Adsorption of Cd(II) and Pb(II) onto Humic Acid–Treated Coconut (*Cocos nucifera*) Husk

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Abstract: This study was conducted to characterize the adsorption of Cd^{2+} and Pb^{2+} by raw coconut husk (RCH) and humic acid–treated coconut husk (HACH). Grounded and sieved coconut husk (CH) from Sri Lanka was treated with humic acid to use as the adsorbent in laboratory experiments. Capacities of HACH and RCH for adsorption of Cd^{2+} and Pb^{2+} at different pH, ionic strengths, initial metal concentrations, and contact times between adsorbent and adsorbate were measured. The effects of binary metal solution, anions, and cations on adsorptions of Cd^{2+} and Pb^{2+} by treated and nontreated CH in batch experiments were also examined. The surface characteristics of HACH and RCH were investigated by scanning electron micrography (SEM), X-ray energy dispersion analysis (EDAX), methylene blue (MB), and the Brunauer, Emmett, and Teller (BET) methods to explain the results. Results showed that adsorption of Cd^{2+} and Pb^{2+} ions by HACH was independent of pH and ionic strength. The maximum adsorption capacities of Cd^{2+} and Pb^{2+} of HACH were 47.28 and 66.26 $mg\,g^{-1}$ and were greater than 24.24 and 21.21 $mg\,g^{-1}$ for RCH. The adsorption of both Cd^{2+} and Pb^{2+} onto HACH was a chemical sorption, and Pb^{2+} adsorption needed a longer reaction time than Cd^{2+} adsorption. The adsorption reaction rates of Cd^{2+} and Pb^{2+} of HACH were 0.056 and 3.17 $mg\,g^{-1}\,min^{-1}$. Some anions and cations affected the adsorption of Cd^{2+} and Pb^{2+} onto HACH. Based on the results from adsorption tests under different conditions, RCH and HACH are effective for individual removal of Cd^{2+} and Pb^{2+} from aqueous solutions. However, humic acid treatment effectively removes metal ions from single metal solutions, although the removal of metal ions in the presence of coexisting ions and other anions and cations could be retarded. **DOI:** 10.1061/(ASCE)HZ.2153-5515.0000196.

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Introduction

Industrial discharge of toxic substances like heavy metals and their accumulation in the environment causes degradation of the ecosystem (Bansal et al. 2009; Bulgariu and Bulgariu 2012; Lesmana et al. 2009; Xu et al. 2008). At present, various sources of heavy metals are recognized: electroplating, batteries, metal surface coating treatments, and industries such as textile, pigments, plastics, and mining (Bulgariu and Bulgariu 2012; Cheng et al. 2012). The removal of heavy metals from industrial wastewater is of great importance because of their impact on the environment. As a result, different treatment methods, including chemical precipitation (Fu et al. 2012; Kornboonraksa et al. 2009), coagulation-flocculation (Amakrone et al. 1997), floatation and electrochemical processes (Belkacem et al. 2008; Raghu and Ahmed Basha 2007), adsorption (Bansal et al. 2009; El-Shafey 2007; Najim et al. 2009; Ofomaja and Ho 2007), membrane filtration (Mavrov et al. 2003), and ion exchange (Dabrowski et al. 2004) have been used in removing heavy metals from wastewater. The use of advanced technologies for treating wastewater, however, has become limited, especially in developing countries, because of their high cost and low feasibility in small-scale industries (Liu et al. 2010; Mahmoud et al. 2010; Pagnanelli et al. 2001).

Among the different methods of removing heavy metals, in contrast, biosorption has become popular recently because of the simplicity of the process, effectiveness, and low cost (Cheng et al. 2012). Different types of biosorbents from agricultural by-products and biowaste materials such as sawdust (Božić et al. 2009; Sewwandi et al. 2012), rice husk (Bansal et al. 2009), algal waste biomass (Bulgariu and Bulgariu 2012), and oil extracts (Rao and Khan 2009) have been used in heavy metal removal. Raw and modified sawdust (SD) have been used by Sewwandi et al. (2012) to remove Cd^{2+} and Pb^{2+} from aqueous solutions. They found that raw SD is more capable of removing mentioned metals than acid- or base-treated SD. Božić et al. (2009) studied the abilities of SD of three different trees to remove Cu^{2+} and Fe^{2+} from synthetic wastewater and reported that the initial concentration of the metals and adsorbent concentration strongly affected the removal process.

Rice husk (RH) has been used with pretreatments such as boiling and formaldehyde treatments to remove Cr^{6+} from synthetic wastewater (Bansal et al. 2009), and the two treatments were not found to be different. Boiled RH would be more prevalent in small-scale industries to remove Cr^{6+}. Green algae waste biomass has been used to remove Pb^{2+}, Cd^{2+}, and Co^{2+} from aqueous solutions. The best removal of heavy metals was obtained at pH 5

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and a contact time of 60 s (Bulgariu and Bulgariu 2012). Rao and Khan (2009) studied the capacity of Neem oil cake to remove Cu^{2+} and Cd^{2+}. The results showed that the maximum sorption of metals onto the biosorbent occurs in acidic medium and that it increases with an increase in the initial metal concentration.

Coconut husk (CH) is a by-product of the coconut industry, and it is abundantly available in tropical countries such as India, Sri Lanka, and Thailand. Coconut husk is rich in short/medium length fibers with a typical diameter of hundreds of micrometers and powdered coir pith/dust with a particle size ranging from a few micrometers to a few millimeters (Nam et al. 2011). According to Abad et al. (2002), the coir dust obtained from Sri Lankan coconut (*Cocos nucifera L.*) averages 476 $\mathrm{g\,kg^{-1}}$ lignin, 329 $\mathrm{g\,kg^{-1}}$ cellulose, and 56 $\mathrm{g\,kg^{-1}}$ hemicellulose on dry weight basis. Raw and treated coir pith have also been used for wastewater treatment. Makehelwala et al. (2009) studied the mechanism of Cr^{6+} adsorption by coir pith and found that reductive adsorption of Cr^{6+} occurred. Moreover, they found that the adsorption is dependent on pH and ionic strength. Adsorptions of Co^{2+}, Cr^{3+}, and Ni^{2+} onto coir pith have been studied as single ions and a mixture of ions (Parab et al. 2006). The results of the study showed that coir pith is efficient as a low cost adsorbent to remove these metals. In addition, coir pith carbon (Kavitha and Namasivayam 2007) and $ZnCl_2$-activated coir pith carbon (Namasivayam and Sangeetha 2004) have been used to remove methylene blue and phosphate in laboratory experiments. However, although modification of different biomass types with chemical substances has given better removal of heavy metals from wastewater (Gode et al. 2008; Liu et al. 2010; Wong et al. 2003), less attention has been paid to the treatment of CH to increase its metal removal efficiency.

