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Effect of chemical extractants on the biosorptive properties of pine cone powder: Influence on lead(II) removal mechanism

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Abstract This study examines the changes in surface properties and lead(II) adsorption mechanism of pine cone powder modified using varying ratios of toluene–ethanol mixtures.

Increasing the ratio of toluene in the extractant mixture increased formation of esters and iodine capacity of the material, but reduced carboxylate ions and surface charge. Values of surface charge and iodine capacity showed no relationship with the bulk densities. Maximum lead(II) adsorption was observed for the 2:1 toluene–ethanol modified sample. Lead(II) ions adsorption was inversely related to surface charge and directly related to iodine capacity.

Ion-exchange was the dominating mechanism followed by chemisorption. Physical adsorption was higher in the sample modified with the 2:1 mixture which also had the least surface negative charge. Shifts in peaks of FTIR spectra indicate that unbounded –OH and acidic groups were responsible for lead(II) bonding and the contribution of these groups were different for each sample.

1. Introduction

An adsorbent is a porous substance having high surface area which can adsorb substances onto its surface by intermolecular forces. A number of materials such as silica gel, zeolites, activated carbon, and activated alumina have been extensively investigated for their use as adsorbents in water pollution control (Bhatnagar and Sillanpää, 2010). Agricultural waste materials usually employed as adsorbent may have potential marketing advantage for wastewater treatment over other adsorbent types because they are of low cost, environmentally friendly, naturally available and efficient (Huang et al., 2010). Adsorbents derived from agricultural wastes are usually called biosorbents. They can either be applied as adsorbents for water

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treatment in their natural, chemically modified or thermally activated forms.

Chemical modification of adsorbents derived from agricultural wastes is usually targeted at (i) extracting plant water soluble or organic soluble constituents which may leach into treated water thereby increasing the chemical oxygen demand (COD), biological chemical demand (BOD) and total organic carbon (TOC) (Gaballah et al., 1997; Nakajima and Sakaguchi, 1990), (ii) improving the adsorption capacity of the biosorbent in question by swelling the material so as to increase the internal and external surfaces (Sciban et al., 2006; Laszlo and Dintzis, 1994; Marshall and Johns, 1996; Wing, 1996; Ahmedna et al., 1979; Sessa and Wing, 1997; Sessa and Wing, 1998) and (iv) modifying the biosorbent surface to allow for penetration of polyfunctional organic compounds into the matrix of the biosorbent to increase binding sites (Marshall et al., 1999; Wartelle and Marshall, 2000).

Wood products especially products of pine wood have been treated using different kinds of chemical extractants to improve surface properties such as mechanical strength, chemical resistance and ability to incorporate organic acid anhydrides through esterification acting as wood preservation agents against decay, etc. (Papadopoulos et al., 2010; Jebrane et al., 2010). These chemical extraction methods have been shown to remove wood extractives such as plant pigments, colored organic compounds, lignin, resin acids and water soluble tannins (Sciban et al., 2006). Recent studies have shown that these methods have been applied for wood materials used as adsorbents for heavy metal removal from solution. For example, Sciban et al. (2006) applied formaldehyde–sodium hydroxide treatment of oak and black locust sawdust before applying it as an adsorbent for removing copper and zinc from aqueous solution. Marchetti et al. (2000) extracted wood meal (*Picea abies*) with a mixture of toluene–ethanol and applied the modified material as an adsorbent for cadmium ions removal from aqueous solution. These authors reported an enhancement in the metal adsorption capacities and an increased interaction of organic ligands with the modified wood materials.

Literature search has shown that wood materials from the pine tree (bark, cone, sawdust) are traditionally extracted using a mixture of toluene–ethanol to improve their surface properties (Papadopoulos et al., 2010). It has been observed from different literatures on this topic that little or no consideration is given to the effect of varying the ratio and time of contact on the surface properties of the pine materials applied. It was also observed that the new surface properties of the extracted materials have never been related to the heavy metal removal ability and metal removal mechanism. Therefore, in this study, the effect of extracting pine cone biomass with toluene:ethanol mixtures of different ratios and the effect of extraction time on surface properties such as bulk density, iodine capacity and surface charge was examined. The metal adsorption capacities and the prevailing adsorption mechanism for the modified adsorbents were also examined.

2. Materials and methods

2.1. Materials

Pine tree cones were collected from a plantation in Sasolburg, Free State. The cones were washed to remove impurities such as sand and leaf. The washed cones were then dried at 90 °C for 48 h in an oven. The scales on the cones were removed and crushed using a pulveriser. The pine cone powder was then sieved and particles between 90 and 45 μm were collected and used for analysis.

2.2. Methods

2.2.1. Sample preparation
Pine cone powder (50 g) was extracted with 250 cm³ mixture of toluene:ethanol of different ratios (1:1, 2:1, 1:2 and 1:3 v/v) in a reflux apparatus at various contact times (2, 4, 8 h) at 100 °C. The solid product from the extraction was then refluxed with water for an additional 8 h, to remove all extractives. The pine cone was filtered and oven-dried at 105 °C for 16 h and cooled to ambient temperature in a desiccator over phosphorus pentoxide. The pine cone powder was transferred to a flask containing pyridine heated to 100 °C for 1 h, then filtered and refluxed in acetone for 1 h to remove the pyridine. Pine cone powder was then filtered and oven-dried at 105 °C.

2.2.2. Bulk density determination
Bulk density measurement was carried out in a 25 cm³ density bottle. The dry pine cone powder was added to the density bottle with gentle tapping to ensure that the particles settle to the bottom 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 cm³ was then obtained from the mass of the bottle and pine cone powder minus the mass of empty bottle.

Mass of PCP which occupies 25 cm³ volume = (mass of bottle + pine cone powder) – mass of empty bottle.

$$\text{Bulk density} = \text{Mass of PCP occupying 25 cm}^3 \text{ volume} / 25 \text{ cm}^3 \tag{1}$$

2.2.3. Iodine capacity determination
An aliquot of 25 cm³ of 0.005 mol/dm³ iodine solution was added to five conical flasks that contain different masses of pine cone powder ranging from 0.031 to 0.500 g. The flasks were then shaken for 24 h to ensure equilibrium adsorption of iodine onto pine cone powder. The iodine number (mg/g) (or adsorption capacity) was determined from the titration of the residual solution of 10 cm³ with 0.10 mol/dm³ sodium thiosulfate in the presence of 1 cm³ of 1.00 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.

