

*Full Length Research Paper*

# **Biosorption of $\text{Cd}^{2+}$ and $\text{Pb}^{2+}$ ions onto mango stone and cocoa pod waste: Kinetic and equilibrium studies**

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**Mango stone (DMS) and cocoa pod (CPC), two agricultural waste materials evaluated for the removal of toxic cadmium ion  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  ions from aqueous media in batch adsorption mode. Adsorption variables such as the nature and composition of electrolyte, pH, adsorbent dose and equilibration time were optimized for the maximum accumulation of the metals to the biosorbents. The optimum contact time of 15 min for  $\text{Cd}^{2+}$  and 40 min for  $\text{Pb}^{2+}$  were found to be independent of the adsorbent in use but on the metal been adsorbed. The presence of alkali electrolyte ions  $\text{Na}^+$  and  $\text{K}^+$  reduced the uptake of  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  as these electrolytes ions competed and reduced the available adsorption sites for heavy metal removal, the effect been more pronounced in DMS than with CPC. Kinetic data obtained in this study fitted satisfactorily to the pseudo-second-order rate equation ( $R^2 > 0.995$ ). Other tested kinetic models however proved useful for describing the adsorption mechanisms at different points in the biosorption process. The Langmuir, Freundlich, Dubinin- Radushkevich (D-R) and Temkin models were applied to describe the isotherms in the study. Based on the assumptions of these equilibrium models and the results obtained, an attempt was made at describing the surface adsorption characteristics of the biosorbents relative to the metals in question. Biosorption capacity of both biomasses for both metals compared well with those of earlier workers.**

**Key words:** Adsorption, kinetics, equilibrium, isotherms, cocoa pods, mango stone.

## **INTRODUCTION**

The presence of metal ions in natural and industrial wastewater, and their potential health implications to man and his environment has been a subject of environmental concern in the last three decades. Metallic species introduced into the environment by anthropogenic activities persist indefinitely and eventually accumulate along the food chain. Virtually every industrial activity utilizing heavy metals in their production process introduces metal ions into the environment via their

effluents or waste. These industrial processes include: electroplating, plastic manufacturing, mining, paint pigment production, alloy preparation, lead, silver-cadmium, and cadmium-nickel batteries manufacture, and metallurgical practices. These industrial activities have introduced metals such as copper (Cu), nickel (Ni), lead (Pb), mercury (Hg), chromium (Cr), zinc (Zn) and cadmium (Cd) and many others into the environment at levels which are above the permissible levels. The health hazards posed by many of these metals have been previously investigated and documented (Forster and Wase, 1997)

Cd, Pb and their related compounds are amongst the 129 so-called 'black-list' substances in the dangerous

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substances directive 76/464/EEC. These metals are also recognized by the World Health Organization (WHO) as metals of most immediate concern (WHO 1984). This is because both metals show acute toxicity and are capable of bioaccumulation and biomagnifications in biological tissues (Friberg et al., 1979) When ingested, they cause accumulative poisoning, cancer, brain damage and other related health disorders. Lead is a general metabolic poison and enzyme inhibitor. It can cause mental retardation and semi-permanent damage in young children. Cd and Pb have the potential to replace Zn and calcium (Ca), respectively, in biological processes and hence interfere with the natural workings of the body system.

Several technologies are presently been utilized for the removal of these metals from industrial wastewater in order to prevent their release into the environment. Conventional technologies used include: chemical precipitation, coagulation, chemical/electrochemical reduction, solvent extraction, and electrolysis (Sheng et al., 2004). These methods of treatment suffer several limitations based on their technical and/or economical viability. Some of these methods do not possess removal efficiencies which are sufficient for meeting the ever increasing environmental requirements been set by regulatory bodies. Also, the possibility of secondary contamination from concentrated sludge and other secondary pollutants is a subject of concern when utilizing these conventional techniques.

Recently, adsorption technology, especially those carried out in the biosorption mode, using non-living biomass has shown to be a promising alternative technology for wastewater treatment. Major advantages include the minimal cost associated with obtaining and preparing the biomass for effluent treatment (Juang and Shiau, 2000; King et al., 2007; Lacour et al., 2001). A variation of this technique utilizes agro-allied waste materials as biosorbents, thus, converting a possible environmental nuisance into a material of economic importance. Several works on the use of biosorbents in the removal of heavy metals are reported in literature and they include: rice husk (Munaf and Zein, 1997), soya bean hulls, cotton seed hulls, rice straw, sugarcane bagasse (Marshall and Champagne, 1995), grape bagasse (Farinella et al., 2008), coconut shell and husk (Hasany and Ahmad, 2006), tea leaves (Malkoc and Nuhoglu, 2007), petiolar felt sheath of palm (Iqbal et al., 2002), maize barn (Singh et al., 2006) and defatted *Carica papaya* seeds (Adie et al., 2011).

Nigeria is the world's 4<sup>th</sup> largest producer of cocoa beans (370,000 metric tons per annum in 2009) (ICO, 2011). The cocoa husk which is the remnant after extraction of the beans is of no economic value. It is mostly burnt in open fires or discarded in dumps and fields where it is allowed to decay (Ajayi et al., 2007). Due to challenges facing the proper disposal of agricultural waste, cocoa husk as with several other

agricultural by-products have been identified as an environmental problem in Nigeria and some other African countries like Ghana and Codevoire (Ojeniyi et al., 2007). Studies by Meunier et al. (2002, 2003) identified cocoa pod (CPC) as a promising biosorbent for metal removal from highly acidic solutions. They proceeded to apply the biomass for the removal of heavy metals from acid soil leachate in batch counter-current adsorption experiments (Meunier et al., 2004). The kinetics of the adsorption of heavy metals (Cu, Cd and Pb) on modified and raw CPC has recently been reported (Odoemelam et al., 2011).

Mango (*Mangifera indica* L., family Anacardiaceae) is a fleshy stone fruit grown in almost all tropical and subtropical regions of the world. Currently, with about 27 million ton production annually, mango ranks 5<sup>th</sup> in production among the major fruit crops. Nigeria ranks as the 8<sup>th</sup> world's largest producer of mangoes (730,000 metric tons per annum). Mango peels and DMS, which make up 40 to 50% of the fruit weight (Medina and García, 2002), are the major by-products after the processing of mangoes. As domestic waste, they are commonly found in refuse dumps where they attract flies and rodents, which can be regarded as unsightly, environmentally undesirable and a non-productive use of resources. After industrial processing of the fruits, considerable amounts of mango seeds are discarded as waste (Puravankara et al., 2000).

Several workers have investigated the possibility of applying parts of the mango plant for adsorption of heavy metals from solution, for example, the bark of mango tree has been applied for the adsorption of  $\text{Hg}^{2+}$ ,  $\text{Cr}^{3+}$  and  $\text{Cd}^{2+}$  from aqueous solution (Tiwari et al., 1999). A high level of metal uptake was reported for  $\text{Hg}^{2+}$  and  $\text{Cr}^{3+}$  within 4 h of contact with the metal solutions, while no significant adsorption of  $\text{Cd}^{2+}$  was observed under various physico-chemical conditions. A recent study has reported the characteristics and mechanism of  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  adsorption by mango peel waste (Iqbal et al., 2009a; Iqbal et al., 2009b).

In this study, we report the batch adsorption of  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  from aqueous solution, onto CPC and mango stone (DMS) (after removal of kernel), two abundant agricultural wastes in Nigeria. The appropriate utilization of these food wastes is a focal point for sustainable development. Adsorption variables such as pH, sorbate-adsorbent contact time, adsorbent dose and varying sorbate concentration are reported. The presence and effect of counter alkali metal ions was also investigated. Surface characterization of the biomass by Fourier transmission infrared (FTIR) and scanning electron microscope (SEM) is also discussed.

## MATERIALS AND METHODS

### Reagents

All reagents used for this study;  $\text{Pb}(\text{NO}_3)_2$ , HCl, NaOH,  $\text{Cd}(\text{NO}_3)_2$

were of analytical grade purchased from Merck South Africa.  $Pb^{2+}$  and  $Cd^{2+}$  stock solutions were prepared by dissolving their corresponding nitrate salt in distilled water. The pH of sorbate solutions were adjusted using 0.1 M HCl or 0.1M NaOH. All experiments were carried out in duplicate and the average values were reported and discussed. Blank experiments were conducted to estimate and correct for adsorptions to the walls of the apparatus used.