Humic acid is a naturally occurring substance in soils, marine and lake sediments, natural waters, and peat that has a comparatively large molecule. It contains functional groups such as $\mathrm{-COOH}$, $\mathrm{-OH}$, $\mathrm{-C = O}$, and $\mathrm{-NH_2}$ that can affect the bonding distribution of cations of trace metals in the environment (Coles and Yong 2006; Lubal et al. 1998). Therefore, the use of humic acid for modification of a biomass may enhance its metal uptake capacity. In addition, real wastewater contains various physical and chemical substances including heavy metals, anions, and cations that can interfere with the adsorption of heavy metals onto biosorbents. Thus, it is important to study the adsorption of heavy metals in binary metal solutions and the effect of anions and cations on adsorption. Certain anions (SO_4^{2-} and PO_4^{3-}) and cations (Mg^{2+} and Ca^{2+}) that are commonly found in natural environment can interfere with the adsorption of heavy metals in actual field conditions. Therefore, the objectives of this study were (1) to determine the adsorption capacity of HACH for Cd^{2+} and Pb^{2+} adsorption at different pH, ionic strength, initial metal concentration, and contact time of adsorbent and adsorbate; (2) to study the effects of Cd^{2+} and Pb^{2+} on adsorption in a binary metal solution; and (3) to study the effects of anions and cations on adsorption.

Materials and Methods

Materials Used

Coconut husk from the species *Cocos nucifera* is abundantly available in Sri Lanka as a by-product of the coconut industry. Coconut husk was collected and sundried for several days after removal of the nut. Collected CH was ground and sieved to obtain the <350 μm fraction for the experiments. Humic acid sodium salt (Sigma Aldrich, St. Louis, Missouri), hereafter called sodium humate, was used to treat CH. Sodium humate salts were dissolved in distilled water to obtain a 50 $\mathrm{mg\,L^{-1}}$ solution. The pH of the sodium humate solution was 6.85. Stock solutions of Cd^{2+} and Pb^{2+} (1,000 $\mathrm{mg\,L^{-1}}$) were prepared in distilled water using $CdCl_2$ and $PbCl_2$ (Sigma Aldrich, St. Louis, Missouri), respectively. Stock solutions were diluted with distilled water as required to obtain the experimental solutions.

Treatment of CH with Sodium Humate

The biomaterial treatment method described by Gode et al. (2008) was adopted to treat the CH in this study. A portion of CH was treated with sodium humate to obtain humic acid–treated CH (HACH). The CH was stirred overnight with 50 $\mathrm{mg\,L^{-1}}$ sodium humate solution at a 1:25 mass:volume ratio at a rate of 400 revolutions per minute (rpm). Then, the suspension was filtered through a Whatman 42 filter, and the residue was washed with distilled water three times to remove the remaining sodium humate. Finally, the residue was dried at 50°C until the weight became constant.

Surface Area and Pore Size Distribution Analysis

The surface area of CH was analyzed by the methylene blue (MB) adsorption and N_2 adsorption techniques (Santamarina et al. 2002) for <350 Fm particles. A spectrophotometer (UV-160A, Shimadzu, Japan) was used for the MB adsorption technique, and the complete cation replacement determined by the titration curve was used to derive the surface area value. The chemical formula of MB is $C_{16}H_{18}ClN_3S$, and in aqueous solution, it is a cationic dye, $C_{16}H_{18}ClN_3S^+$, that can be adsorbed to negatively charged surfaces. The amount of adsorbed MB is used to determine the surface area of the particles (Chen et al. 1999). A TriStar II 3020 surface area and porosity analyzer (Micromeritics, Norcross, Georgia) was used in this study to analyze the surface area using the Brunauer, Emmett, and Teller (BET) method. Surface area measurement by the N_2 adsorption technique was performed on a dry specimen obtained by heating and degassing. The measurement was carried out in triplicate. The pore size distribution of the material was determined using the adsorption isotherms obtained from the N_2 adsorption technique.

Scanning Electron Microscopy and X-Ray Energy Dispersion Analysis

Scanning electron microscopy (SEM) and energy dispersion analysis (EDAX) were carried out to study the surface microstructures of the CH particles and to obtain the elemental mapping on the surfaces of metal-adsorbed CH particles, respectively. A scanning electron microscope [Quanta 200 Field Emission Gun (FEG), Hillsboro, OR] and EDAX analyzer (Oxford INCA Energy+, Cardiff, United Kingdom) were used in this study.

Surface Charge Characterization

The surface charge characterization of CH was done in terms of ξ potential as a function of pH. The pH of the solution was adjusted using 0.1 M HCl or 0.1 M NaOH. The experiment was conducted to determine the electrophoretic mobility of the CH particles at different pH values using a Zeta meter (Model 502, Nihon Rufuto, Japan). The ξ potential values were calculated at every pH using the Smoluchowski equation (Sze et al. 2003).

Fourier Transform Infrared Spectroscopy Analysis

The infrared spectra of RCH, HACH, and separately Cd^{2+}- and Pb^{2+}-treated HACH were analyzed by Fourier transform infrared spectroscopy (FT-IR) (Nicolet 6700 USA series, Waltham, MA). Transmission spectra were obtained between 400–4,000 cm^{-1}, with 4 cm^{-1} resolution and 128 scans. Sample pellets were prepared for FT-IR by mixing 20 mg of vacuum-dried samples (<350 μm) with FT-IR grade 100 mg of KBr. Each pellet contained approximately 70 mg of the aforementioned mixture. Spectral analyses were performed using OMNIC (version 7.3) software.

Effect of pH and Background Ion Concentration on Adsorption

Adsorption experiments were conducted for HACH at 0.01, 0.005, and 0.001 $\mathrm{M\,NaNO_3}$ ionic strength levels. To avoid the effect of precipitation on adsorption, it was decided to use the values measured in the pH range from 4–8. At the same time, the experiment was conducted using RCH at 0.001 $\mathrm{M\,NaNO_3}$ concentration at the same pH range. The adsorbent concentration used was 2.5 $\mathrm{g\,L^{-1}}$. The pH of solutions was adjusted using 0.1 $\mathrm{M\,HNO_3}$ or 0.1 M NaOH, and 10 mL samples at each pH were withdrawn to polypropylene tubes and shaken in a water bath shaker for 24 h at 100 rpm (EYELA B603, Japan). Next, the samples were centrifuged (2,500 rpm, 10 min), filtered with a membrane filter (Millipore 0.45 μm, Billerica, MA) after measuring the final pH of the samples, and used in data analysis. The filtrate was acidified for analysis by flame atomic absorption spectrometry (GBC 933; NSW, Australia). The initial concentrations of $\mathrm{Cd^{2+}}$ and $\mathrm{Pb^{2+}}$ used were 20 and 100 $\mathrm{mg\,L^{-1}}$, respectively.