2.2.4. Surface negative charge
A modification of the method of Boehm (1994) was used to determine total negative charge. The 'total' negative charge could be obtained only on samples at pH < 3.0. At this pH even the most easily ionizable negative groups (i.e. carboxyl groups) were fully protonated as indicated by no change in titratable negative charge when the pH was at or below 3.0. With fully protonated pine cone powder, the presence of a strong base (NaOH) deprotonated both strongly and weakly ionizable groups which contribute to the total negative charge.

One-half gram of pine cone powder, which had pH values < 3.0, was suspended in 25 cm³ of 0.10 mol/dm³ NaOH

and stirred at 300 rpm for 16–20 h in glass stoppered 100 cm³ Erlenmeyer flasks. The flasks were kept stoppered during stirring to minimize the dissolution of carbon dioxide gas in the NaOH and the subsequent formation of Na_2CO_3. The flask contents were filtered by vacuum filtration through Whatman #4 filter paper and 10 cm³ of the filtrate added to 15.0 cm³ of 0.10 mol/dm³ HCl. The addition of excess HCl prevented any possible adsorption of carbon dioxide by the base and was particularly important if the solutions were required to stand for extended time periods before analysis. The solution was titrated with 0.10 mol/dm³ NaOH until an endpoint. The results were expressed in mmoles H^+ neutralized by excess OH^- per gram of pine cone powder.

2.2.5. Fourier transform infrared (FTIR)
The FTIR spectra of pine cone powder before and after treatment were recorded on a Fourier transform infrared spectrometer (Perkin–Elmer infrared spectrophotometer) to elucidate the functional groups present on the pine cone powder.

2.2.6. Metal adsorption
A volume of 100 cm³ of lead(II) solution of concentration 300 mg/dm³ was added to six 250 cm³ beakers and the initial solution pHs of the solutions adjusted to pH 5. An amount (0.5 g) of the raw or toluene–ethanol extracted pine cone powder samples were then added to the prepared lead(II) solution. The mixtures were then shaken at room temperature for 2 h at 200 rpm. At the end of the agitation, the mixture was separated by centrifugation at 200 rpm and the clear liquid analyzed by atomic absorption spectrophotometer for the lead(II) left in solution.

2.2.7. Desorption
Biosorbent residues used in the system of 0.5 g of pine cone in contact with 100 ml of 300 mg/dm³ of lead(II) solution were separated by centrifugation and washed with distilled water. The washed residue solids were then stirred in 100 cm³ of 0.1 mol/dm³ of each of the desorbing solvents (NaOH, HCl and CH_3COOH and distilled water). After shaking the flasks for 2 h at 200 rpm, the pine cone solids were separated by filtration and the leached amount of lead(II) ions in the filtrate analyzed by atomic absorption spectrophotometer.

3. Results and discussion

The motivation for this study comes from the fact that toluene–ethanol mixture has been applied for treating pine wood before modification to improve certain wood properties. Therefore, it is our aim to examine the effect of toluene–ethanol mixture on the surface properties of pine cone powder at different solvent ratios and contact times and how these factors affect the adsorption properties such as bulk density, surface negative charge, surface functional groups, removal of lead(II) ions from solution and the removal mechanism.

3.1. Bulk density

Bulk density of a powder material is a measure of the amount of void spaces present in the material. The larger the amount of void spaces, the lower the bulk density (Ofomaja et al., 2010a). Plant materials are known to contain voids spaces that may be filled with plant components such as sugars, pigments,

lignin, resin acids, water soluble tannins and so on (Wartelle and Marshall, 2000). Extraction of these plant components have been shown to be achieved by washing with base solutions, water, mixtures of toluene–ethanol, formaldehyde, etc. (Sciban et al., 2006; Marshall et al., 1999; Marchetti et al., 2000; Vaughan et al., 2001).

In the present study, the effect of extracting pine cone powder with different ratios of toluene–ethanol mixtures at different time interval on the bulk density was examined and the results shown in Fig. 1. The results revealed that the bulk density of the raw pine cone powder is 0.6457 g/cm³. On refluxing 50 g of pine cone powder with toluene–ethanol mixture of ratios 1:1, 2:1, 1:2 and 1:3 (v/v) for 2 h at 100 °C, the bulk density was found to have been altered. The bulk density for pine cone powder washed with toluene–ethanol mixture of ratios 1:1, 2:1, 1:2 and 1:3 was found to reduce by 28.9%, 32.9%, 30.2% and 31.6%, respectively. These results show that pine cone treated with 2:1 mixture of toluene–ethanol produced the greatest reduction in bulk density. Previous studies have shown that pine cone consists of about 15.4% alcohol–benzene extractive (Micales et al., 1994). The reduction of bulk density can be attributed to extraction of plant pigments, resin acids, tannins and sugars in the pine cone material. Koncsag et al. (2011) extracted rice straw degraded by *Pleurotus ostreatus* using different types of organic solvents and observed the extractable phenols and sugars increased as the temperature of extraction increased. Wartelle and Marshall (2000) observed a percentage decrease in bulk density of 31.0%, 36.4% and 60.1% when corn cob, soybean hull and almond hull were treated with 0.1 mol/dm³ of NaOH for 1 h.

