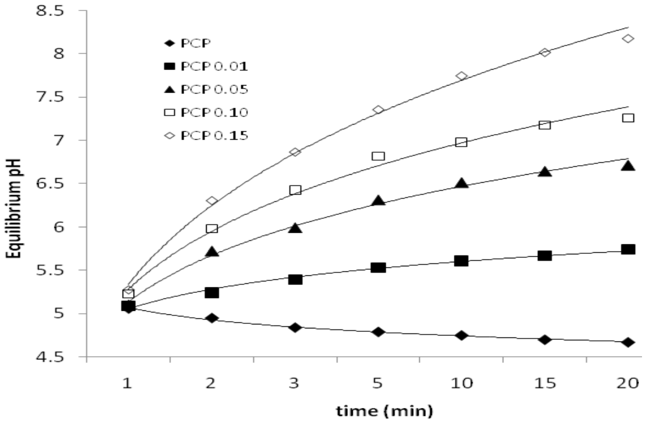

Fig. 9. Variation of copper(II) capacity with time for copper(II) removal (biosorbent mass: 4 g; solution pH 5.0; temperature: 291 K; agitation speed: 160 rpm; initial Cu(II) concentration: 70 mg dm^{-3}).

cal equations can be derived to show the relationships between the contact time and the equilibrium solution pH so as to predict the equilibrium pH at any biosorbent dose within the range of pine cone dose 1–8 g dm^{-3} having high correlation coefficients, r^2, below:

$$\text{PCP: } \text{pH}_{ea} = 5.023\,t^{-0.025} \quad \left(r^2 = 0.997\right) \tag{18}$$

$$\text{PCP 0.01: } \text{pH}_{ea} = 5.117\,t^{0.039} \quad \left(r^2 = 0.971\right) \tag{19}$$

$$\text{PCP 0.05: } \text{pH}_{ea} = 5.039\,t^{0.085} \quad \left(r^2 = 0.925\right) \tag{20}$$

$$\text{PCP 0.10: } \text{pH}_{ea} = 5.388\,t^{0.101} \quad \left(r^2 = 0.938\right) \tag{21}$$

$$\text{PCP 0.15: } \text{pH}_{ea} = 5.336\,t^{0.136} \quad \left(r^2 = 0.928\right) \tag{22}$$

The increase in equilibrium pH was found to follow the trend of increasing concentration of NaOH in wash solution. The increase in equilibrium pH was also accompanied by the increase in copper(II) biosorption capacity. Therefore, the biosorption mechanism is likely to be complexation for the NaOH treated pine cone powder and a mixture of ion-exchange and complexation for the untreated pine cone powder.

3.9. Kinetics of copper(II) ion removal

The batch biosorption kinetics of copper(II) removal from aqueous solution using pine cone powder and NaOH modified pine cone powder was studied by contacting 0.4 g of biosorbent with 100 ml of 100 mg dm^{-3} copper(II) solution at 18°C in a batch reactor agitated at 160 rpm. The kinetic data for the biosorption is shown in Fig. 10, as the plot of equilibrium concentration of copper(II) in the solution vs. the contact time. The plots show that there is a sharp reduction of copper(II) in the solution at the initial stage of the biosorption (within the first 5 min), this reduction slowed down after 5 min of contact and there was little or no change in the copper(II) removed from solution thereafter.

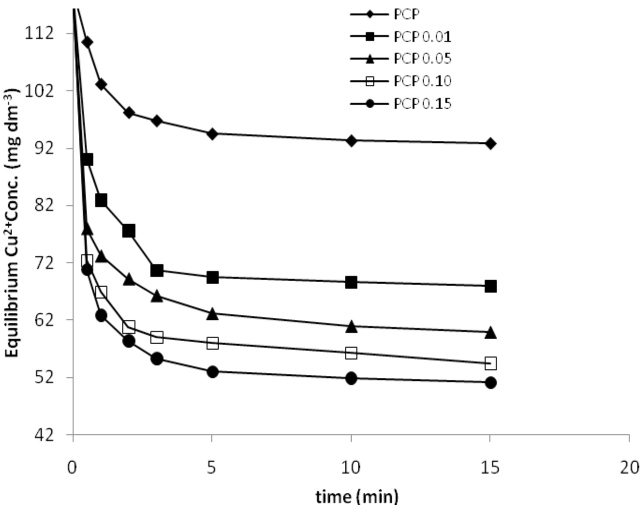

Fig. 10. Kinetics of copper removal with reducing copper concentration (biosorbent mass: 0.4 g; solution pH 5.0; temperature: 291 K; agitation speed: 160 rpm).

The order of increasing copper(II) removal from aqueous solution with time was PCP 0.15 > PCP 0.10 > PCP 0.05 > PCP 0.01 > PCP. The high initial removal rate is attributed to the large amount of active sites available at the initial stage of the biosorption which then reduced with increasing coverage of the biosorbent surface. The difference in the initial removal rates among the pine cone powder samples is in line with the iodine capacity of the different samples indicating that, the larger the surface of the sample, the higher the rate of copper(II) biosorption at the initial contact period.