Effect of Initial Metal Ion Concentration on Adsorption

Batch adsorption experiments were carried out for 2.5 $\mathrm{g\,L^{-1}}$ raw and modified coconut husk samples at pH ~7. Suspensions of RCH and HACH were stirred for 2 h at a speed of 300 rpm to hydrate the surfaces of the material. The 10 mL samples from each RCH and HACH suspension were transferred to capped polypropylene tubes. Initial $\mathrm{Cd^{2+}}$ and $\mathrm{Pb^{2+}}$ concentrations varied from 2.5–200 and 25–200 $\mathrm{mg\,L^{-1}}$, respectively. The ionic strength of the solutions was maintained at 0.001 $\mathrm{M\,NaNO_3}$ concentration. Tubes were equilibrated for 24 h at 100 rpm in a water bath shaker. After that, the supernatant was centrifuged (2,500 rpm, 10 min) and filtered for metal analysis. Detection of $\mathrm{Cd^{2+}}$ and $\mathrm{Pb^{2+}}$ were carried out using the flame method of an atomic adsorption spectrophotometer (AAS).

The data of $\mathrm{Cd^{2+}}$ and $\mathrm{Pb^{2+}}$ adsorption onto adsorbents was fitted to the Langmuir isotherm model [Eq. (1)] and Freundlich isotherm model [Eq. (2)] (Bulgariu and Bulgariu 2012; Cheng et al. 2012; Demirbas 2008; Sari et al. 2011). The essential characteristic and feasibility of the Langmuir isotherm model, which is known as the separation factor, R_L [Eq. (3)], was determined (Bansal et al. 2009; Rao and Khan 2009). Model fitting was done using Origin 7 software (OriginLab Corporation, Northampton, Massachussets)

$$q_e = \frac{q_m b C_e}{(1 + bC_e)} \tag{1}$$

$$q_e = K_f C_e^{1/n} \tag{2}$$

where q_e = weight of metal ions adsorbed per gram of adsorbent at equilibrium ($\mathrm{mg\,g^{-1}}$); C_e = equilibrium aqueous metal ion concentration ($\mathrm{mg\,L^{-1}}$); q_m = maximum adsorption capacity ($\mathrm{mg\,g^{-1}}$); b = Langmuir constant related to the energy of adsorption ($\mathrm{L\,mg^{-1}}$); K_f = adsorption capacity ($\mathrm{mg\,g^{-1}}$); and n = adsorption intensity

$$R_L = \frac{1}{1 + bC_i} \tag{3}$$

where C_i = initial metal concentration ($\mathrm{mg\,L^{-1}}$).

The value of R_L is a positive number, and the magnitude of R_L determines the feasibility of adsorption. If $R_L = 1$, biosorption isotherm becomes linear; $R_L = 0$–1, favorable for biosorption; $R_L > 1$, unfavorable for biosorption; and $R_L = 0$, biosorption is irreversible.

Effect of Contact Time on Adsorption

To investigate the mechanism of adsorption of $\mathrm{Cd^{2+}}$ and $\mathrm{Pb^{2+}}$ onto HACH, the effect of contact time on adsorption was studied using a 2.5 $\mathrm{g\,L^{-1}}$ suspension of HACH at pH ~7. The ionic strength was maintained at 0.001 $\mathrm{M\,NaNO_3}$ for all experiments. The suspensions of HACH were hydrated by stirring at 300 rpm for 3 h. Then, the suspension was spiked with the required amount of metal solutions to maintain the initial concentrations of 20 $\mathrm{mg\,L^{-1}}$ and 100 $\mathrm{mg\,L^{-1}}$ for $\mathrm{Cd^{2+}}$ and $\mathrm{Pb^{2+}}$, respectively. Samples of 10 mL were taken from the solution at known time intervals. After centrifugation, the supernatant was transferred by membrane filtration (0.45 μm) for metal analysis. Detections of $\mathrm{Cd^{2+}}$ and $\mathrm{Pb^{2+}}$ were carried out using the flame method of the AAS. The data from adsorption kinetic experiments were analyzed using pseudo first order [Eqs. (4*a*) and (4*b*)] and pseudo second order [Eq. (5)] models (Javed et al. 2007; Jústiz-Smith et al. 2008; Ofomaja and Ho 2007). The pseudo first order model assumes nondissociating molecular adsorption, whereas the pseudo second order model assumes the chemisorptions of the adsorbate onto the adsorbent where exchange or sharing of electrons occurred between the adsorbate and active sites of the adsorbent (Rajapaksha et al. 2011)

$$\frac{dq}{dt} = k_1(q_e - q_t) \tag{4a}$$

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \tag{4b}$$

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{5}$$

where q_t = amount adsorbed per g of adsorbent at time t ($\mathrm{mg\,g^{-1}}$); q_e = amount adsorbed per g of adsorbent at equilibrium ($\mathrm{mg\,g^{-1}}$); k_1 = Lagergren rate constant ($\mathrm{min^{-1}}$); t = time (min); and k_2 = pseudo second order constant ($\mathrm{g\,mg^{-1}\,min^{-1}}$).

Further, the initial adsorption rate, h ($\mathrm{mg\,g^{-1}\,min^{-1}}$) as $t \to 0$ can be defined as Eq. (6)

$$h = k_2 q_e^2 \tag{6}$$

The best fitting model was selected based on the correlation coefficient, fitting, and measured amount of metals adsorbed onto the HACH at the equilibrium.

Desorption Experiments

Desorption experiments were conducted to study the effect of water on leaching of adsorbed metals from HACH. After the adsorption of metals in batch tests, the adsorbent was washed with distilled water twice, mixed with distilled water, and filtered in a Büchner funnel. Then, the adsorbent was shaken with 10 mL of distilled water at 300 rpm for 3 h. After that, suspension was filtered and analyzed for heavy metals using the flame method on the AAS.