When refluxing time was increased from 2 to 4 h, the percentage reduction in the bulk density was found to increase for all samples except for the sample extracted with 2:1 mixture which had a slightly higher value as compared to the value after 2 h of extraction. Koncsag et al. (2011) also observed further decreases in sugar and phenol content as reflux time increases to 3 h when toluene–ethanol mixture was employed as extraction solvent for rice straw. The reduction in bulk densities of pine cone became 31.7%, 32.3%, 33.3% and 36.0% as the pine cone samples were extracted with 1:1, 2:1, 1:2 and 1:3 mixture of toluene–ethanol. The trend in these percentages was
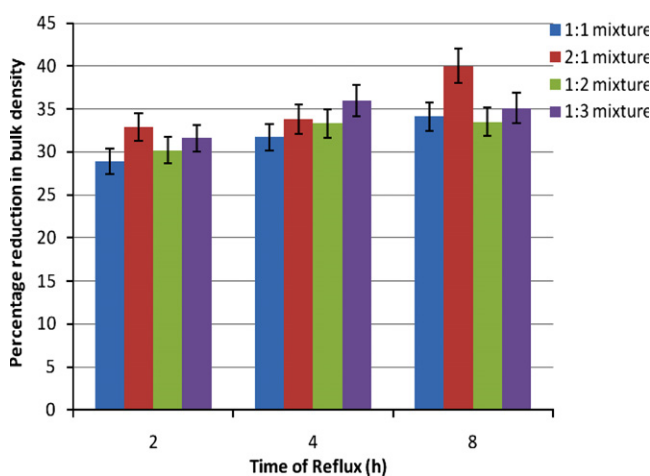

Figure 1 Relationship between ratio of toluene–ethanol mixture, contact time and bulk densities of extracted pine cone powder.

different from those observed for 2 h of reflux. The result for 4 h extraction reveals that greater extraction was observed for samples extracted with 1:2 and 1:3 mixtures than for the 1:1 and 2:1 mixtures.

On increasing the reflux time from 4 to 8 h, the bulk densities were found to reduce further for the 1:1 (34.1 %) and 2:1 (33.5%) treatments, the reduction was almost constant for 1:2 (33.5 %), and the 1:3 treatment had a value of reduction of 35.4 % which was slightly less than that for 4 h treatment. In conclusion, extraction of pine cone using 1:2 and 1:3 toluene–ethanol mixtures above 4 h was not found to alter the bulk densities much while 8 h of contact with 1:1 and 2:1 toluene–ethanol mixtures produced further reduction in bulk density.

From these results, it can therefore be concluded that for the 1:1, 2:1 and 1:2 mixtures, the reduction in bulk densities continues with increasing contact time, while for the 1:3 mixture, bulk density reduces to its optimum values at 4 h of contact and reduces only slightly at 8 h of contact.

3.2. FTIR analysis

Pine cone is a lignocellulosic material with chemical composition of approximately hemicelluloses (46.5%), lignin (37.4%), celluloses (18.8%) and extractive (15.4%). These chemical components of pine cone are known to contain organic functional groups that can be detected by UV/visible spectroscopy. On analysis of the raw pine cone powder using FITR (Fig. 2); it was observed that the sample's spectra bands can be divided into four main sections: (i) the section covering 3100–3600 cm^{-1} which is a broad band indicative of unbounded –OH group (Perez-Marın et al., 2007), (ii) the section covering between 2700 and 2900 cm^{-1} which is a peak attributed to aliphatic C–H stretching (Brown et al., 2001; Inglesby et al., 2005), (iii) the section between 1500 and 1750 cm^{-1} which represents the carbonyl group stretching (Shin et al., 2007) and (iv) the finger print region which covers wave numbers below 1500 cm^{-1} (Min et al., 2004).

Prominent peaks on the spectra include the peak at 3334.19 cm^{-1} representing unbounded hydroxyl group (–OH), peaks at 2700–2900 cm^{-1} which comprises the majority of aliphatic fraction of waxes (Inglesby et al., 2005), peaks at 1627.20 and 1547.68 cm^{-1} which are indicative of asymmetric and symmetric stretching vibrations of ionic carboxylic acid groups (–COO$^-$) (Iqbal et al., 2009). The peak at 1026.93 cm^{-1} is associated with C–O–C functionalities (Moosavi-Nasab and Yousefi, 2011). The peak at 1511.41 cm^{-1} is due to aromatic ring vibrations likely from the lignin fraction of the plant material (Shin et al., 2007), while peaks between 812.30 and 659.47 cm^{-1} represent bending modes of these aromatic compounds (Bansal et al., 2009). The peak at 1262.69 cm^{-1} is indicative of aliphatic acid group vibration due to deformation vibration of C=O and stretching formation of –OH of carboxylic acid and phenol (Iqbal et al., 2009). The peak at 1372.43 cm^{-1} can be assigned to C–N stretching vibration, which corresponds to the amine groups (Xu et al., 2011).

A comparison of the FTIR spectra of the extracted pine cone samples with the raw pine cone is discussed for 8 h treatment only (Fig. 3). The results show that changes in peak intensities as well as a significant increase in intensity of the peak around 1720–1738 cm^{-1} were observed for the extracted samples (Doczekalska et al., 2007).