### Preparation of biosorbents

CPCs were collected from a disposal site at the Cocoa Research Institute of Nigeria, Ibadan, Nigeria (CRIN) in April, 2010. The sample was washed to removed dirt and debris, air dried, crushed and milled. Disposed mango fruit was obtained from a disposal site in Ibadan, washed free of the pericarp and the stone air dried. The dry DMS was crushed and milled to obtain biomass of fine aggregates size. The ground biomasses (CPC and DMS) were washed with distilled water to remove surface adhering ions and oven dried at 70°C for 72 h. The CPC cake obtained upon drying was ground using a mortar and pestle and sieved using a 40 mesh sieve (US, 0.42 mm). The biomasses were then stored in high density polyethylene bottle, labeled and used for adsorption studies without any chemical treatment. The crushed DMS biomass were called DMS biomass and that for cocoa pod was called CPC biomass

### Characterization of biosorbents

FTIR absorption spectra of DMS and CPC biomass were obtained using the potassium bromide (KBr) pellet method. Approximately 1 mg of finely powdered dry sample was mixed with 250 mg of dry KBr and ground to fine powder in an agate mortar. The mixture was transfer into a die and compressed to form a pellet (13 mm diameter) by the use of hydraulic press. The pellet was carefully removed from the die, placed in the holder and the spectra of the samples were recorded over the range 4 000 to 400  $cm^{-1}$  using FTIR (Perkin Elmer<sup>TM</sup> Spectrum 1000). For the SEM analysis, a thin layer of carbon glue was spread on a stub and small quantity of the biomass samples was spread on the thin layer of the glue. Excess particles were then dusted off by means of a compressed gas duster. The stub was coated with carbon to make the samples conductive by means of a carbon coater (Balzers model BSV 202) for 1 h. The micrograph of the sample was then view by a FEI<sup>TM</sup> SEM (Nova Nano SEM 230)

### Biosorption experiments

Biosorption experiments were carried out by suspending 200 mg CPC and 300 mg of DMS in separate 20 mL of 250 mg/L metal ion solution in 60 mL polythene bottles. After appropriate agitation, biomass suspensions were filtered using a 0.45  $\mu m$  filter paper and the clear supernatant analyzed for the residual metal content using atomic absorption spectroscopy (Buck Scientific 210/211) working with air acetylene flame (flow rate: 1.5 L/min) and equipped with hollow cathode lamps used for the metals. Detection limit for  $Cd^{2+}$  and  $Pb^{2+}$  was 0.01 and 0.08 ppm, respectively. The amount of metal absorbed by each biomass was calculated from the difference between metal quantity added to the biomass and metal content of the supernatant using the Equation 1.

$$q = \frac{(C_o - C)V}{M} \quad (1)$$

Where  $q$  is the metal uptake (mg/g),  $C_o$  and  $C$  are the initial and equilibrium metal concentration in the solution (mg/L), respectively.  $V$  is the volume of the solution (L) and  $M$  is the mass of the biosorbent (g). The effect of operating variables on the adsorption of Pb and Cd by both biomasses was investigated. The effect of pH was studied by equilibrating 200 mg CPC and 300 mg DMS with 20 mL of metal solution after pH adjustment with 0.1 M  $H_2SO_4$  and NaOH. The pH of adsorbate solutions were in the range of 3.0 to 9.0, in intervals of 1 pH unit. The effects of counter electrolyte ion (sodium and potassium), contact time and sorbate concentration were also examined.

### Kinetic study

Metal adsorption rate is considered to be an important factor for designing any adsorption process. Batch experiments were carried out at a constant temperature 27°C. 200 mg of CPC and 300 mg of DMS (optimized from preliminary studies) were added to 60 mL polyethylene bottles containing 20 mL of 250 mg/L single metal ion ( $Cd^{2+}$  or  $Pb^{2+}$ ) solutions. After appropriate pH adjustments, mixtures were agitated on an end-to-end shaker and withdrawn at desired time intervals. The mixtures were filtered and the supernatant analyzed for residual metal content. Percentage metal adsorbed relative to initial metal in solution for the biomasses was calculated using Equation 1.

### Adsorption Isotherms

Adsorption isotherms of  $Cd^{2+}$  and  $Pb^{2+}$  unto both biomasses were obtained by batch experiments working at optimized adsorbent dose, pH and contact time established after optimization of working parameters. Initial metal concentration was varied from 5 to 300 mg/L for both metals. The amount of metal adsorbed  $q$  was determined using Equation 1. The following isotherms were applied to describe the adsorption process;

1) Langmuir isotherm (Langmuir 1918) is the most commonly used adsorption isotherm and is linearized by Equation 9:

$$\frac{1}{q_e} = \frac{1}{q_m K_L} \left[ \frac{1}{C_e} \right] + \frac{1}{q_m} \quad (2)$$

Where  $C_e$  is the concentration of the adsorbate solution (mg/L) at equilibrium,  $q$  is the adsorption capacity (mg/g) and  $b$  is related to the energy of adsorption (L/mg). Values of  $q_m$  were calculated from the linear plot of  $1/q_e$  against  $1/C_e$  (Lawal et al., 2010).

2) Freundlich isotherm (Freundlich, 1907): The Freundlich isotherm is most frequently used to describe the adsorption of inorganic and organic compounds in solution. In its logarithmic form it can be represented as follows:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (3)$$

Where  $K_f$  and  $n$  are constants incorporating all factors affecting the adsorption process (adsorption capacity and adsorption intensity). Values of  $K_f$  and  $n$  were calculated from the slope and intercept of the plot of  $\log q_e$  against  $\log C_e$ .

3) Dubinin-Radushkevich (D-R) isotherm (Dubinin and Radushkevich, 1947): This is a more general isotherm than the Langmuir and Freundlich and does not assume a homogeneous surface or constant adsorption potential. The linear form of the model is represented as follows:

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \quad (4)$$

Where  $\beta$  is a constant related to the mean free energy of adsorption per mole of adsorbate ( $\text{kJ}^2/\text{mol}^2$ ),  $q_m$  is the theoretical saturation capacity ( $\text{mg/g}$ ) and  $\varepsilon$  is the polanyi potential which is related to the equilibrium concentration  $C_e$  by the expression;

$$\varepsilon = RT \ln \left( 1 + \frac{1}{C_e} \right) \quad (5)$$

The polanyi potential is the work required to move a molecule or ion away from its location in the sorption space.  $R$  is the gas constant ( $\text{J/molK}$ ), and  $T$  is absolute temperature in Kelvin. Hence, the plot of  $\ln q_e$  against  $\varepsilon$  obtains a straight line whose slope and intercept can be related to  $\beta$  and  $q_m$ , respectively. The value of  $\varepsilon$  is related to the adsorption energy by the expression;

$$E = \frac{1}{(-2\beta)^2} \quad (6)$$

4) Temkin model: In its linearized form, the Temkin isotherm is represented as follows:

$$q_e = B_T \ln K_T + B_T \ln C_e \quad (7)$$

Where  $B_T$  and  $K_T$  are Temkin constants.

### Kinetic Isotherms

In order to investigate the mechanism of the biosorption of  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  ions by DMS and CPC, and the potential rate determining steps, such as mass transport and chemical reactions, reaction - based and diffusion - based kinetic models were used to stimulate the experimental adsorption data. These empirical mathematical models which describe laboratory batch adsorption data are proven useful tools for scale up process optimization (Sciban and Klasnja, 2003; Senthilkumaar et al., 2006). The kinetic data on quantity adsorbed as a function of time were fitted to five kinetic models:

1) The pseudo first order kinetic model (Lagergren, 1898).

$$\log(q_e - q_t) = \log q_e - \frac{K_1 t}{2.303} \quad (8)$$

Where  $q_e$  and  $q_t$  are amount of the adsorbate sorbed at equilibrium and at time  $t$ , respectively in  $\text{mg/g}$ ,  $K_1$  is the first order rate constant ( $\text{min}^{-1}$ ) and  $t$  is time ( $\text{min}$ ).

2) The pseudo second order kinetic model as proposed by Ho and McKay (1999).

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (9)$$

Where  $k_2$  is the pseudo second order rate constant. The product of the pseudo second order rate constant  $k_2$  and the square of the equilibrium quantity  $q_e$  is defined as  $h$ , the initial adsorption rate ( $\text{mg/g min}$ ). Equation then becomes

$$\frac{t}{q_t} = \frac{1}{h} + \frac{t}{q_e} \quad (10)$$

3) Intraparticle diffusion model was also tested according to the Equation 11 to identify the mechanism of adsorption (Weber and Morris, 1963)

$$q_t = f(t^{1/2}) \quad (11)$$

Where  $f$  is the intraparticle diffusion constant ( $\text{min}^{-1/2}$ )

4) Elovich model as described by Basha and Murthy (2007):

$$q_t = (1/b) \ln(ab) + (1/b) \ln t \quad (12)$$

Where  $a$  is regarded to as the initial adsorption rate ( $\text{mg/g min}$ ) and  $b$  is related to the extent of surface coverage and activation energy for chemisorption ( $\text{g/mg}$ ). ( $a$  and  $b$  are constants).

5) Fractional power model is a modified form of the Freundlich model and the linearized form has been applied in previous studies (Sciban and Klasnja, 2003):