The kinetic data from the experiments were then tested with four kinetic models via first order, second order, pseudo-first order, pseudo-second order and the fit of the experimental data to the kinetic models determined using the correlation coefficient, r^2, method. The various kinetic models and their linear forms are given in Table 1. Since the trend in the plot of experimental data along with kinetic models were similar for all samples, Fig. 11 showing the curves for PCP was taken as a representative plot and the different kinetic parameters for the samples shown in Tables 2–4.

The plot revealed that for all samples the pseudo-first order kinetics deviated further away from the experimental data than any of the other kinetic model. The second order model and the pseudo-second order model were closest to the experimental data, with the pseudo-second order model describing the biosorption more accurately. This good fit of the pseudo-second order model can also

Table 2
First order parameters for copper(II) sorption on to pine cone and NaOH treated pine cone powder

Sample	k (min^{-1})	C_0 (mg dm^{-3})	r^2
First order			
PCP	0.0203	102.82	0.5570
PCP 0.01	0.0350	81.09	0.5550
PCP 0.05	0.0359	76.64	0.7385
PCP 0.01	0.0343	65.83	0.6364
PCP 0.15	0.0389	62.54	0.5926
Second order			
PCP	8.82×10^{-5}	103.09	0.5770
PCP 0.01	2.00×10^{-4}	80.83	0.5770
PCP 0.05	2.3×10^{-4}	72.60	0.7657
PCP 0.01	5.6×10^{-4}	65.71	0.6718
PCP 0.15	6.7×10^{-4}	62.32	0.6268

Table 4
Pseudo-second order parameters for copper(II) sorption on to pine cone and NaOH treated pine cone powder

Sample	q_e (exp)	q_e (cal)	k (gmg^{-1}min^{-1})	h (mgg^{-1}min^{-1})	r^2
PCP	6.80	7.19	0.1878	9.71	0.9994
PCP 0.01	13.01	13.51	0.1889	34.48	0.9997
PCP 0.05	15.03	15.32	0.1990	45.29	0.9998
PCP 0.01	16.38	16.54	0.2396	66.43	0.9998
PCP 0.15	17.22	17.47	0.2500	74.96	1.0000

Table 3
Pseudo-first order parameters for copper(II) sorption on to pine cone and NaOH treated pine cone powder

Sample	q_e (exp)	q_e (cal)	k (min^{-1})	r^2
PCP	6.80	3.48	0.3595	0.9510
PCP 0.01	13.01	4.20	0.3703	0.8600
PCP 0.05	15.03	4.32	0.2906	0.9788
PCP 0.10	16.38	3.21	0.2153	0.8388
PCP 0.15	17.22	3.75	0.3278	0.9213

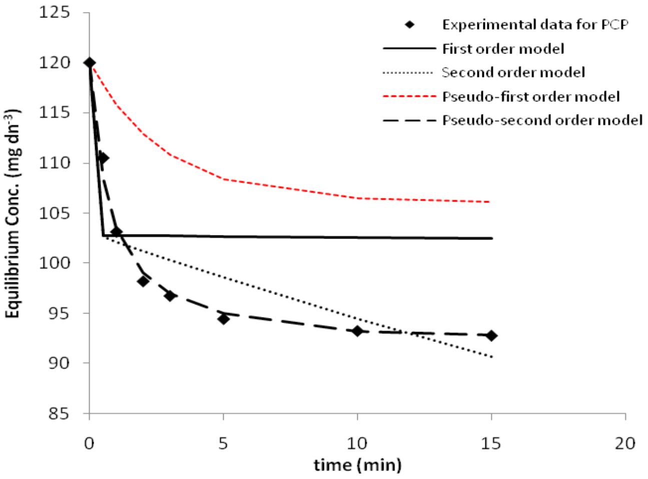

Fig. 11. Kinetic modeling of experimental data with various kinetic models for PCP (biosorbent mass: 0.4 g; solution pH 5.0; temperature: 291 K; agitation speed: 160 rpm).

be seen from the higher values of the correlation coefficient, r^2, and the ability of the pseudo-second order model to closely predict the equilibrium capacities for each sample. Therefore, the biosorption process may be said to proceed by chemical reaction or ion-exchange mechanism with organic functional groups. The biosorption of nickel(II) biosorption [23], chromium(VI) biosorption [37] and cationic dye (Acid Blue 40) [38] onto pine cone powder have all been shown to be best described by the pseudo-second order sorption kinetics.

4. Conclusion

Chemical modification of pine cone powder with NaOH solution of different concentrations has been carried out and the variation in chemical properties of the modified pine cone powder studied. Properties such as bulk density, point zero charge, iodine number and amount of acid and basic groups were found to be affected by the concentration of NaOH solution. Sodium hydroxide washing modified the amounts of acidic groups on the biosorbent surface leading to different mechanism for copper(II) biosorption as compared with the unwashed pine cone powder and optimum NaOH concentration is 0.15 mol dm^{-3}.

The initial rate of biosorption of copper(II) from solution was faster and the equilibrium copper(II) capacity were higher for the pine cone powder samples with higher iodine number. Pseudo-second order kinetics was the better fitting kinetic model for the biosorption for all pine cone powder samples.

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