The peak observed between 1720 and 1738 cm^{-1} is attributed to C=O of esters and non-ionic carboxylic acid groups (–COOH, –COOCH$_3$) stretching vibration (Iqbal et al., 2009)
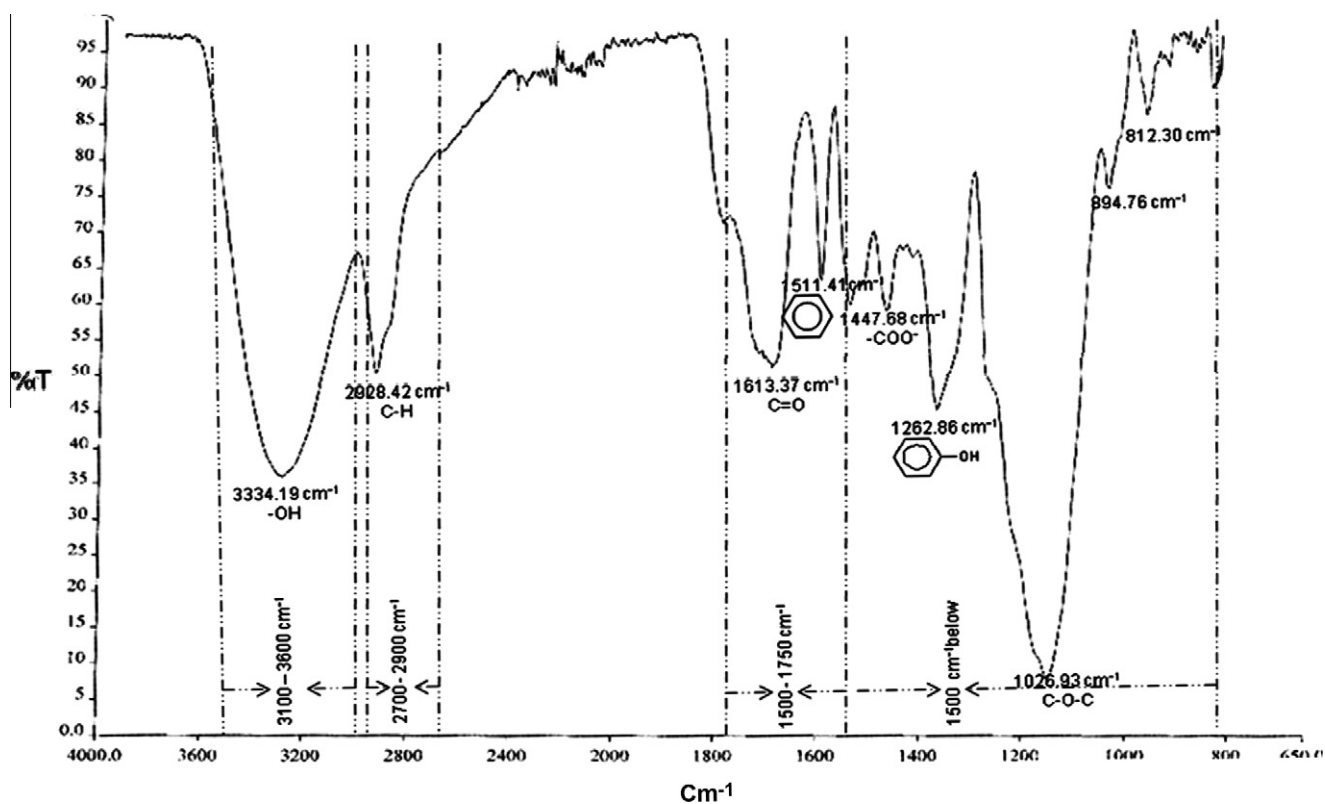

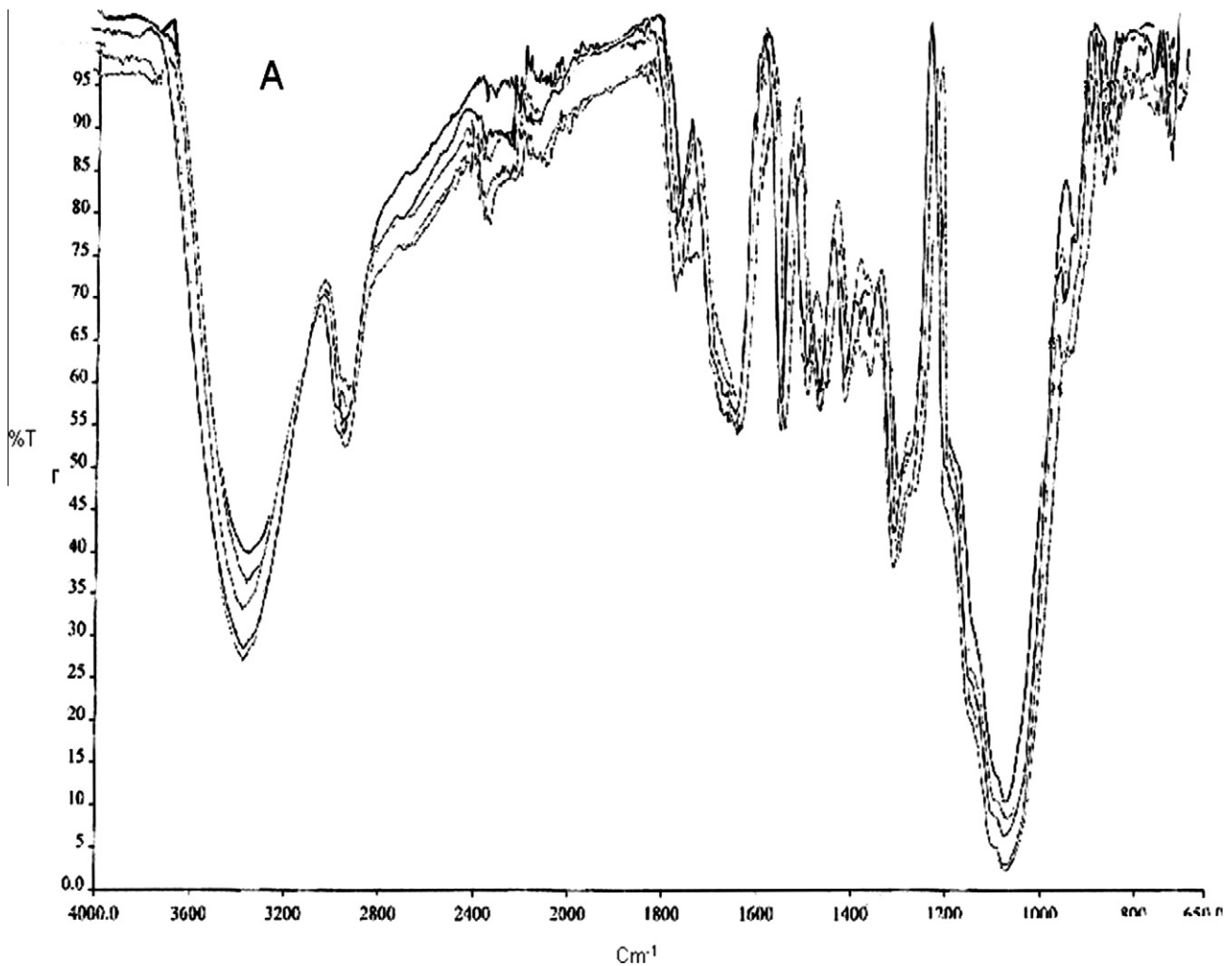**Figure 2**   FTIR spectra of raw pine cone powder.