$$\ln q_t = \ln k + v \ln t \quad (13)$$

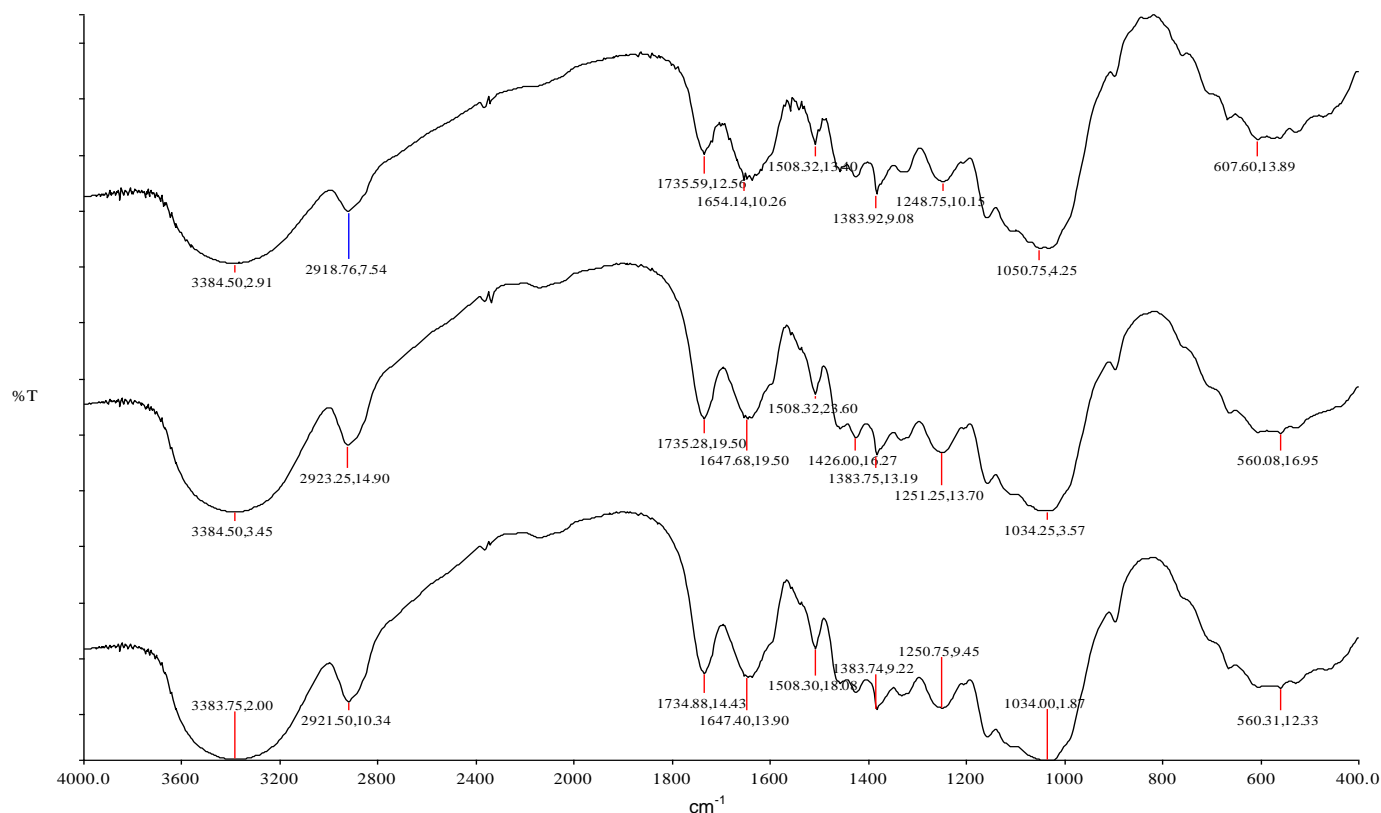
The product  $kv$  is defined as the specific biosorption rate a unit time.

## RESULTS AND DISCUSSION

### FTIR analysis

The FTIR spectrum for DMS and CPC in their raw state and where the biomass was loaded with  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  ions is shown in Figures 1 and 2, respectively. Peaks appearing in the native and loaded biomass were assigned various functional groups and bands in accordance with their respective wave numbers ( $\text{cm}^{-1}$ ). The broad peak at  $3383 \text{ cm}^{-1}$  (DMS) and  $3382 \text{ cm}^{-1}$  (CPC) was assigned to the stretching of O-H group due to inter- and intra-molecular bonding of polymeric compounds such as alcohols, phenols and carboxylic acids, as in pectin, cellulose and lignin. The broad range for this O-H band indicates the presence of 'free' hydroxyl groups of carboxylic acids (Gnanasambandam and Protor, 2000; Iqbal et al., 2009b). The band at  $2921 \text{ cm}^{-1}$  (DMS) and  $2924 \text{ cm}^{-1}$  (CPC) is assigned the symmetric and asymmetric C-H stretching vibrations, respectively of aliphatic acids (Li et al., 2007). The peak at  $1734 \text{ cm}^{-1}$  corresponding to the stretching vibrations of C=O in non-ionic carboxyl groups such in esters and carboxylic acids (Iqbal et al., 2009b), was present only in the DMS spectra and noticeably absent in the raw CPC sample before metal loading. Upon loading of the CPC sample with  $\text{Pb(II)}$  and  $\text{Cd(II)}$  ions, the  $1734 \text{ cm}^{-1}$  bands indicating the presence of a non-ionic carboxyl group appeared in the spectra. The appearance of the  $1734 \text{ cm}^{-1}$  and  $1513 \text{ cm}^{-1}$  band in the metal CPC-FTIR spectra may be attributed to a chemical interaction between the metals and the biomass.

The asymmetric stretching vibration of ionic carboxylic groups ( $-\text{COO}^-$ ) appeared at  $1654$  and  $1624 \text{ cm}^{-1}$  for the raw DMS and raw CPC, respectively. This band shifted



**Figure 1.** Showing FTIR spectrum of DMS and metal loaded DMS; from above DMS, DMS-Pb and DMS-Cd

to higher wave number in CPC (Figure 2) after loading with the metals (that is, 1624 to 1635  $\text{cm}^{-1}$ ), while the shift in DMS was to a lower wave number (that is, 1654 to 1647  $\text{cm}^{-1}$ ). Metal adsorption by biomass has been attributed to interactions between the ionic-carboxyl group and the metal. The pectin peak at 1383  $\text{cm}^{-1}$  (Farinella et al., 2008) was identified in both CPC and DMS samples. The 1057 to 1060  $\text{cm}^{-1}$  bands in CPC spectra and 1050 to 1034  $\text{cm}^{-1}$  bands in DMS spectra were assigned the C-OH stretching in alcohols (Lawal et al., 2010). The shifts in the ionic carboxylate and hydroxylate anions observed after loading of both biomasses may be attributed to changes in counter ions associated with these ions suggesting their contribution to metal uptake (Farinella et al., 2008; Subbaiah et al., 2011).

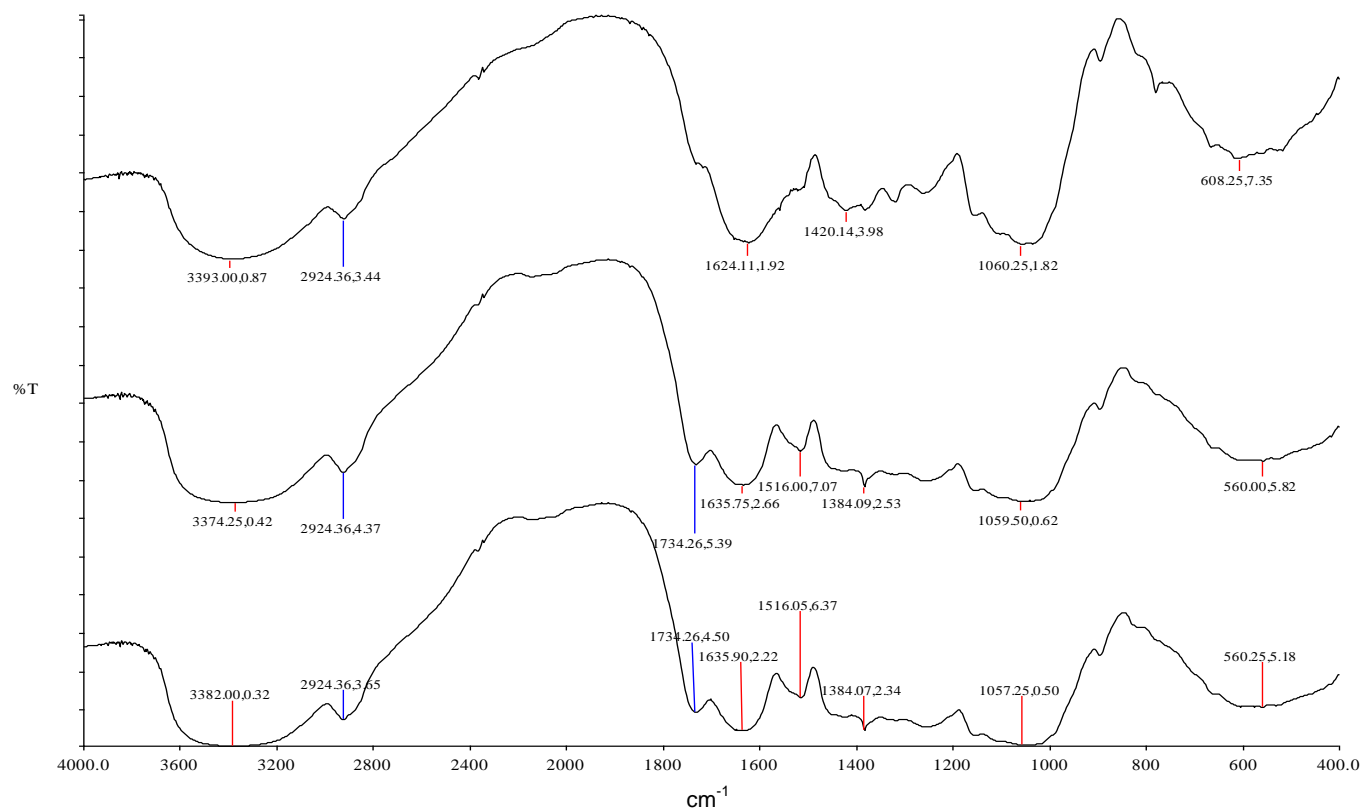
### SEM analysis

The scanning electron microscopy results of CPC and DMS are shown in Figures 3 to 6. At magnification  $\times 1000$  (Figure 3), the surface of CPC shows rough micro porous particles which becomes visible as single surface particles at magnification  $\times 15000$  (Figure 4). The surface of DMS on the other hand does not display any individual

