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RESEARCH ARTICLE

Investigation on adsorption kinetics of heavy metals by rice husk

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Abstract: Removal of heavy metal ions and their derivative forms from the environment has become a priority to safeguard the quality of the ecosystem. In this context, the present study is based on the removal of Cd(II), Cr(III), Cu(II), Ni(II), Pb(II) and Zn(II) from synthetic industrial effluents using heat-treated rice husk, which can be used to develop cost-effective and eco-friendly effluent treatment procedures. The characterisation experiments reveal that Si available in rice husk in high percentage and many chemical functional groups present on the surface are involved in the adsorption mechanism. Metal ions commonly present in effluents of metal finishing industries were specially considered for their removal. The optimum firing temperature of rice husk, determined using 10.0 mg L^{-1} solutions of each metal ion, was 100 ºC. The effect of other experimental parameters, such as contact time and pH were also investigated using rice husk fired at the optimised temperature of 100 ºC. Kinetics studies conducted for the interaction of the above metal ions and rice husk lead to the validity of pseudo second order kinetics with high regression coefficients. The initial rate of adsorption (h_o) of metal ions varies in the order of Pb(II) > Zn(II) > Cd(II) > Cu(II) > Ni(II) > Cr(III). According to the diffusion models investigated, Weber and Morris intra-particle diffusion model supports the data for rate constant of particle diffusion, which varies in the same order as observed in initial adsorption rate measurements (h_o).

Keywords: Adsorption, heavy metals, intra-particle diffusion model, kinetics, rice husk.

INTRODUCTION

Many industries produce effluents containing hazardous materials, such as oil, dyes, heavy metal ions and their compounds, pesticides and anions, which are harmful to the ecosystem (Khan *et al.*, 2004; Chieng *et al.*, 2014). Even after treatment of industrial effluents, they may still contain pollutants to some degree, and consequently, these pollutants end up in natural water bodies. Among various hazardous materials, heavy metals are non-biodegradable and affect living tissues *via* bioaccumulation, causing many diseases and disorders to the human being (Naja & Volesky, 2009; Saikaew & Kaewsarn, 2009).

Physical, chemical and biological treatment methods are commonly in practice for the removal of harmful substances present in water (Scott & Ollis, 1995; Kurniawan *et al.*, 2006). Many industries use physical and biological treatment methods to treat biodegradable waste, while chemical treatment methods are typically used to treat industrial effluents containing toxic substances such as heavy metal ions and their compounds. Coagulants, flocculants and pH controlling agents are especially needed for effective chemical treatment processes, but the excess of added chemicals would mix up with water bodies deteriorating their quality. Products formed during treatment could also pose another environmental problem (Wang *et al.*, 2011).

Attempts have been made to use environmental friendly substances to remove heavy metal ions from industrial effluents to minimise the above stated threats. Natural substances, such as agricultural waste, coconut shell, peat, brick clay, fruit peel waste, tea leaf, coir dust and saw dust, have been used to remove heavy metal ions

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from wastewater (Zaggout, 2005; Zehra *et al*., 2015). The use of natural, environmental-friendly substances to remove pollutants from effluents has become highly attractive as compared to classical methods involving chemicals.

Rice husk is excessively produced in rice processing areas as a waste, and hence its disposal often creates environmental problems. Use of rice husk in solving an environmental problem is thus be an important approach, and further, the use of rice husk for treatment of heavy metal containing effluents would be cost-effective and eco-friendly. Contamination with these metal ions would cause health hazards to human beings as well as to many other living organisms (Ahmaruzzaman & Gupta, 2011; Gupta *et al*., 2015). Renal and liver failures, allergies, vomiting and diarrhoea are some health hazards of heavy metal contamination, and fumes of metallic compounds may even cause death of humans (Dayan & Paine, 2001; Singh *et al*., 2011). Therefore, it is very important to remove heavy metal ions and their compounds from industrial wastewater, as it is the main source of heavy metals contaminating natural water bodies.

Although it has been reported that rice husk has the ability to remove heavy metal ions (Nhapi *et al*., 2011; Navaratne *et al*., 2013; Priyantha *et al*., 2015), adsorption kinetics of heavy metal ions on rice husk have not been reported to the best of our knowledge despite the necessity of rate measurements of adsorption of heavy metal ions in designing efficient treatment plants using such materials. In this context, the main objective of the current research was to investigate adsorption kinetics of heavy metal ions on rice husk under static conditions after optimisation of experimental and process parameters. For kinetics studies, individual aqueous metal ion solutions of Cd(II), Cr(III), Cu(II), Ni(II), Pb(II) and Zn(II) were used. The extent of removal of each metal ion by heat-treated rice husk was determined within a short period of time prior to the establishment of adsorption equilibrium, beyond which reliable results for rate of reaction cannot be obtained. It has already been reported that heat treatment of adsorbents leads to variation of adsorption characteristics (Priyantha & Bandaranayake, 2010). Further, the pseudo order kinetics models were investigated for this heterogeneous system as it was difficult to vary the concentrations of the adsorbent and the adsorbate simultaneously. These results could be used as background information to design industrial wastewater treatment systems.