Figure 3 Comparison of FTIR spectrum for raw and modified pine cone powder extracted with various ratios of toluene–ethanol mixtures for 8 h.
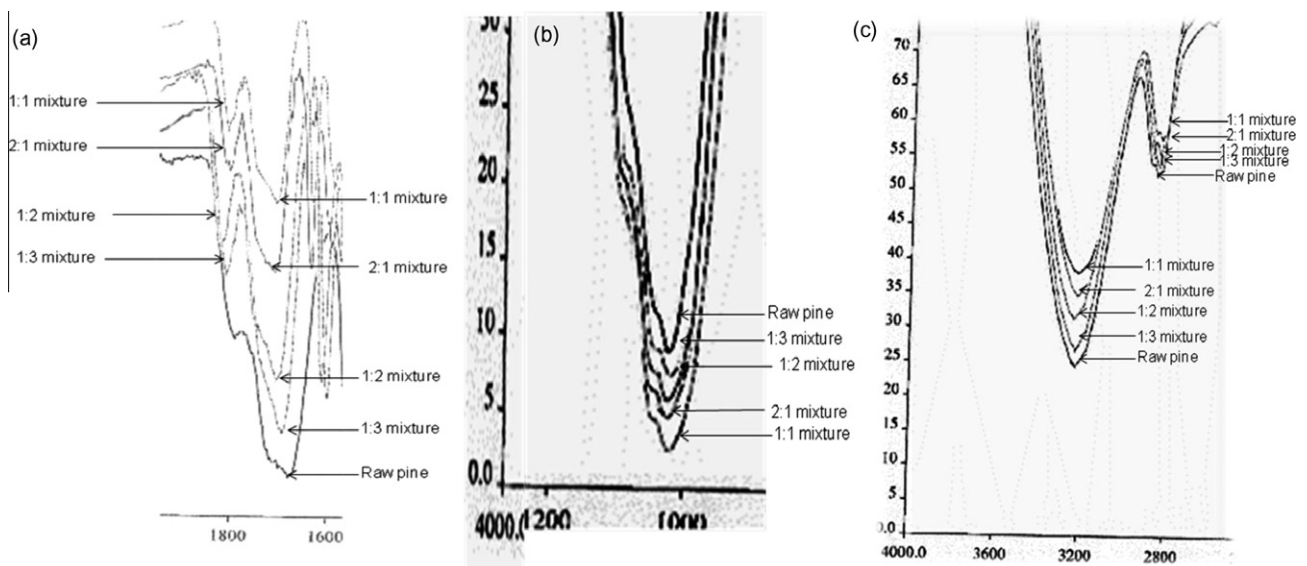

Figure 4 Comparison of characteristic peaks for raw and extracted pine cone: (a) the peaks between 1800 and 1600 cm^{-1}, (b) peaks between 1200 and 1000 cm^{-1} and (c) peaks at 3334 cm^{-1}.

(Fig. 4a). This means that toluene–ethanol extraction interacted with the pine cone to produced non-ionic carboxylic acid groups or esters (Fig. 4a). The increase in the intensity of the peak at 1020–1029 cm^{-1} representing the C–O–C functionality (Fig. 4b) in all the extracted samples therefore confirms that the new peaks 1720–1738 cm^{-1} is due to ester formation (Papadopoulos et al., 2010). The raw pine cone contains more of the carboxylate ions than the extracted sample and little ester groups as can be seen from Fig. 4a. The intensity of the ester group increased in the order of raw < 1:3 < 1:2 < 2:1 < 1:1 (i.e., as the ethanol proportion decreased).

It was observed that the unbounded –OH peaks were found to decrease in intensity as compared with the raw sample, indicating the possibility of decrease of hydroxyl groups during the extraction (Fig. 4c) (Inglesby et al., 2005). Fig. 4c also shows a decrease peaks at 2700–2900 cm^{-1} for the extracted samples as compared with the raw pine cone. It has been shown that the CH$_2$-group stretching comprises the majority of aliphatic fraction of waxes (Inglesby et al., 2005). Inglesby et al. (2005), in the solvent extraction of rice straw with toluene–ethanol mixture observed a reduction of these peaks and associated the reduction to the extraction of waxes on the straw surface. The peaks representing the carboxylate ions at 1627.20 and 1547.68 cm^{-1} were also found to reduce in intensity for samples treated with toluene–ethanol mixture of ratios 1:1 and 2:1 while for samples treated with toluene–ethanol mixture of ratios 1:2 and 1:3, the intensities changed only slightly from the raw sample. This will support the results above that ester formation was more with samples treated with 1:1 and 2:1 mixtures. The intensities of the peaks lying between 1311 and 1375 cm^{-1} representing C–N stretching of amine were also observed to increase slightly in intensity, indicating that basic functional groups of amine (C–N) were not extracted during the treatment process but are likely exposed with increasing internal surface. Finally, The peaks between 1500 and 1513 cm^{-1} due to benzene ring and that between 1200 and 1260 cm^{-1} representing carboxylic/aromatic hydroxyl (–OH) stretching formation of phenol were found to decrease after extraction. This may likely be due to extraction of lignin containing pine cone material.

3.3. Iodine capacity (I)

Significant information on the internal surface of powder materials can be obtained from the iodine capacity (I mg/g) of the material. In the present investigation the iodine capacity of the pine cone was obtained to be 23.7 ± 0.09 mg/g. When pine cone powder was treated with toluene–ethanol mixture of ratios 1:1, 2:1, 1:2 and 1:3 (v/v) for 2 h, the iodine capacities for the samples were increased to 24.39 ± 0.10 and 24.96 ± 0.07 mg/g for toluene–ethanol mixtures of 1:1 and 2:1 but decreased to 22.73 ± 0.20 and 22.39 ± 0.40 mg/g for the 1:2 and 1:3 mixture (Fig. 5). It may be interpreted that the 1:2 and 1:3 toluene–ethanol mixtures caused contraction of the pine cone surface due to the higher ethanol ratio.