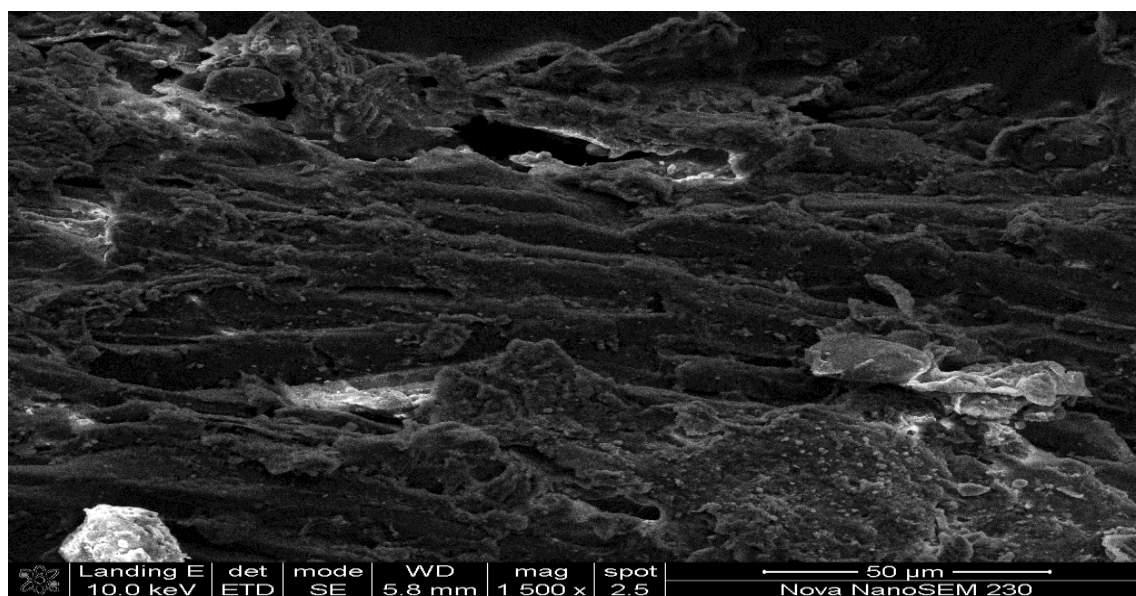
particle (Figure 5) at magnification  $\times 1000$ . It shows a flat sheet of biomass with a few large lobe-like particles which are well defined at higher resolution (Figure 6)

### Effect of pH

Metal adsorption on surface of biomass materials has been described in terms of molecular mechanisms which may include cation exchange in the interlayer, and specific adsorption resulting from surface complexation. Hydrogen ions affect metal complexation because they have great affinity for adsorption sites. It is well established that the adsorption of heavy metal ions by biosorbents is dependent on the pH (Al-Rub et al., 2004; Gong et al., 2005). Figure 7 shows that the effect of pH on the adsorption of  $\text{Cd}^{2+}$  from aqueous solution is more significant with DMS biosorbent than it is with CPC biosorbent. The optimal pH for removal of  $\text{Cd}^{2+}$  was pH 4, where both biomasses had their highest adsorption. Above pH 4, the increase in metal adsorption is insignificant for CPC and reduces for DMS from 64 to 54% at pH 5. Though it was shown in Figure 7 that highest removal for DMS was at pH 9, this could not be assumed to be true as Cd precipitated after pH 6, thus, precipitated Cd were inaccessible for measurement after



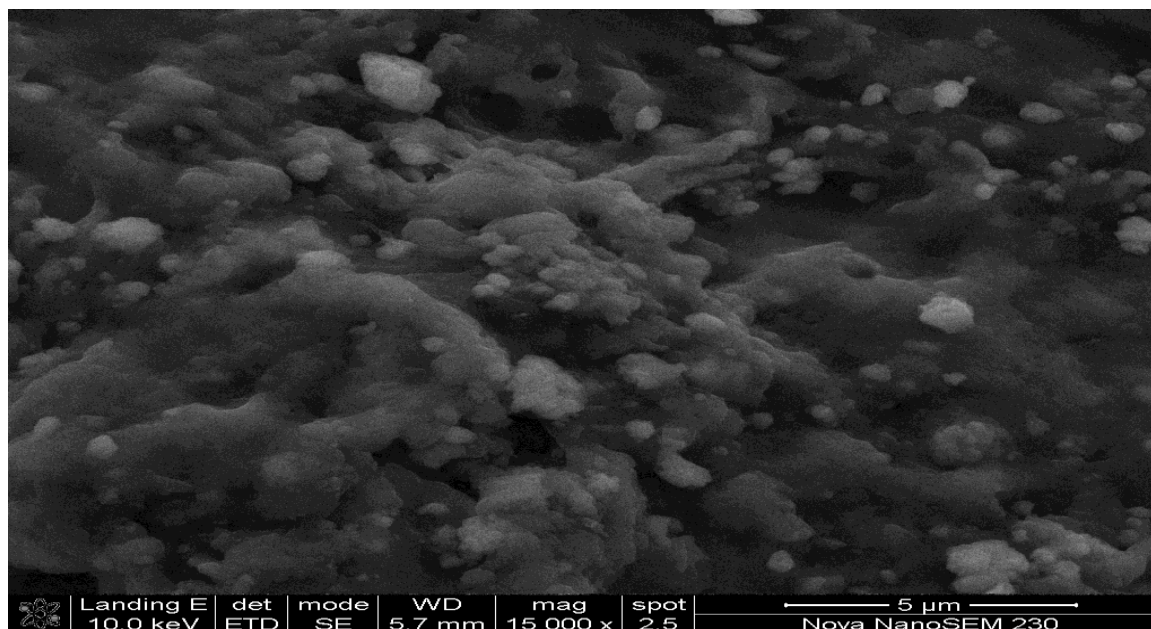
**Figure 2.** FTIR spectrum of CPC and metal loaded CPC. From above, raw CPC, CPC-Pb and CPC-Cd.



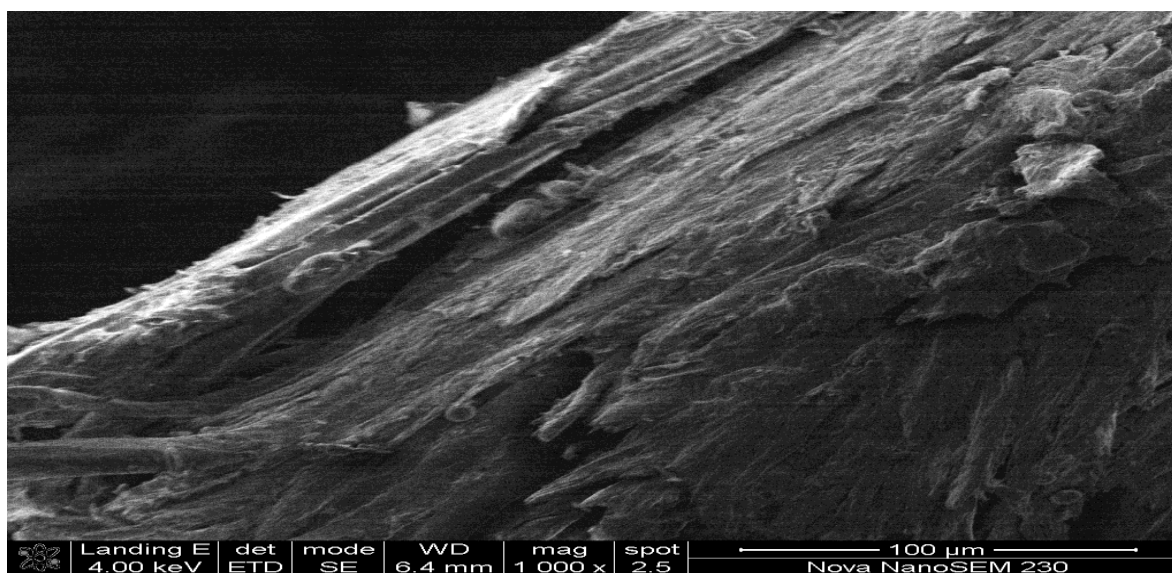
**Figure 3.** Scanning electron micrograph of (CPC) (mag.  $\times 1500$ ).

filtration. Lodeiro et. al, (2006) have shown that free  $\text{Cd}^{2+}$  ions are the predominant species between pH 3.5 and pH 5. At high pH (pH = 8 for Cd), several hydroxyl and low

soluble species are formed such as  $\text{Cd}(\text{OH})_2$  and  $\text{Cd}(\text{OH})_3^-$ , which are inaccessible to the biosorbents for adsorption. Their presence in solution after biomass



**Figure 4.** Scanning electron micrograph of CPC (mag.  $\times 15000$ ).



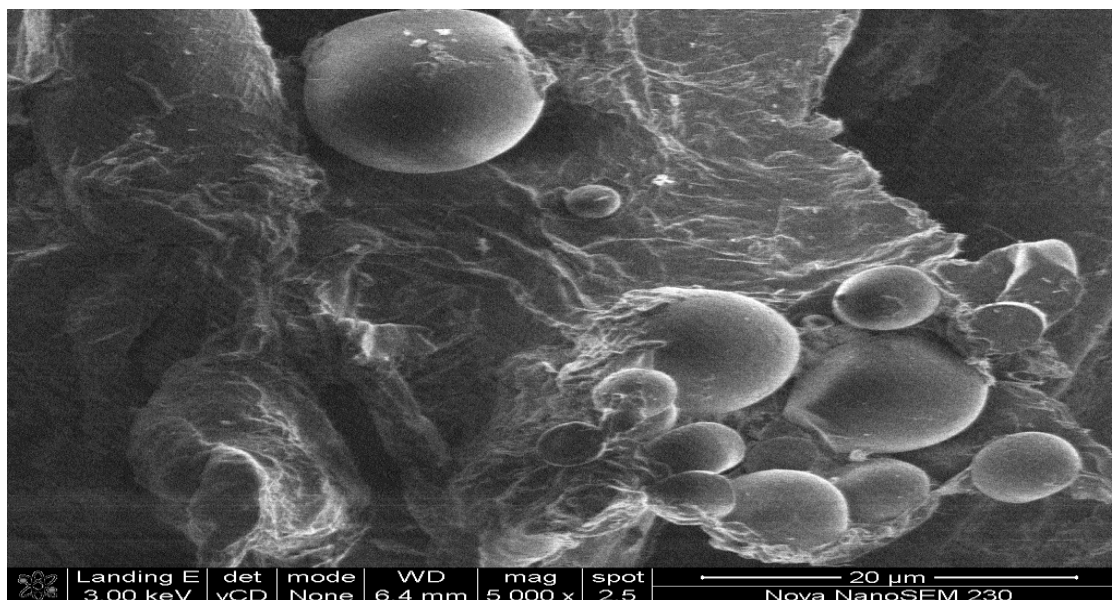
**Figure 5.** Scanning electron micrograph of DMS (mag.  $\times 1000$ ).

removal accounts for the high residual metal content in supernatant after this pH.