Effect of Competitive Ion on Adsorption

Adsorption experiments were conducted to study the effect of competitive ions on adsorption onto HACH as described by Sewwandi et al. (2012). The effect of Cd^{2+} on Pb^{2+} adsorption onto HACH and the effect of Pb^{2+} on Cd^{2+} adsorption onto HACH were studied. Initial concentrations of Cd^{2+} and Pb^{2+} used for the experiments were 20 and 100 $mg\,L^{-1}$, respectively. In addition, the effects of other ions commonly found in wastewater (Ca^{2+}, Mg^{2+}, SO_4^{2-}, and PO_4^{3-}) were studied. The concentrations of these ions were the same as those that Sewwandi et al. (2012) used. Concentrations of anions and cations were selected based on World Health Organization standard values of the respective ion (Ramakrishnaiah et al. 2009).

Results and Discussion

Characterization of Coconut Husk

Coconut husk surface areas determined by the MB adsorption and N_2 adsorption techniques were 270.49 and 1.83 $m^2\,g^{-1}$, respectively. The difference in experimental conditions used by the two methods could be the reason for the difference in surface area. The MB adsorption technique is performed under wet conditions, whereas the N_2 adsorption technique is performed on a dry sample, which is accomplished by heating and degassing the sample (Santamarina et al. 2002). Because the adsorbate can reach the interlayer surfaces under wet conditions, the surface area determined by the MB adsorption technique is higher than in the N_2 adsorption technique, in which gas cannot cover the interlayer surfaces. Similar variations from the two methods have been observed by Chen et al. (1999) for montmorillonite soil and Santamarina et al. (2002) for soils. In addition, the results from the N_2 adsorption showed that more than 60% of the total volume was occupied by <10 nm size pores.

Zeta potential analysis of RCH and HACH with pH shows that both materials were negatively charged in the pH range of 3–11 (not shown). The ξ potential values varied from -8 to -12 mV within the pH range studied.

SEM and EDAX Analysis

Scanning electron micrographs of RCH and HACH are shown in Figs. 1(a and b), respectively, with a magnification of x400. Surface texture and porosity can reveal the morphological features and surface characteristics of biosorbents. It is clear from the SEM images that both RCH and HACH have numerous voids with an irregular structure and are rich in fine pores. Figs. 2 and 3 showed the SEM images and SEM-EDAX spectrum of Cd^{2+}- and Pb^{2+}-adsorbed HACH, respectively. The SEM-EDAX spectra for Cd^{2+} and Pb^{2+} indicate the adsorption of the respective metal onto the active sites of HACH. Accordingly, the weight percentage of Cd^{2+} and Pb^{2+} adsorbed onto HACH are 1.3 and 4.36%, respectively.

FT-IR Analysis

The FT-IR spectrums of RCH, HACH, and Cd^{2+}- and Pb^{2+}-adsorbed HACH are shown in Fig. 4. Only slight differences were observed between RCH and HACH. The characteristic peak at around 1,637 cm^{-1} can be observed as the —OH bending of adsorbed water and —OH groups (Oh 2005). The bands observed at 1,514 cm^{-1} are because of $C = C$ stretching vibrations of aromatic bonds (Makehelwala et al. 2009). Peaks at $1{,}525 - 1{,}460$ cm^{-1} can be assigned to $-CH_3$ and $-CH_2$ deformations (Pretsch et al. 1989). Symmetric stretching vibrations at around 1,412 cm^{-1} are assigned to $-COO^-$ groups (Kitadai et al. 2009). The C—H deformation vibration and O—H deformation modes of alcohol and phenolic groups of cellulose appeared around 1,375 cm^{-1} (Pretsch et al. 1989).

Disappearance of C—H deformation vibration and O—H deformation modes of alcohol and phenolic groups of cellulose at 1,375 cm^{-1} (Pretsch et al. 1989) were observed in HACH. Bands between 1,250–1,550 cm^{-1} shifted to low wave numbers after humic acid treatment. However, several changes in infrared (IR) spectra can be identified between HACH before and after metal

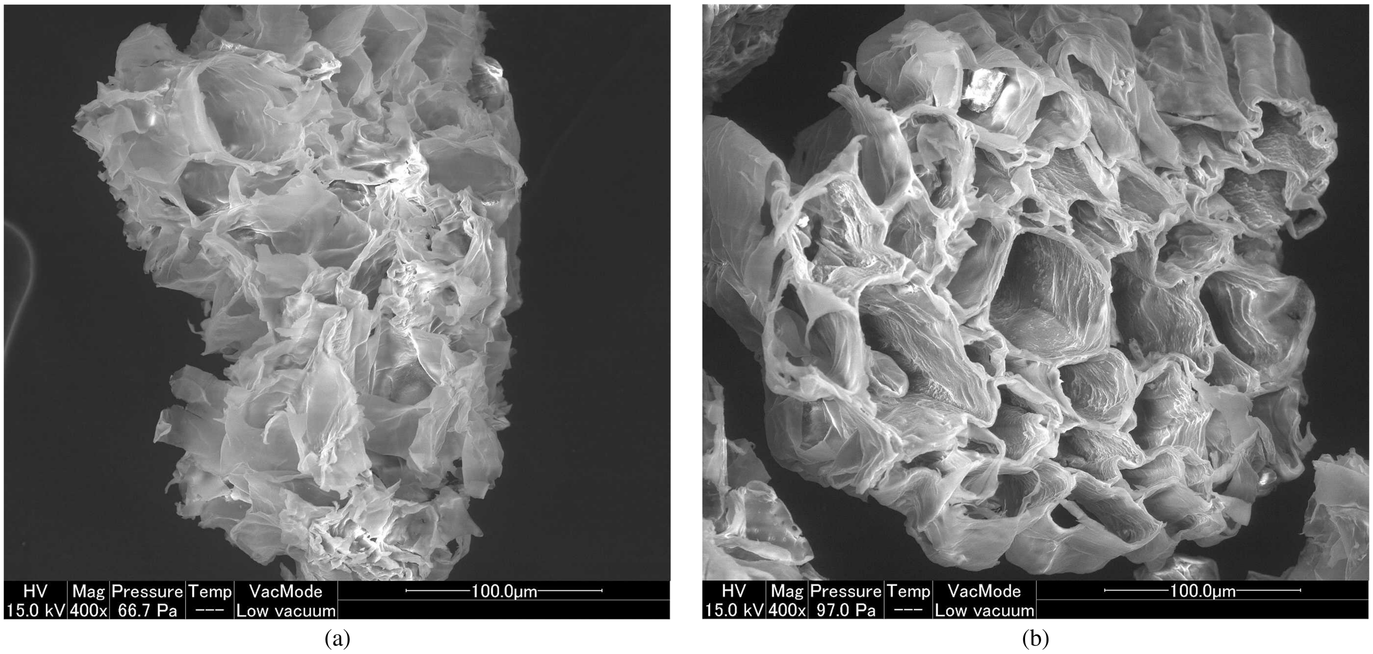
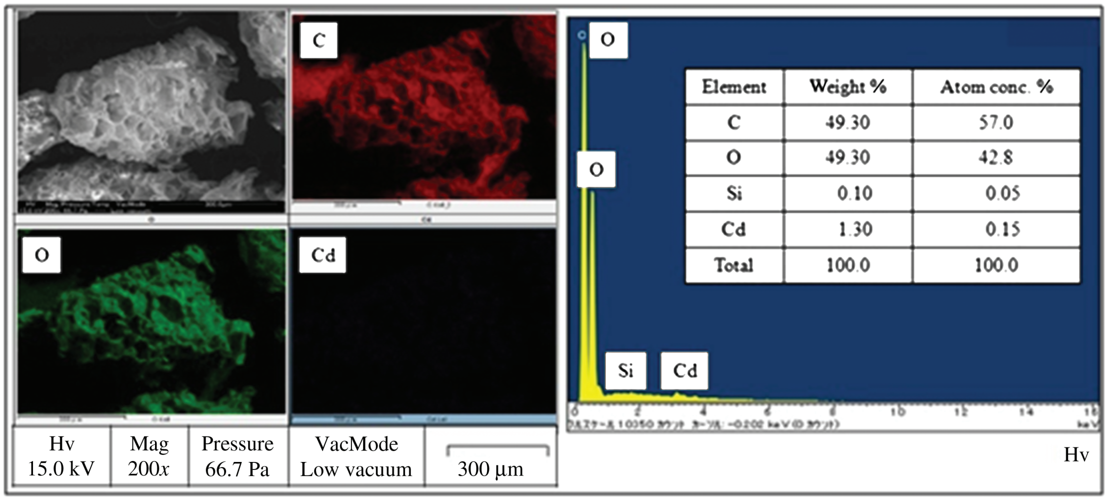