On increasing the contact time from 2 to 4 h, the iodine capacities increased to 26.98 ± 0.30, 26.1 ± 0.30, 23.55 ± 0.40 and 24.70 ± 0.50 mg/g for the 1:1, 2:1, 1:2 and 1:3, respectively. These results suggest that 4 h of heating may have increased the amounts of pore spaces in the pine cone material by extracting more of the organic plant components as was observed from the high percentage reduction in bulk densities
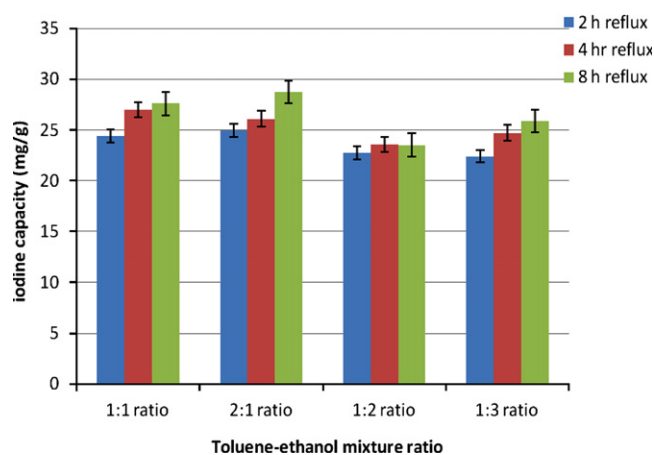

Figure 5 Relationship between iodine capacity and toluene–ethanol mixture ratio at different reflux time.

for all samples. The magnitude of increase was higher for samples treated with toluene–ethanol mixture of ratios 1:1, 2:1 than for the 1:2 and 1:3 treatments (Fig. 5).

Finally, reflux for 8 h further increased the iodine capacities for 1:1, 2:1 and 1:3 treated samples to 27.60 ± 0.40, 28.72 ± 0.50 and 25.88 ± 0.50 mg/g while for the 1:2 mixture, the iodine capacities reduced slightly to 23.49 ± 0.50 mg/g. It will be observed here that the increases in iodine numbers were not as rapid between 0–4 h and 4–8 h of reflux as compared to the 2–4 h of reflux accept with the 2:1 mixture treatment. The results show that the iodine capacity increased continuously with the increasing time of reflux and this trend is quite similar to the percentage decrease in bulk densities of the samples. The 2:1 mixture treatment producing the highest percentage decrease in bulk density at each reflux time also had the highest increase in iodine capacity; this can be attributed to the extraction of organic components of pine cone present within the material matrix. Similar extraction has been reported by Koncsag et al. (2011).

3.4. Surface negative charge

The surface negative charge of a biological material is attributed to ionization of acidic functional groups on the material surface (Ofomaja et al., 2010a). These sites are usually responsible for interaction with positively charged spices in solution (Ofomaja and Ho, 2007). The surface negative charge value of the raw pine cone powder was found to be 3.82 ± 0.02 mmol/g. On the treatment of pine cone powder with toluene–ethanol mixture of ratios 1:1, 2:1, 1:2 and 1:3 (v/v) for 2 h, the values of surface negative charge obtained were 0.73 ± 0.04, 0.68 ± 0.03, 0.78 ± 0.03, 0.77 ± 0.04 mmol/g. The results revealed that the values for surface negative charge reduced significantly from that of the raw pine cone after 2 h of extraction. The implication of these results is that the initial extraction may have removed surface components of the pine cone samples that are negatively charged. For example, pine cone is known to contain diterpinoid resin acids which make up a significant percentage of the extractives and carry negative charges. These acids act as defense mechanism against fungi attack (Ofomaja et al., 2009). Marshall et al. (1999) observed a reduction in surface negative charge from 1.33 ± 0.00 to 1.01 ± 0.00 mmol/g for soybeans extracted with 0.1 mol/dm^3 NaOH for 1 h at 23 °C.

When the contact time of reflux was increased from 2 to 4 h, the values of surface negative charge were found to increase slightly for all samples. The new values of surface negative charge obtained were 0.74 ± 0.05 mmol/g for ratio 1:1, 3.78 ± 0.03 mmol/g for ratio 2:1, 3.80 ± 0.04 mmol/g for ratio 1:2 and 3.80 ± 0.05 mmol/g for ratio 1:3. It was explained earlier that the initial reduction in surface charge was attributed to the removal of charged components such as resin acids. Therefore, further increase in surface negative charge with increased time of contact can be attributed to two possible reasons: (i) extraction of plant components blocking the pore spaces in the pine cone particles which causes the exposure of hidden negative sites within the pores and (ii) release of functional groups on the material surface which leads to increased charges. From the calculated values of iodine number in the previous section, the increase in iodine capacities was highest between 2 and 4 h of reflux than between 0 and 2 reflux signifying that opening of blocked pores may have caused that increase in the magnitude of surface negative charge.

Finally, increasing contact time of refluxing to 8 h increased the values of surface negative charge of the samples extracted with toluene–ethanol mixtures of ratio 1:2 (4.02 ± 0.02 mmol/g) and 1:3 (3.92 ± 0.04 mmol/g) higher than the values for the raw pine cone. The surface negative charges for toluene–ethanol mixtures of ratio 1:1 (3.80 ± 0.05 mmol/g) and 2:1 (3.76 ± 0.03 mmol/g) had values lower than the original raw pine cone. The lower values of surface negative charge for samples treated with 1:1 and 2:1 mixtures may be attributed to the high formation of esters from carboxylic acid group which contributes largely to the total negative charge. On the other hand, samples treated with 1:2 and 1:3 mixtures with lower proportions of esterification had higher surface charge values.

3.5. Adsorption experiments

Batch adsorption experiments of lead(II) ion removal from aqueous solution were performed using the raw and toluene–ethanol (1:1, 2:1, 1:2, 1:3 at 8 h) extracted samples. An amount (0.5 g) of each of the samples were contacted with 100 cm^3 of 300 mg/dm^3 lead(II) solution adjusted to pH 5 and agitated at 200 rpm for 2 h at room temperature. The results of the adsorption experiment revealed that the adsorption capacities were different for the various samples. The lead(II) adsorption capacities (q_e, mg/g) obtained were 13.6, 16.1, 17.2, 12.8, and 14.7 mg/g for the raw, 1:1, 2:1, 1:2 and 1:3 toluene–ethanol extracted samples, respectively. From these results it can be seen that all treated samples had higher values for equilibrium capacity than the raw pine cone. Therefore it can be said that toluene–ethanol extraction improved the lead(II) adsorption capacity of pine cone powder. The order of increasing lead(II) adsorption capacity within the samples is raw < 1:2 < 1:3 < 1:1 < 2:1.