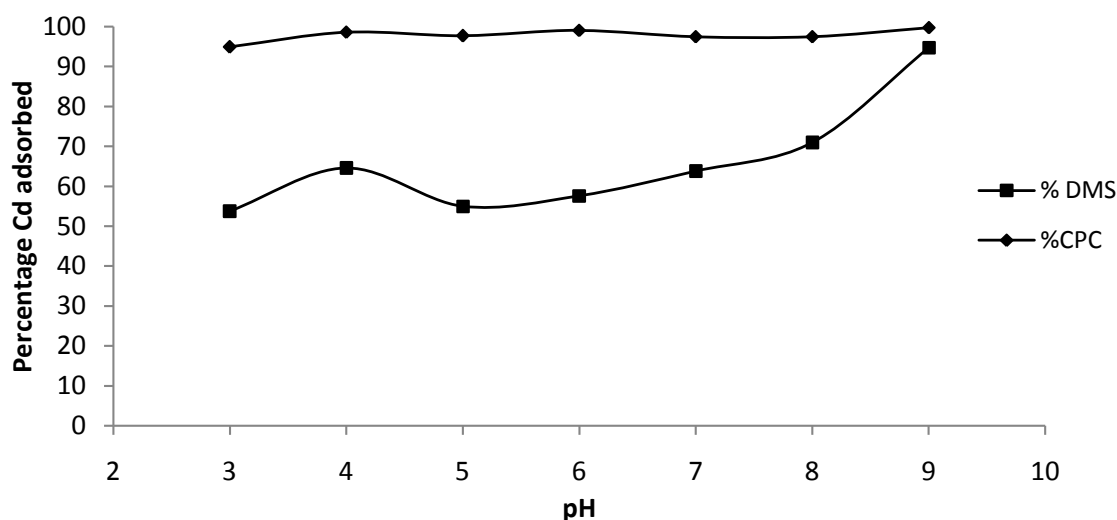
Figure 8 shows the effect of pH on the adsorption of  $Pb^{2+}$  onto both biosorbents. The percentage removal of  $Pb^{2+}$  by DMS increased from 66.1 to 96% with an increase in pH from 3.0 to 4.0 and thereafter no significant change was observed. The percentage removal of  $Pb^{2+}$  by CPC reduced gradually with increase in pH from 3.0 to 9.0. Adsorption experiments were

therefore carried out at the established optimized pH of 4.0 and pH 3.0 for DMS and CPC, respectively. Below pH 6.0, Pb is predominating as free  $Pb^{2+}$  ion which is responsible for maximum adsorption in this pH range. Above this pH, several hydroxide species cause a gradual decrease in adsorption (Jean and Bancroft, 1986; Singh et al., 2006). Similar results were also reported in literature for different biomass materials (King et al., 2007; Matheickal and Yu, 1999; Sag et al., 1998; Zhou et





**Figure 6.** Scanning electron micrograph of DMS (mag.  $\times 5000$ ).



**Figure 7.** Effect of pH on the adsorption of  $\text{Cd}^{2+}$  adsorption (%) onto DMS and CPC. Concentration, 250 mg/L; time, 60 min; sorbate volume, 20 ml.

al., 1998).

#### Effect of adsorbent dose

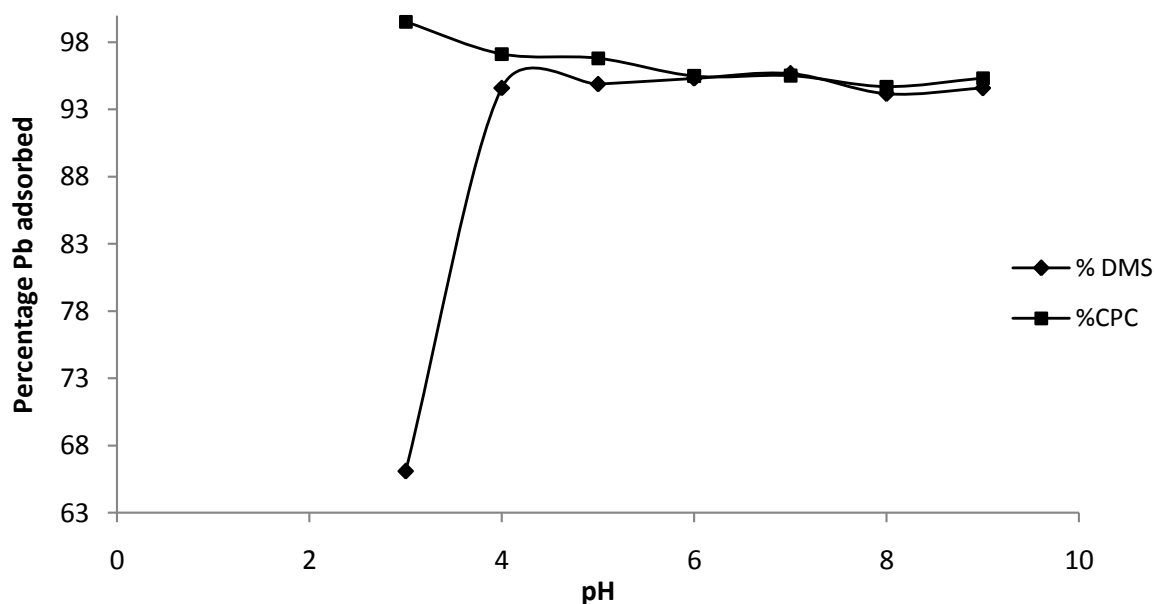
Figure 9 shows the effect of adsorbent dose on the percentage removal of  $\text{Pb}^{2+}$ . The percentage of  $\text{Pb}^{2+}$  ions adsorbed by DMS and CPC increased with an increase in the weight of adsorbent from 0.1 to 0.3 g for DMS and 0.1 to 0.2 g for CPC after which the percentage adsorbed remained constant. Optimal masses for  $\text{Pb}^{2+}$  ions

removal by DMS and CPC were therefore established at 0.3 g and 0.2 g, respectively. Similar experiments were conducted to establish optimal masses (results not shown) for  $\text{Cd}^{2+}$  ion removal by DMS and CPC as 0.3 and 0.2 g, respectively.

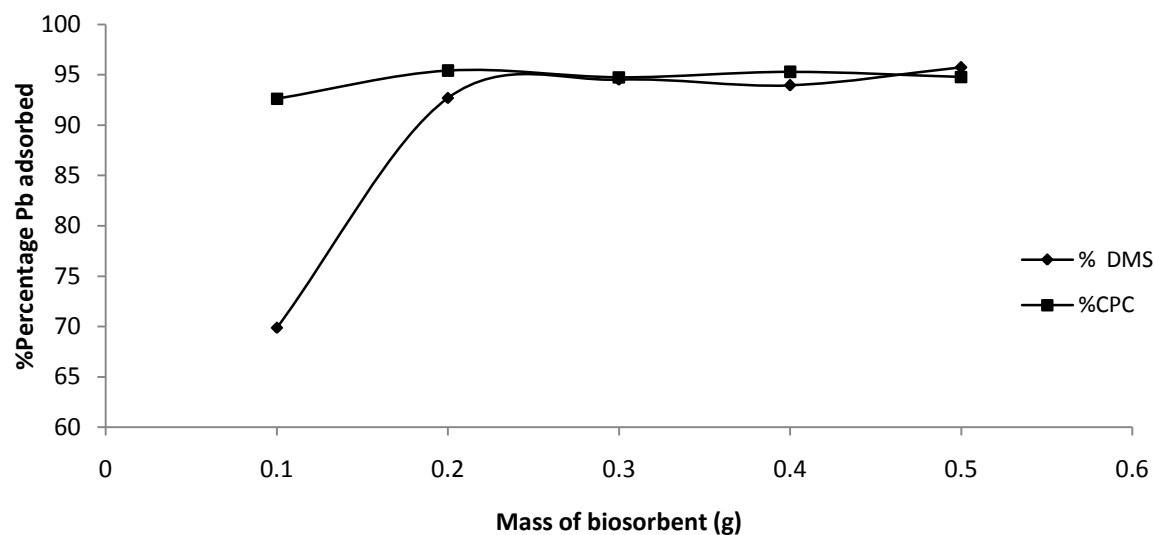
#### Effect of counter electrolyte ions

Figures 10 and 11 show the effect of counter ions from electrolyte  $\text{Na}^+$  and  $\text{K}^+$  (introduced as their chloride salts)





**Figure 8.** Effect of pH on the adsorption of  $Pb^{2+}$  adsorption (%) onto DMS and CPC. Concentration, 250 mg/L; time, 60 min; sorbate volume, 20 ml.