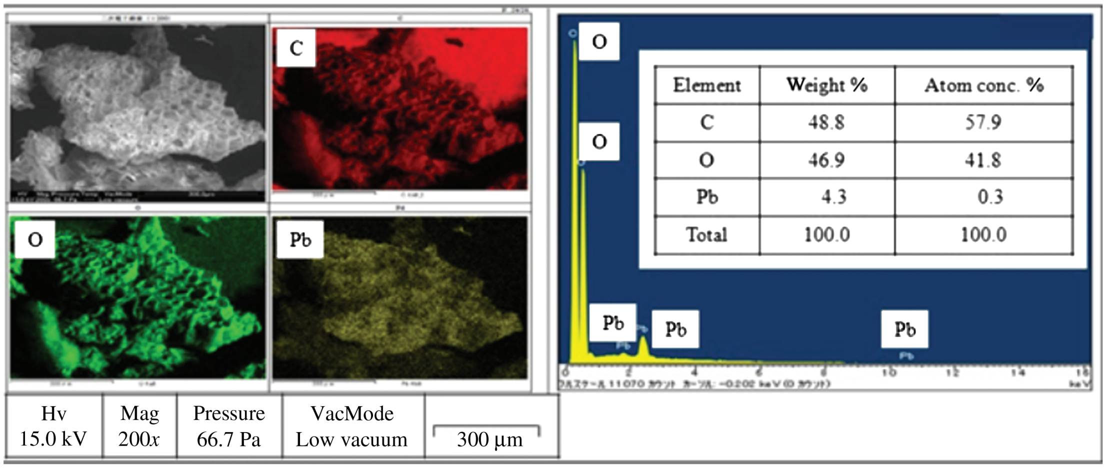
Fig. 1. Scanning electron micrograph of (a) RCH; (b) HACH



Element	Weight %	Atom conc. %
C	49.30	57.0
O	49.30	42.8
Si	0.10	0.05
Cd	1.30	0.15
Total	100.0	100.0

Hv	Mag	Pressure	VacMode	
15.0 kV	200x	66.7 Pa	Low vacuum	300 μm

Fig. 2. (Color) Scanning electron micrograph and SEM-EDAX spectrum of Cd^{2+} adsorbed HACH



Element	Weight %	Atom conc. %
C	48.8	57.9
O	46.9	41.8
Pb	4.3	0.3
Total	100.0	100.0

Hv	Mag	Pressure	VacMode	
15.0 kV	200x	66.7 Pa	Low vacuum	300 μm

Fig. 3. (Color) Scanning electron micrograph and SEM-EDAX spectrum of Pb^{2+} adsorbed HACH

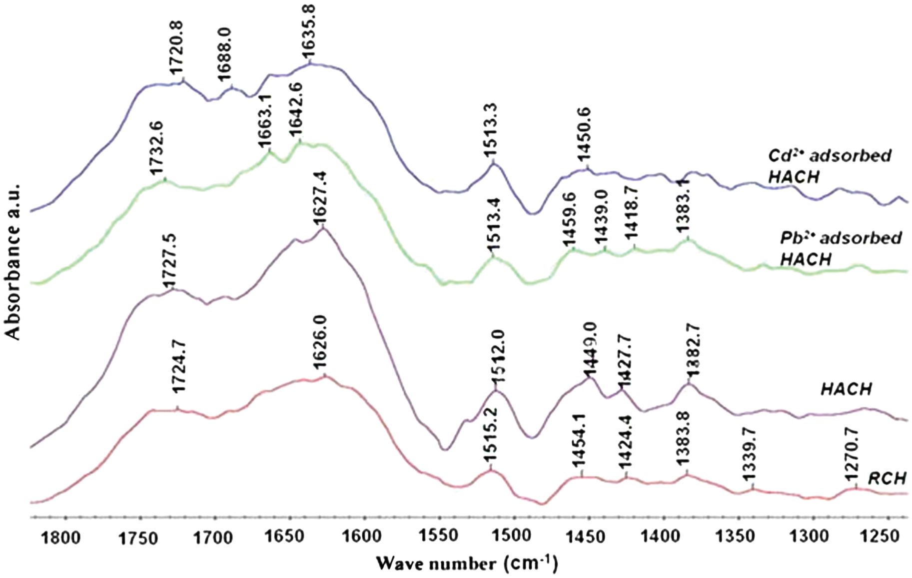


Fig. 4. (Color) FT-IR spectra of RCH, HACH, and Cd^{2+} and Pb^{2+} adsorbed HACH

adsorption. The board band intensity at around 1,730 cm^{-1}, which is assigned to stretching modes of the carbonyl ($C = O$) bond in the $-COOH$ groups (Anirudhan et al. 2010), has shifted to low wave numbers after both Cd^{2+} and Pb^{2+} adsorption (Fig. 4).