The trend in the percentage lead(II) removal from solution was compared with the surface properties of the samples. The comparison showed that the trend in the values of bulk density was not in line with the lead(II) equilibrium capacities, i.e. no correlation was observed between lead(II) adsorption capacities and bulk densities. When the trend in the values of surface negative charge of the extracted samples were compared with equilibrium lead(II) capacity, it was observed that the sample with the highest lead(II) adsorption capacity of 17.2 mg/g (2:1 toluene–ethanol extracted sample) corresponded to the least surface negative charge of 3.76 mmol/g. On the other hand, the sample

with the least equilibrium lead(II) adsorption capacity of 12.8 mg/g (1:2 toluene–ethanol extracted sample) had a high surface negative charge of 4.02 mmol/g. It was also found that the trend in surface negative charge with lead(II) adsorption capacity gave an inverse relationship with a correlation coefficient $r^2 = 0.972$. This suggests that the surface negative charge of the pine samples does not control the adsorption performance of the pine cone sample. Wartelle and Marshall (2000) investigating the relationship between surface negative charge of agricultural waste materials extracted with 1.0 mol/dm^3 NaOH and copper(II) adsorption observed that although soybean hulls did not have a high negative charge (1.24 ± 0.01 mmol/g) as compared with almond shell (1.99 ± 0.12 mmol/g) and Black walnut shell (1.30 ± 0.11 mmol/g), the copper(II) capacity was higher for soybean (0.55 mmol Cu^{2+}/g) than for almond hull (0.27 mmol Cu^{2+}/g) and Black walnut shell (0.51 mmol Cu^{2+}/g). Wartelle and Marshall (2000) suggested that the amount of copper(II) removal may be related to reactive surface of the agricultural waste material.

Comparing the trend of equilibrium lead(II) capacities with the iodine capacity of the extracted pine cone samples, it was observed that a trend can be seen between equilibrium lead(II) capacity and iodine adsorption capacity. The highest value for iodine capacity which is 25.72 mg/g (2:1 toluene–ethanol extracted sample) corresponds to the highest values for equilibrium lead(II) adsorption capacity of 17.2 mg/g, while the least value of iodine capacity of 21.49 mg/g (1:2 toluene–ethanol extracted sample) corresponded to the least equilibrium lead(II) adsorption capacity of 12.8 mg/g. When the relationship between iodine capacity and lead(II) equilibrium capacity was plotted, a linear relationship was found with correlation coefficient, $r^2 = 0.998$ and a mathematical equation representing the relationship:

$$q_e = 0.8332(I) - 6.8158 \tag{2}$$

The good correlation between the iodine capacity (I) and equilibrium lead(II) adsorption capacity suggests that the internal surface of the adsorbent controls the lead(II) adsorption onto the pine cone surface. One explanation to these results is that, although the 1:2 and 1:3 toluene–ethanol extracted samples have higher surface negative charges, their internal surfaces are smaller than those of the 1:1 and 2:1 extracted samples. This will therefore affect their ability to remove lead(II) ions from aqueous solution, while for the 1:1 and 2:1 toluene–ethanol ratios the inner surface is larger and accounts for the higher lead(II) adsorption capacity.

3.6. Desorption studies and adsorption mechanism

Desorption studies are vital in determining the mechanism of an adsorption process and its applicability in industrial practice. The desorption characteristics of an adsorbent can be evaluated by extracting absorbed metal ions by different solvents. If the metal ion adsorbed can be desorbed by water, it is believed that the attachment of the metal ion onto the adsorbent is by weak bonds (physical bonds). If a strong acid or base solution such as HCl or NaOH can desorb the metal ion, it is believed that the attachment of metal is by ion-exchange. If a solution of acetic acid can desorb the metal, it is believed that the adsorption of metal is by chemisorption.

The desorption experiment was carried out using the residual pine cone powder used in the adsorption experiments (after
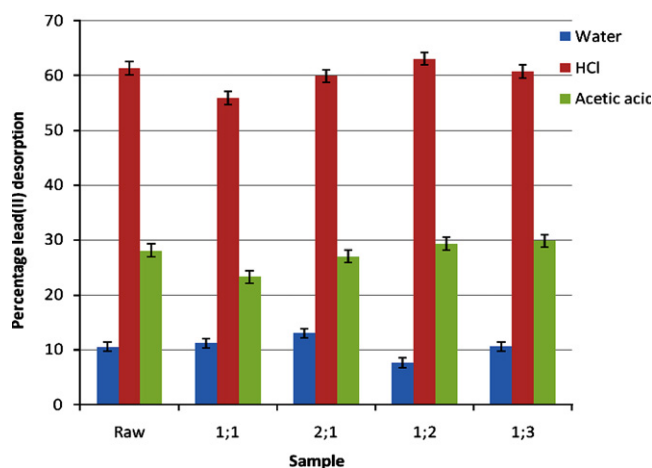
Figure 6 Desorption efficiencies of lead(II) from pine and extracted pine cone powder by various solvents. Temperature: 299 K, time: 4 h, C_o (desorbing solvent): 0.1 mol/dm^3.

filtrating and washing with excess water to remove unbounded lead(II) ions). Results of the desorption analysis are shown in Fig. 6. The results show that the pattern of desorption with the different desorption agents was the same for all the pine samples. The amount of lead(II) desorbed using 0.1 mol/dm^3 of HCl was highest for all the samples while lead(II) desorbed using 0.1 mol/dm^3 of acetic acid had the next highest values. This pattern in the desorption studies shows that lead(II) was mostly bounded by ion exchange followed by the irreversible bonding of lead(II). The results also revealed that weakly bounded lead(II) were only a small fraction of the total lead(II) adsorbed for all samples. Ofomaja (2010) in the desorption studies of copper(II) ions from palm kernel fiber observed that desorption with strong acid solution followed by acetic acid accounted for the highest percentage of copper(II) removed, Ofomaja et al. (2010b) also reported similar observation for the desorption of copper(II) and lead(II) ions from KOH treated pine cone powder.