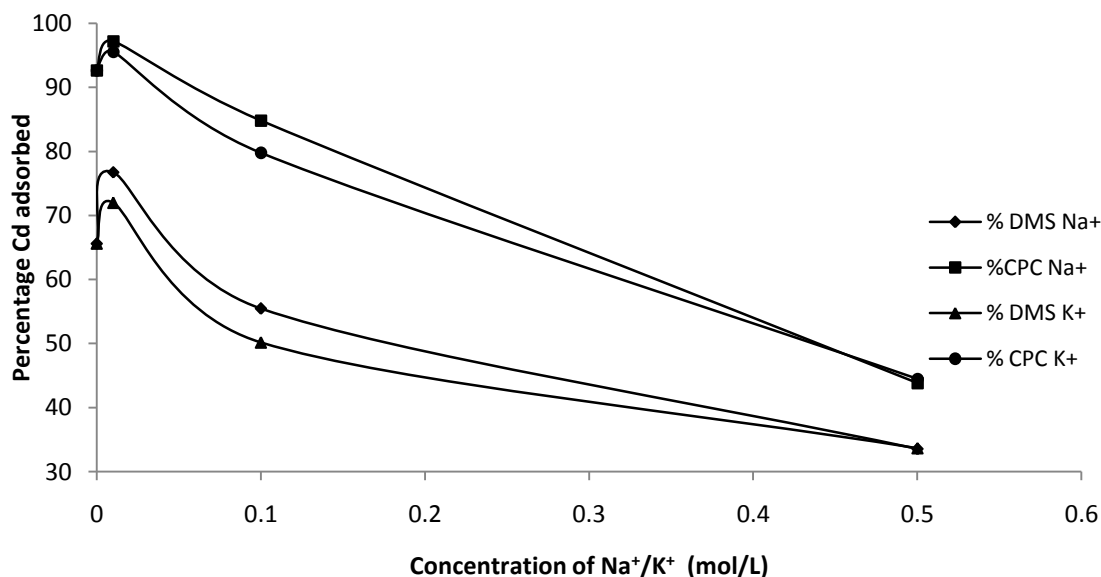


**Figure 9.** Plot showing variation of adsorbent doses for DMS and CPC and quantity of  $Pb^{2+}$  adsorbed from aqueous solution.

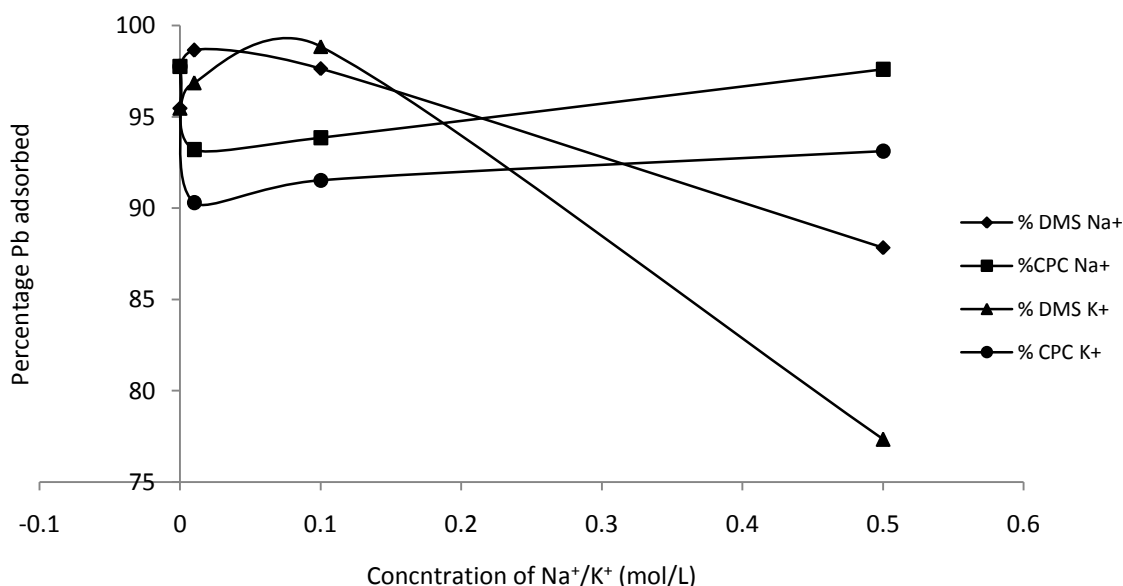
on the uptake capacity of DMS and CPC biosorbents for  $Cd^{2+}$  and  $Pb^{2+}$ , respectively.

Increasing concentration of  $Na^+$  and  $K^+$  from 0.01 to 0.5 M decreased the percentage uptake of  $Cd^{2+}$  ions by the biomasses. Percentage removal of DMS reduced from 76 to 33% in the presence of  $Na^+$ , and from 72 to 34% in the presence of  $K^+$ . CPC biosorbent showed a reduction in metal removal from 97 to 43% in the presence of  $Na^+$  and from 96 to 45% in the presence of  $K^+$ . This is in

agreement with other biomass behavior previously reported (Lodeiro et al., 2006; Schiewer and Volesky, 2000). It is important to note that increased adsorption of  $Cd(II)$  by DMS and CPC was observed when the experiments were conducted in the presence of either 0.01 M  $Na^+$  or 0.01 M  $K^+$  ions compared to experiments conducted in the absence of the ions. However, for the removal of  $Pb^{2+}$ , an increase in concentration of  $Na^+$  and  $K^+$  increased the percentage uptake by CPC only.



**Figure 10.** Chart showing variation in percentage removal of  $\text{Cd}^{2+}$  from aqueous solution by DMS and CPC as a function of varying concentration of electrolyte ions ( $\text{Na}^+$  and  $\text{K}^+$ ). Zero concentration indicated an absence of electrolyte ions.

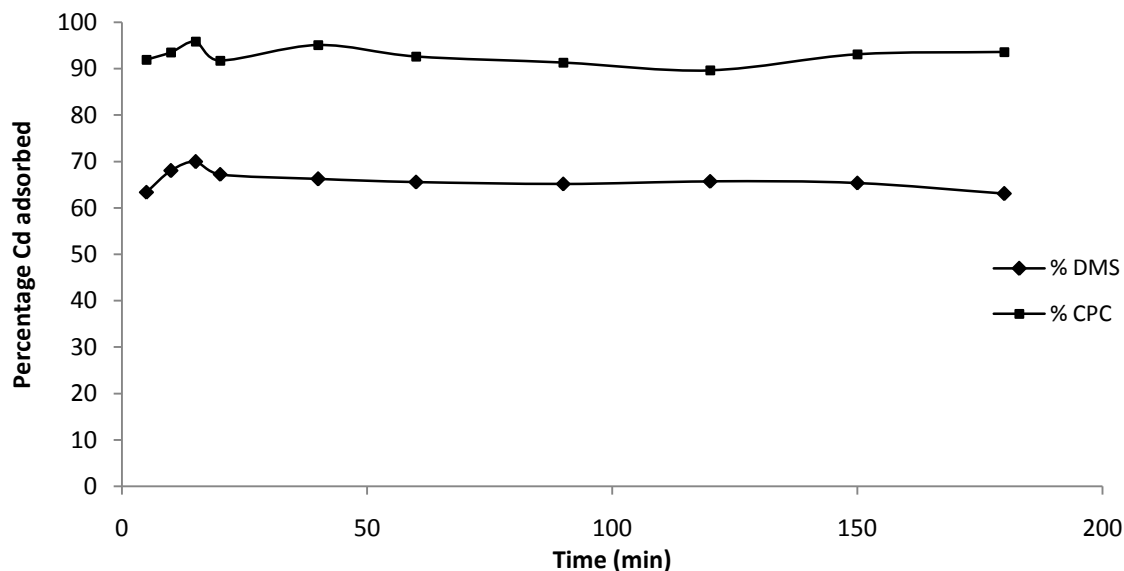


**Figure 11.** Chart showing variation in percentage removal of  $\text{Pb}^{2+}$  from aqueous solution by DMS and CPC as a function of varying concentration of electrolyte ions ( $\text{Na}^+$  and  $\text{K}^+$ ). Zero concentration indicated an absence of electrolyte ions.