The wave numbers that have been shifted to lower values in $C = O$ stretching for metal-adsorbed HACH strongly indicate the interaction between $-COOH$ groups and metal ions. Therefore, this result suggests the adsorption of metal ions to $-COOH$ groups through the $C-O-M$ bond ($M = Cd^{2+}$ or Pb^{2+}) through monodentate adsorption (Hug and Bahnemann 2006).

Effect of pH and Ionic Strength on Adsorption

The adsorption process is affected by pH because it affects the surface charge of the adsorbent, species of adsorbate, and the degree of ionization (Naiya et al. 2009a). The variations of Cd^{2+} and Pb^{2+} adsorption onto HACH with final pH at different ionic strength levels are given in Fig. 5. The adsorption process is independent of the pH range studied in this study. Because of the reactions that have taken place in the adsorption of metal ions to the adsorbent, the pH of the solution is changed. However, Naiya et al. (2009a) found that when the pH of the solution is higher ($pH > 6$), total Pb^{2+} removal is increased because of the formation of $Pb(OH)_2$ precipitate, though there is a decrease in adsorption.

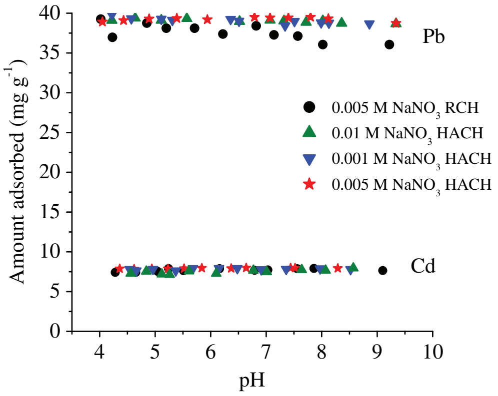


Fig. 5. (Color) Variation of Cd^{2+} and Pb^{2+} adsorption with pH and ionic strength

The mechanism of adsorption of metals onto the biosorbents can be determined by examining the ionic strength dependency of the process. Thus, if the adsorption process shows an ionic strength dependency, the mechanism of adsorption is binding to the outer sphere of surface complexes. In contrast, in the inner sphere bonding mechanism, the effect of ionic strength on adsorption is not observed (Bansal et al. 2009; Tang et al. 2009). The results shown in Fig. 5 indicate that adsorption of Cd^{2+} and Pb^{2+} onto CH shows no dependence on ionic strength of the solution, which indicates that an inner sphere bonding mechanism is involved in adsorption. Because the adsorption capacities are independent of ionic strength of the solutions, 0.001 M $NaNO_3$ was used in later experiments.

Effect of Initial Metal Concentration on Adsorption

Langmuir and Freundlich isotherm models were used to analyze the data. Langmuir isotherm model fitting curves for the data obtained along with the fitted equation from the isotherm experiments are given in Fig. 6. Adsorption of Cd^{2+} onto RCH was higher than HACH up to the initial concentration of ~100 mg L^{-1} (equilibrium concentration ~10 mg L^{-1}), and after that, the reverse occurred [Fig. 6(a)]. The Pb^{2+} adsorption was significantly higher onto HACH than onto RCH for the entire range of the initial concentration [Fig. 6(b)]. Adsorption of both Cd^{2+} and Pb^{2+} was well fitted to the Langmuir isotherm model, which indicates that monolayer adsorption is predominant. In monolayer adsorption, metal ions are adsorbed onto the homogenous surfaces of the adsorbent without interaction between adsorbed molecules (Cheng et al. 2012; Sari et al. 2011). Langmuir model fitting parameters are shown in Table 1. Higher correlation coefficient values may indicate that the heavy metal ions utilize their single molecular forms to adsorb metal ions onto both RCH and HACH within the concentration range used in this study (Cheng et al. 2012; Rao and Khan 2009; Sari et al. 2011).

Table 1. Langmuir Adsorption Parameters for Adsorption of Cd^{2+} and Pb^{2+}

Metal	Adsorbent	b (L mg^{-1})	q_m (mg g^{-1})	r^2	R_L
Cd^{2+}	RCH	0.953	24.2	0.89	0.005–0.290
	HACH	0.092	47.3	0.92	0.005–0.010
Pb^{2+}	RCH	3.680	21.2	0.95	0.001–0.010
	HACH	0.989	66.1	0.85	0.060–0.080

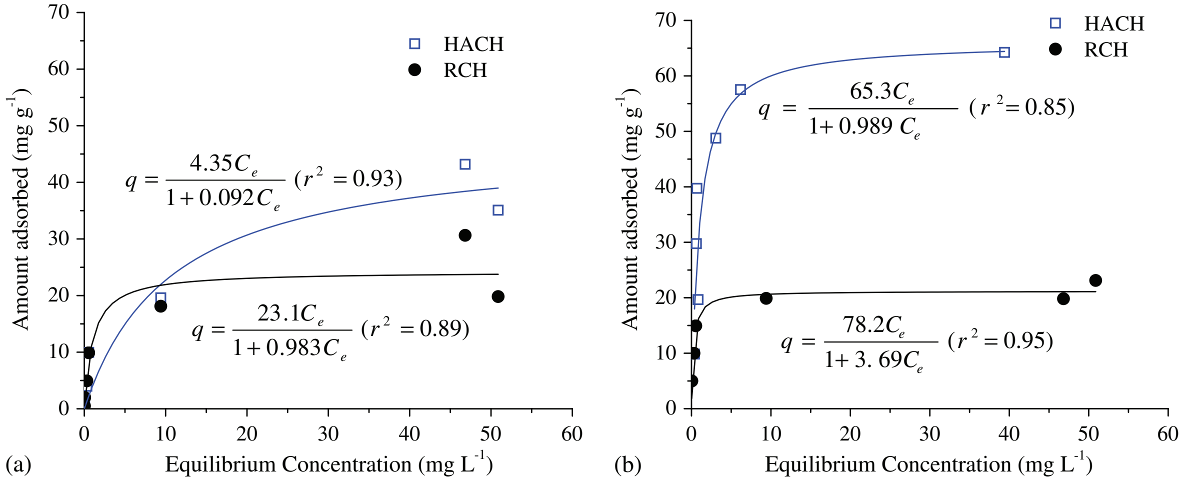


Fig. 6. (Color) Langmuir isotherm model fitted curves of (a) Cd^{2+}; (b) Pb^{2+}

The adsorption capacities of Cd^{2+} and Pb^{2+} onto HACH were 47 and 66 $mg\,g^{-1}$, and those onto RCH were 24 and 21 $mg\,g^{-1}$, respectively. The higher adsorption of Pb^{2+} than Cd^{2+} by HACH is clearly shown by SEM-EDAX elemental mapping (Figs. 2 and 3). Similar results were observed by Cheng et al. (2012), who found that the smaller hydration radius, low free energy of hydration, and higher reactivity of Pb^{2+} than Cd^{2+} were the reasons for higher adsorption of Pb^{2+} than Cd^{2+}.