The percentage of lead(II) ions desorbed using HCl gives an indication of the fraction of lead(II) ions bounded by ion exchange on the sample surface, this mechanism accounted for the largest fraction of lead(II) desorbed with all pine samples. The desorption results therefore reveal that the highest percentage of lead(II) desorbed was obtained for the 1:2

toluene–ethanol extracted pine cone powder (63.1%) followed by the raw pine (61.4%) and then the 1:3 toluene–ethanol extracted pine cone powder (60.7%). This trend in the percentage of lead(II) bounded by ion exchange to the pine samples was observed to follow the trend in the surface negative charge of the samples. The 1:1 (55.9%) and 2:1 (59.9%) toluene–ethanol extracted pine cones were observed to have the least values of percentage lead(II) desorbed by HCl which is also the trend in the surface negative charge. The percentage of lead(II) desorbed by 0.1 mol/dm^3 acetic acid on the other hand, which accounts for irreversibly bounded lead(II) is the mechanism responsible for the second highest fraction of lead(II) desorbed from the pine samples. The irreversible mechanism was again dominant in the 1:2 (29.3%) and 1:3 (29.8%) toluene–ethanol extracted pine cone powder. Acetic acid desorbed a lower fraction for lead(II) adsorbed in the 1:1 (23.3%) and 2:1 (27.1%) ratio toluene–ethanol extracted pine cone powder. Finally, the trend was opposite for the percentage lead(II) desorbed by water which accounted for the weakly bounded lead(II) ions. The results showed that there was a higher fraction of lead(II) ions held by weak adsorption on the 1:1 (11.2%) and 2:1 (13.0%) ratio toluene–ethanol extracted pine cone powder. While lower percentage desorption of lead(II) ions was recorded for the raw sample (10.6%), 1:2 (7.6%) and 1:3 (10.6%) ratio toluene–ethanol extracted pine cone powder. This trend in results may be due to the fact that the 1:1 and 2:1 ratio toluene–ethanol extracted pine cone powder had lower values of surface negative charge and higher surface area which permitted more interaction of lead(II) ions to the adsorbent surface increasing the chances for physical interaction.

The spectra peaks for the pine cone samples before and after lead(II) ions adsorption are recorded in Table 1. The peak values in the table suggest that certain peaks have been shifted slightly after lead(II) adsorption from solution and the extent of the shift of the affected peaks were not the same in all samples. Peaks that were involved include the unbounded –OH peak, the carbonyl and carboxylate peaks and the carboxylic/phenolic –OH peaks. These results suggest that both –OH groups and acidic functional groups on the pine cone samples are responsible for lead(II) ion binding.

The peaks at 3334.19, 3332.78, 3332.15, 3334.99 and 3333.49 cm^{-1}, representing the unbounded –OH in the raw, 1:1, 2:1, 1:2 and 1:3 ratio toluene–ethanol extracted pine cone samples were observed to have shifted to 3338.85, 3339.13, 3338.33, 3332.04 and 3339.77 cm^{-1}, respectively. It was

Table 1 FTIR peaks for unbounded water and acidic functional groups before and after lead(II) adsorption.

FTIR peak	Raw	1:1 (8 h)	2:1 (8 h)	1:2 (8 h)	1:3 (8 h)
Hydroxyl (–OH)					
Before	3334.19	3332.78	3332.15	3334.99	3333.49
After	3338.85	3339.13	3338.33	3332.04	3339.77
Carboxylate (–COO$^-$)					
Before	1613.37	1607.20	1606.84	1606.73	1611.10
After	1609.91	1608.53	1607.65	1608.13	1608.72
Carboxylic –OH					
Before	1447.68	1422.59	1421.58	1423.29	1422.94
After	1451.86	1423.16	1422.76	1421.28	1421.00
Phenol –OH					
Before	1262.89	1264.01	1264.21	1263.29	1263.27
After	1263.02	1263.91	1263.99	1264.19	1264.44

observed that change in the position of the peaks were higher for samples with higher percentage desorption of lead(II) when water was applied as desorption agent. This suggests that the unbounded –OH groups actually play a role in the physical bonding to lead(II) to these samples. The peaks for carbonyl/carboxylate groups at 1613.37/1447.68 cm^{-1}, 1607.20/1422.59 cm^{-1}, 1606.84/1421.58 cm^{-1}, 1606.73/1425.29 cm^{-1} and 1611.10/1422.94 cm^{-1} were also found to shift slightly to 1609.91/1451.86 cm^{-1}, 1608.53/1423.16 cm^{-1}, 1606.84/1422.76 cm^{-1}, 1608.13/1421.28 cm^{-1} and 1608.72/1421.00 cm^{-1}. It was found that samples were raw, 1:2 and 1:3 had higher shifts in the carbonyl/carboxylate peaks. These samples have also been shown to have higher surface negative charge. The peak representing the carboxylic/phenolic –OH bond was found to shift more for raw, 1:1 and 1:3 ratio toluene–ethanol extracted samples than for 1:1 and 2:1 samples. These samples had the lower values for iodine capacity and higher intensities of the carboxylic/phenolic –OH peak, indicating that the carboxylic/phenolic –OH participated strongly in these samples.

4. Conclusion

The effect of solvent extraction as an adsorbent modification method on the surface properties of pine cone powder has been examined and valuable information as to the importance of extraction time and solvent ratio obtained. Increasing the proportion of ethanol in the mixture improved the surface negative charge but reduced iodine capacity. Lead(II) adsorption was found to increase with increasing iodine capacity and reducing surface negative charge. The 2:1 8 h toluene–ethanol mixture was found to be the best modification procedure that gives the optimum biosorption properties.

Desorption studies revealed that ion-exchange and chemisorption accounts for a large percentage of the lead(II) binding mechanism. FTIR studies before and after lead(II) adsorption reveal that unbounded –OH and acidic functional groups are responsible for the lead(II) binding.

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