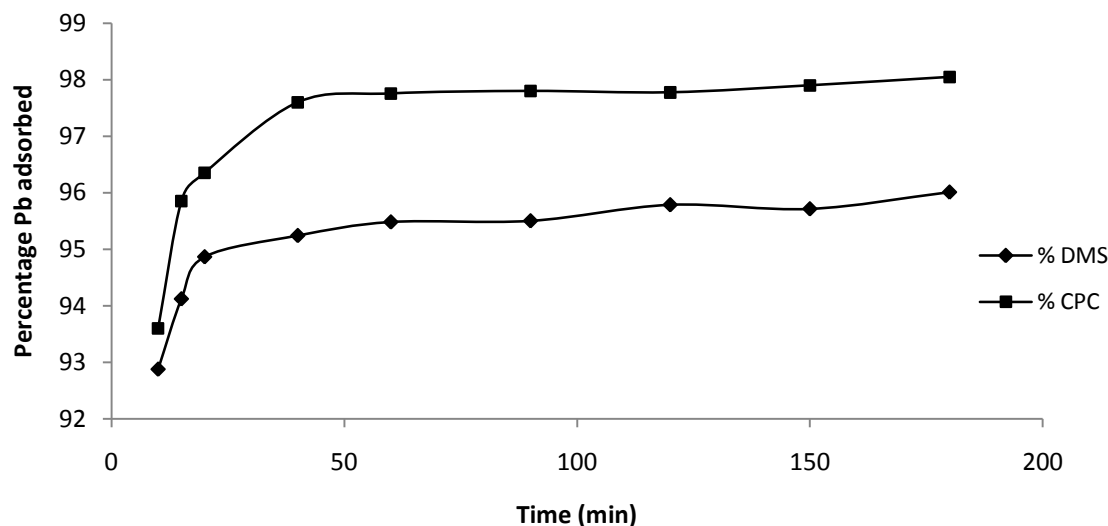
A reverse trend was observed for DMS.

Industrial effluents often contain a mixture of cations. Light metals like Na, K and Ca are usually present especially after pretreatment by precipitation and other agglomeration techniques. These metals can interfere with biosorption exercise and compete for binding sites with metal ions under study (Schiewer and Wong, 2000).

An increase in ionic strength has been shown to suppress metal ion uptake as a result of screening of electrostatic charge (Schiewer and Volesky, 1997). More so, the ions of the metal salts that balance the positive charge of the metal ion are necessarily present in solution and these ions could also affect the metal uptake by forming complexes.



**Figure 12.** Effect of contact time on the adsorption of  $\text{Cd}^{2+}$  by DMS and CPC. Concentration, 250 mg/L.



**Figure 13.** Effect of contact time on the adsorption of  $\text{Pb}^{2+}$  by DMS and CPC. Concentration 250 mg/L

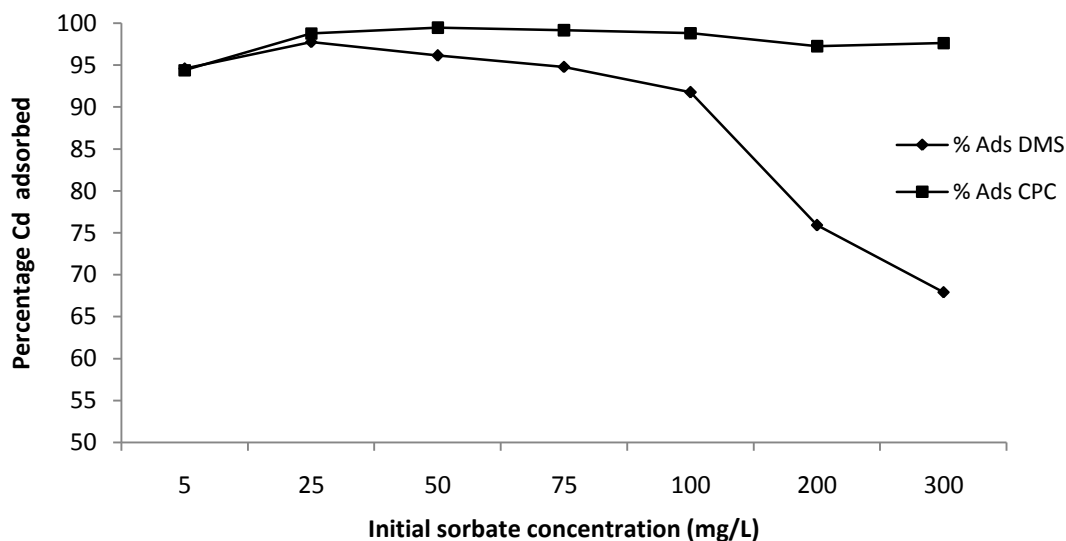
### Effect of contact time

The effect of contact time on the biosorption of  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  ions by both biosorbents are shown in Figures 12 and 13. Figure 12 showed that 15 min was sufficient contact time for both biomasses to achieve equilibrium with  $\text{Cd}^{2+}$  ions, with a removal of 70 and 96% for DMS and CPC, respectively at this time, after which the percentage adsorption reduces gradually with a few percent over the 180 min shaking period. Adsorption of  $\text{Pb}^{2+}$  by both biomasses was optimized after 40 min of contact with the biosorbents as shown in Figure 13.

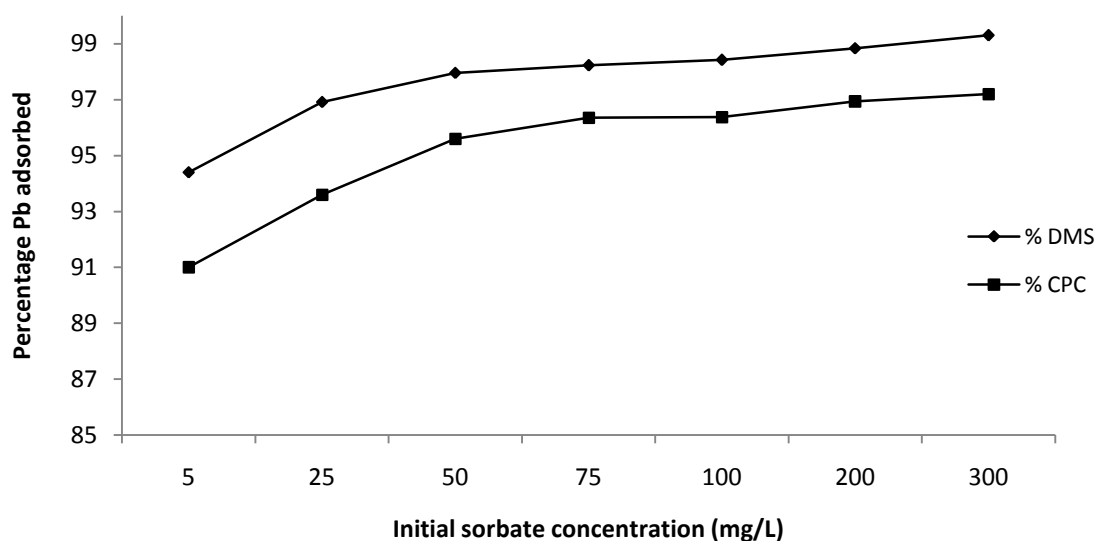
### Effect of initial metal concentration

The effect of adsorbate concentration on CPC and DMS adsorption for  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  was determined at different initial metal concentrations (5 to 300 mg/L). Figure 14 shows that DMS biomass is more effective for  $\text{Cd}^{2+}$  removal at low concentrations when compared to results obtained at higher concentrations. Above 100 mg/L  $\text{Cd}^{2+}$  ions, the percentage removal by DMS drops sharply from 91.7 to 75.91%. Such a biomass presents attractive potential for removing  $\text{Cd}^{2+}$  from dilute solutions.

Percentage  $\text{Cd}^{2+}$  ion removal by CPC increased with



**Figure 14.** Plot of  $\text{Cd}^{2+}$  adsorption by DMS and CPC at various initial metal concentrations.



**Figure 15.** Plot of  $\text{Pb}^{2+}$  adsorption by DMS and CPC at various initial metal concentrations.

increase in  $\text{Cd}^{2+}$  ions, reaching a maximum at 50 mg/L after which percentage removal dropped gradually. Figure 15 shows that an increase in initial  $\text{Pb}^{2+}$  ions brought about an increase in percentage removal for both CPC and DMS. The increase may be attributed to an increase in the driving forces that is, concentration gradient as noted by King et al. (2007).

### Kinetics of adsorption process

Kinetic data obtained in this study was fitted to Equations 8 to 13. Kinetic parameters obtained are shown in Table

1. The results obtained indicate that only the pseudo second order equation was able to satisfactorily fit the kinetic data for DMS and CPC on  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  in the whole data range.  $R^2$  values as shown in Table 1 and are very high (0.9993 to 0.9998). Also, the theoretical  $q_{e2cal}$  values were closer to the experimental  $q_{e2exp}$  values. In this model, the rate-limiting step is a biosorption mechanism involving chemisorption, where metal removal from solution is due to physicochemical interactions between biomass and metal solution (Aksu, 2001). According to the pseudo-second order kinetic model, the rate of biosorption reaction non-linearly decreases with time.