The R_L values respective to the maximum adsorptions of Cd^{2+} and Pb^{2+} given in Table 1 indicate that the adsorption of Cd^{2+} and Pb^{2+} onto CH is favorable and that the metal ion binding to the surfaces of CH is strong. Moreover, the values of R_L became very close to zero, indicating that the process was closer to the irreversible adsorption (El-Shafey 2007). However, isotherm data was not fitted to the Freundlich isotherm model (data not shown).

Effect of Contact Time on Adsorption

Table 2 shows pseudo first order kinetic parameters and correlation coefficient values obtained from the plot of log $(q_e - q_t)$ with time. The correlation coefficient values and/or measured and fitted values of equilibrium adsorption capacities are not correlated, indicating that the kinetic data do not fit the pseudo first order model. Therefore, the rate of occupation of biosorption sites is not likely to be proportional to the number of occupied sites (Najim et al. 2009; Vinodhini and Das 2010).

Table 2. Pseudo First Order Kinetic Model Parameters and Correlation Coefficient Values for Adsorption of Cd^{2+} and Pb^{2+} onto HACH

Metal	$q_{e,\text{measured}}$ ($mg\,g^{-1}$)	$q_{e,\text{fitted}}$ ($mg\,g^{-1}$)	k_1 (min^{-1})	r^2
Cd^{2+}	7.88	4.31	0.059	0.91
Pb^{2+}	38.5	0.362	0.002	0.14

Table 3. Pseudo Second Order Kinetic Model Parameters and Correlation Coefficient Values for Adsorption of Cd^{2+} and Pb^{2+} onto HACH

Metal	$q_{e,\text{measured}}$ ($mg\,g^{-1}$)	k_2 ($g\,mg^{-1}\,min^{-1}$)	H ($mg\,g^{-1}\,min^{-1}$)	r^2
Cd^{2+}	7.93	3.17	200	0.99
Pb^{2+}	38.46	0.056	83.3	0.99

In contrast, adsorption kinetic data was well fitted to the pseudo second order model (Table 3). This suggests that the rate-limiting factor in adsorption of Cd^{2+} and Pb^{2+} onto HACH is a chemical sorption that involves valence forces through sharing or exchange of electrons between metal ions and the functional groups of HACH, as shown in previous studies (Ho and McKay 1999; Naiya et al. 2009b; Najim et al. 2009). As indicated by the reaction rate constant values, Cd^{2+} adsorption onto HACH reached equilibrium faster than Pb^{2+} adsorption.

Desorption Experiment

Desorption studies were conducted to study the regeneration of used biomaterials for repeated biosorption. The results of the experiments showed that desorption of the metals adsorbed onto CH is very low (not detectable) in the pH range studied with water. Therefore, this confirms that the main process of adsorption is a chemisorption process (Kavitha and Namasivayam 2007).

Effect of Competitive Ions on Adsorption

Figs. 7(a and b) show the adsorption variations of Cd^{2+} and Pb^{2+} in the presence of different concentrations of the other metal ion, respectively. As shown in Fig. 7(a), almost 100% adsorption of Cd^{2+} was observed when there was no Pb^{2+} in the solution. However, when the Pb^{2+} concentration in the aqueous solution increased, the adsorption of Cd^{2+} decreased drastically. Similarly, 96% removal of Pb^{2+} was observed when there was no Cd^{2+} present in the aqueous solution. Removal of Pb^{2+} decreased from 95 to 80% when the Cd^{2+} concentration was the same as the Pb^{2+} concentration in the solution. However, a further increase in Cd^{2+} in the solution did not affect further reduction of Pb^{2+} removal from the aqueous solution. Competitive adsorption of metal ions could be attributable to the differences in the radius of the hydrated ions, free energy of adsorption, and activity of metal ions (Cheng et al. 2012). Srivastava et al. (2009) studied the competitive adsorption of Cd^{2+} and Ni^{2+} onto rice husk ash (RHA) and found that the affinity of RHA for Ni^{2+} is greater than that of Cd^{2+} in binary metal mixtures. The competitive effects of different metals on adsorption of other metals are different (Qin et al. 2006). Qin et al. (2006) studied the mechanisms of competitive adsorption of Cd^{2+}, Pb^{2+}, and Cu^{2+} onto peat and found that the competitive adsorptions of the studied metals are in the order of $Pb^{2+} > Cu^{2+} > Cd^{2+}$, similar to the results observed in the present study.

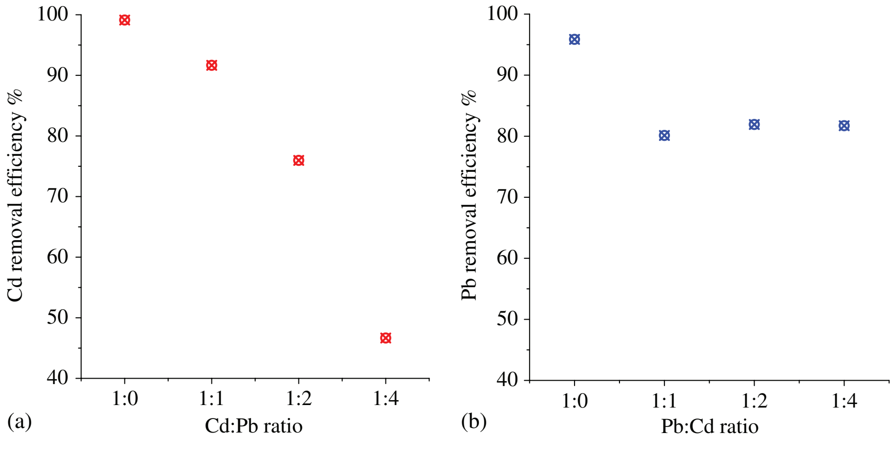


Fig. 7. (Color) (a) Cd^{2+}; (b) Pb^{2+} adsorption variation in binary metal solutions

Table 4. Adsorption of Cd^{2+} and Pb^{2+} in the Presence of Anions and Cations

Ion added	Concentration of ion ($mg\,L^{-1}$)	% Adsorption	
		Cd^{2+}	Pb^{2+}
Ca^{2+}	10	85.7	89.8
	25	61.5	85.5
	50	34.4	80.0
	75	21.4	73.4
Mg^{2+}	25	75.9	95.8
	50	51.5	89.0
	75	31.5	82.9
	100	29.8	80.3
	125	23.9	76.2
SO_4^{2-}	50	97.7	96.9
	100	95.5	90.8
	250	94.9	80.9
	400	84.4	84.8
PO_4^{3-}	1.0	99.7	88.8
	2.5	91.8	64.0
	5.0	99.0	33.6
	10.0	98.8	8.8

The impact of cations (Ca^{2+} and Mg^{2+}) and anions (SO_4^{2-} and PO_4^{3-}) on the adsorption of Cd^{2+} and Pb^{2+} when their availability in the environment was higher and their effect on the adsorption of metals onto adsorbents was studied. The results of the experiment are shown in Table 4. Adsorption of Cd^{2+} onto HACH was decreased in the presence of Ca^{2+} and Mg^{2+} ions in the aqueous solution. It was observed that the adsorption of Cd^{2+} was decreased from 86 to 21% when the Ca^{2+} concentration in the solution increased from 10 to 75 $mg\,L^{-1}$. Moreover, Cd^{2+} adsorption was decreased from 76 to 24% when the Mg^{2+} ions are present in the aqueous solution (Table 4). However, only a few changes in the adsorption of Pb^{2+} were observed at the presence of Ca^{2+} and Mg^{2+}.

Neither Cd^{2+} nor Pb^{2+} adsorption was affected much by the availability of SO_4^{2-} in the solution. Similarly, Cd^{2+} adsorption did not show a change attributable to PO_4^{3-} ions in the solution, whereas Pb^{2+} adsorption was affected by PO_4^{3-} ions. Thus, removal of Pb^{2+} decreased from 89 to 9% when the PO_4^{3-} concentration increased from 1 to 10 $mg\,L^{-1}$. The differences in the adsorption of the two metals by HACH could be attributable to differences in the chemistry of Cd^{2+} and Pb^{2+} ions. Wang and Xing (2002) found that the presence of phosphate enhanced the Cd^{2+} adsorption process. Both Cd^{2+} and Pb^{2+} ions form complexes with phosphate, and the forms of the complexes are different and their solubility is also different in aqueous solution (Ayati and Lundager Madsen 2000). Therefore, it shows the importance of using a pretreatment to remove inorganic contaminants that can affect the adsorption of heavy metals in wastewater.

Comparison of Cd^{2+} *and* Pb^{2+} *Adsorption onto Biosorbents*

The Cd^{2+} and/or Pb^{2+} adsorption capacities of HACH with the other biosorbents in batch experiments are compared in Table 5. The adsorption capacity of raw coconut husk is similar to most of the biosorbents that other researchers studied (Table 5). However, humic acid-treated coconut husk shows higher adsorption capacity than untreated biosorbents. Similar results were obtained by Igwe and Abia (2007) and Wong et al. (2003) for modified maize husk and rice husk, respectively.

Table 5. Comparison of Adsorption Capacity of HACH with Other Biosorbents

Adsorbent	Maximum adsorption ($mg\,g^{-1}$)		Reference
	Cd^{2+}	Pb^{2+}	
RCH	24.24	21.21	Present study
HACH	47.28	66.06	Present study
Grape bagasse	53.84	42.27	Farinella et al. (2007)
Neem oil cake	11.80	—	Rao and Khan (2009)
Sawdust of deciduous trees	3.50	—	Božić et al. (2009)
Sugar beet pulp	0.13	0.37	Pehlivan et al. (2008)
Rose waste biomass	—	151.15	Javed et al. (2007)
Green algae waste biomass	39.20	74.30	Bulguriu and Bulguriu (2012)
Lemon peel	52.20	180.00	Arslanoglu et al. (2009)
Tea waste	—	65.00	Amarasingha and Williams (2007)
Coconut copra meal	4.92	—	Ho and Ofomaja (2006)
Rice husk ash	—	91.74	Naiya et al. (2009b)
Rice husk (tartaric acid modified)	—	108.0	Wong et al. (2003)
Maize husk (unmodified)	−151.5	−217.4	Igwe and Abia (2007)
Maize husk (EDTA modified)	833.3	714.3	Igwe and Abia (2007)

Conclusions

The results of this study indicate that HACH can be used effectively for removal of Cd^{2+} and Pb^{2+} from single-metal ion solutions and that adsorption could be retarded by the presence of coexisting metal ions and other cations and anions. Adsorption of Cd^{2+} and Pb^{2+} ions onto HACH is independent of the pH and ionic strength used in this study. Adsorption by HACH is higher than RCH of Cd^{2+} and Pb^{2+} over the range of initial concentrations studied and shows a monolayer adsorption onto the adsorbent. The maximum adsorption capacities of Cd^{2+} and Pb^{2+} onto HACH were 47.28 and 66.26 $mg\,g^{-1}$, respectively, and 24.24 and 21.21 $mg\,g^{-1}$, respectively, for RCH. The metal ion adsorption process by CH tends more toward an irreversible process that is endothermic in nature. Moreover, the Cd^{2+} and Pb^{2+} adsorption mechanism of CH involves the formation of inner-sphere complexes by metal ions with the active sites of CH. Because the adsorption process is irreversible, regeneration of the biomaterial with water is difficult, and therefore desorption methods with chemical solutions need to be studied.

Adsorption of Cd^{2+} and Pb^{2+} onto HACH is a chemical sorption in which Pb^{2+} adsorption needs a longer reaction time, whereas Cd^{2+} adsorption reaches equilibrium faster. The adsorption reaction rates of Cd^{2+} and Pb^{2+} onto HACH are 0.056 and 3.17 $mg\,g^{-1}\,min^{-1}$, respectively. The presence of several anions and cations affected the adsorption of Cd^{2+} and Pb^{2+} by HACH, and therefore it is important to have a pretreatment unit to remove other ions and suspended solids in wastewater when HACH is used for actual wastewater treatment.

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