**Table 1.** Kinetic model parameters for Cd<sup>2+</sup> and Pb<sup>2+</sup> biosorption by DMS and CPC.

Model	Cd <sup>2+</sup>		Pb <sup>2+</sup>	
	DMS	CPC	DMS	CPC
<b>Pseudo first order</b>				
k <sub>1</sub> (min <sup>-1</sup> )	9.9 × 10 <sup>-3</sup>	7.8 × 10 <sup>-3</sup>	6.909 × 10 <sup>-2</sup>	1.6121 × 10 <sup>-1</sup>
q <sub>e</sub> (mg/g)	0.22	0.268	0.34	0.36
R <sup>2</sup>	0.1728	0.0986	0.789	0.155
<b>Pseudo second order</b>				
k <sub>2</sub> (g/mg min)	8.05 × 10 <sup>-2</sup>	4.35 × 10 <sup>-1</sup>	2.023 × 10 <sup>-1</sup>	1.33 × 10 <sup>-1</sup>
q <sub>e</sub> cal. (mg/g)	10.66	23.148	16.129	25.00
h (mg/g min)	91.476	233.086	52.63	83.33
R <sup>2</sup>	0.9993	0.9994	0.9998	0.9998
q <sub>e</sub> exp. (mg/g)	11.66	23.96	16.00	24.51
<b>Elovich</b>				
a (mg/g min)	7.128	8.44 × 10 <sup>10</sup>	1.55 × 10 <sup>19</sup>	1.97 × 10 <sup>11</sup>
b (g/mg)	0.989	1.174	3.067	1.213
R <sup>2</sup>	0.9932	0.9354	0.935	0.96
<b>Fractional power</b>				
k (mg/g)	9.12 × 10 <sup>-2</sup>	3.63 × 10 <sup>-2</sup>	2.00 × 10 <sup>-2</sup>	3.40 × 10 <sup>-2</sup>
v (min <sup>-1</sup> )	9.14	21.64	14.79	21.71
R <sup>2</sup>	0.9913	0.9382	0.933	0.957
<b>Intraparticle diffusion</b>				
k <sub>p</sub> (mg/g min <sup>0.5</sup> )	6.781 × 10 <sup>-1</sup>	5.862 × 10 <sup>-1</sup>	1.36 × 10 <sup>-1</sup>	3.47 × 10 <sup>-1</sup>
R <sup>2</sup>	0.9756	0.9669	0.874	0.919

DMS, Mango Stone; CPC, cocoa pod; Cd, cadmium; Pb, lead.

The pseudo first order kinetic model did not appropriately describe the kinetic data in the whole data range. The other three kinetic models (intraparticle diffusion model, elovich model and the fractional power model) also did not give satisfactory fits when fitted for their applicability to the kinetic data. However, it was observed that the biosorption process presented by these models comprised of two phases suggesting their applicability to a particular period of the adsorption process. The three models were then tested on the two phases presented. It was observed that all data obtained before the saturation point of the biomass followed the assumptions of these models as indicated by their regression values. A similar method had been adopted for describing kinetic data (Basha and Murthy, 2007).

### Isotherms of the adsorption process

As shown from the results in Table 2, The Langmuir isotherm showed good correlation for the adsorption of Pb<sup>2+</sup> ions on both biosorbents with a regression R<sup>2</sup> >

0.98, while the regression for Cd<sup>2+</sup> on CPC was poor with R<sup>2</sup> < 0.4. This indicates that Cd<sup>2+</sup> ions do not form a monolayer coverage over the interface between the adsorbent (CPC) as against the kind of coverage formed on DMS. The equilibrium parameter R<sub>L</sub> often referred to as dimensionless separation factor was the calculated for the adsorption of the metal ions on DMS and CPC by the expression (Adebowale et al., 2006)

$$R_L = \frac{1}{(1 + K_L C_i)} \quad (14)$$

Where K<sub>L</sub> is the Langmuir constant obtained from the initial Langmuir plot, and C<sub>i</sub> is the initial concentration (mg/L). The values of R<sub>L</sub> obtained from Equation 14 all fall within 0 and 1 (0 < R<sub>L</sub> < 1), indicating that the adsorption process is favorable (Adebowale et al., 2006; Singh et al., 2006; Zafar et al., 2007). A similar result was presented by Jiang et al. (2009) for the adsorption of Cu<sup>2+</sup> unto amidoximated bagasse. Table 3 shows the comparison of biosorption capacity (q<sub>m</sub>: mg/g) of DMS and CPC for Cd<sup>2+</sup>

**Table 2.** Isotherm constants of two-parameter models for Cd<sup>2+</sup> and Pb<sup>2+</sup> biosorption by DMS and CPC.

Model	Cd <sup>2+</sup>		Pb <sup>2+</sup>	
	DMS	CPC	DMS	CPC
<b>Langmuir</b>				
$K_L$ (L mg <sup>-1</sup> )	0.063	0.305	0.513	0.175
$q_m$ (mg/g)	21.05	12.15	1.90	5.31
$R^2$	0.908	0.3313	0.9868	0.992
$K_R$	0.05-0.76	0.01-0.40	0.01-0.28	0.02-0.53
<b>Freundlich</b>				
$K_F$ (L g <sup>-1</sup> )	1.532	6.184	3.139	1.44
$1/n$	0.543	0.822	1.879	1.118
$R^2$	0.8578	0.6892	0.9755	0.9937
<b>Dubinin-Redushkevich</b>				
$q_{RD}$ (mg/g)	7.07	22.94	22.80	28.31
$\beta$ (kJ <sup>2</sup> /mol <sup>2</sup> )	$4.93 \times 10^{-7}$	$3.97 \times 10^{-7}$	$6.21 \times 10^{-7}$	$9.14 \times 10^{-7}$
$E$ (kJ/mol)	1.007	1.122	0.707	0.739
$R^2$	0.897	0.892	0.905	0.913
<b>Temkin</b>				
$K_T$ (L/g)	$1.01 \times 10^{-1}$	$1.60 \times 10^{-5}$	$3.51 \times 10^{-3}$	$1.25 \times 10^{-1}$
$b_T$ (J/mol)	0.451	0.130	0.080	0.125
$R^2$	0.967	0.920	0.604	0.789

DMS, Mango Stone; CPC, cocoa pod; Cd, cadmium; Pb, lead.

**Table 3.** Comparison of biosorption capacity of DMS and CPC for Cd<sup>2+</sup> and Pb<sup>2+</sup> with that of other biosorbents.

Biosorbent	Cd <sup>2+</sup>	pH	Pb <sup>2+</sup>	pH	Reference
<i>Mucor rouxii</i>	20.3	6.0	-	-	Yan and Viraraghavan (2003)
<i>Phanerochaete chrysosporium</i>	15.2	4.5	-	-	Li et al. (2004)
<i>Ulva lactuca</i>	29.2	5.0	-	-	Sarı and Tuzen (2008)
<i>Phanerochaete chrysosporium</i>	23	6.0	-	-	Say et al. (2001)
<i>Amanita rubescens</i>	27.3	-	-	-	Sarı and Tuzen (2009)
Barley straw	-	-	15.2	5.5	Conrad and Bruun Hansen (2007)
Rice husk	-	-	4	5.5	Conrad and Bruun Hansen (2007)
Hazelnut shell	-	-	1.78	5.5	Conrad and Bruun Hansen (2007)
<i>Zoogloea ramigera</i>	-	-	10.4	4.5	Sağ et al. (1995)
<i>Rhizopus arrhizus</i>	-	-	15.5	5.0	Sağ et al. (1995)
<i>Aspergillus flavus</i>	-	-	13.5	5.0	Akar and Tunalı (2006)
Cocoa shells	-	-	2.60-3.35	2.0	(Meunier et al. 2002)
Cocoa shells	-	-	4.16-6.54	2.0	Meunier et al. (2003)
Cedar bark	-	-	1.32-3.17	2.0	Meunier et al. (2002)
DMS	21.1	5.0	1.90	4.0	Present study
CPC	12.5	4.0	5.31	3.0	Present study

and Pb<sup>2+</sup> ions with that of various biomasses reported in literature. The  $q_m$  values calculated for Cd<sup>2+</sup> was

comparable with those in earlier published work. The biosorption capacity of both biomasses for Pb<sup>2+</sup> was

lower than that for  $\text{Cd}^{2+}$ . Similar values had been reported by other workers using agricultural waste.

The adsorption of  $\text{Pb}^{2+}$  ions onto DMS and CPC was equally described by the Freundlich model. The Freundlich adsorption isotherm supports the heterogeneity of the surface and the exponential distribution of the sites and their energies. The  $K_F$  and  $1/n$  values obtained for the adsorption of  $\text{Cd}^{2+}$  were DMS (1.532 and 0.543) and CPC (6.184 and 0.822), respectively. The  $K_F$  and  $1/n$  values obtained for the adsorption of  $\text{Pb}^{2+}$  were DMS (3.139 and 1.897) and CPC (1.44 and 1.11), respectively.  $1/n$  is an empirical parameter relating to the biosorption intensity and varies with the heterogeneity of the material (Anayurt et al., 2009; Sari and Tuzen, 2008b). Values between 0 to 1 for  $\text{Cd}^{2+}$  indicated that biosorption of the metal onto CPC and DMS was favorable at studied conditions. The D-R isotherm assumes a fixed volume or 'adsorption space' where adsorption takes place. It also describes heterogeneity of adsorption energies within this space independent of temperature. It was observed that the D-R isotherm gave a good fit for the adsorption of both metals to both biomasses when compared with Langmuir, Freundlich and Temkin models. The E values obtained of the biosorption processes were all in the range of ion-exchange reactions (Basha and Murthy, 2007).

## Conclusion

The results of this study indicate that DMS and CPC waste are promising materials for the development of low cost biosorption technology that can be used for the removal of  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  from wastewater effluents. The adsorption processes were strongly affected by pH and the presence of electrolyte ions (Na and K). The extent of competition by the electrolyte ions was influenced by the nature and concentration of the ion. The fast kinetics of the adsorption process and the high percentage removal from concentrated solutions under optimized conditions are useful properties of the adsorbent which can be developed by modification.

Kinetic models evaluated include fractional power model, intraparticle diffusion model, Elovich model and pseudo first and second order models. While the kinetic data for all the adsorption experiments satisfactorily fitted to the pseudo-second order model, the assumptions of the Elovich, intraparticle diffusion and the fractional power models were apparently important before and after the saturation points of the biosorbents. Equilibrium adsorption of both metals could not be described by the simple Langmuir and Freundlich models alone. However, a combination of other two-parameter equilibrium models suggestively describes the nature of the adsorption processes. The R-D model, amongst the evaluated models gave the best fit for all the adsorption processes studied.

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