METHODOLOGY

Materials

Standard aqueous solutions of Cd(II), Cr(III), Cu(II), Ni(II), Pb(II) and Zn(II) were prepared using analytical grade reagents of their nitrates or sulphates in deionised water. All the experiments were conducted under static conditions using individual metal ion solutions. Rice husk samples consisted of husks of different rice varieties obtained from a rice mill in Kandy, Sri Lanka, and used in its natural size after thorough mixing and washing.

Instrumentation

The samples of rice husks were heated up to pre-determined temperatures using Carbolite CTF 12/100/900 tube furnace. Spectro-electronic M series atomic absorption spectrophotometer (AAS) was used to determine the total concentration of each metal in solutions. Metals present in adsorbents were also determined using X-ray fluorescence (XRF) spectrophotometer (Fischerscope Model-DF500FG-456) and X-ray diffractometer (XRD) (Siemens Model D50000) using Cu-K X-ray beam (1.54056 Ǻ). Fourier transform infrared (FTIR) spectra were recorded on Thermo Nicolet Model-Avater 320 FTIR spectrophotometer, while scanning electron microscopic (SEM) images of rice husk samples before and after treatment with metal ion solutions were taken using Oxford Instruments - EVO LS 15 (Zeiss) instrument.

Research design

Representative samples of rice husks, being a natural substance having a variable composition, were prepared by mixing large portions of samples, heated for 4.0 h at various temperatures and allowed to cool down to room temperature through natural convection. All the experiments were performed under static conditions using individual adsorbate solutions containing each cation at 10.0 mg L^{-1} concentration level. Aliquots of 50.0 cm^3 of each metal ion solution were shaken for pre-determined time periods with 2.50 g of heat treated rice husk samples. The extent of removal of each metal ion by rice husk samples in each experiment was determined as percentage removal using equation (1),

$$\text{Percentage removal} = \frac{C_i - C_f}{C_i} \times 100\ \% \qquad \text{...(1)}$$

where C_i is the initial concentration of metal ion and C_f is the total concentration of metal ions present in the supernatant of the treated solution.

Effect of contact time on adsorption was observed by varying the shaking time and settling time separately. All other variables were made constant and only the effect of the above two variables were initially checked for the maximum removal. Shaking rate was taken as 150 rpm in all experiments. Thereafter, the initial pH of solutions was varied to optimise the solution pH for most effective removal. For this purpose, each heavy metal ion solution was prepared at 10.0 mg L^{-1} concentration, and its initial pH was adjusted to different values between 2 and 10 using 0.1 mol dm^{-3} solutions of HNO_3 and/or NaOH. High pH values were not employed to avoid precipitation of some metal ions.

Kinetics modelling

To investigate the validity of kinetics models, 1000 cm^3 aliquots of 10.0 mg L^{-1} solutions of each metal ion were stirred with rice husk samples heated at 100 ºC in 1:100 w/v composition. Thereafter, samples were withdrawn at every 1.0 min period, immediately filtered and the remaining concentration of each metal ion was determined using AAS.

Kinetics modelling was done for better understanding of the rate process. Assuming that the activity of the adsorbent is constant during the initial stage of adsorption, the generalised equation for kinetics can be written as (Priyantha & Bandaranayaka, 2011),

$$\frac{d(q_t)}{dt} = k'(q_e - q_t)^n \quad ...(2)$$

where k' is the apparent rate constant, t is the contact time, and q_e and q_t are the masses of metal ions adsorbed by unit mass of the sorbent at equilibrium and at time t, respectively. A linearised integrated form of the above equation leads to the following kinetics models (Igwe *et al*., 2008; Priyantha & Bandaranayaka, 2011);

Pseudo first order:

$$\log(q_e - q_t) = -\frac{k'}{2.303}t + \log q_e \quad ...(3)$$

Pseudo second order:

$$\frac{t}{q_t} = \frac{1}{q_e}t + \frac{1}{k'{q_e}^2} \quad ...(4)$$

If the initial adsorption rate is h_0,

$$h_0 = k'q_e^2 \quad ...(5)$$

The Elovich kinetic model can be expressed as (Kumar *et al.*, 2011; Patil *et al*., 2012),

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln t \quad ...(6)$$

where α is the initial adsorption rate in mg g^{-1} min^{-1}, and β (g mg^{-1}) is related to the extent of surface coverage.

In order to identify the boundary layer diffusion, the external mass transfer diffusion model and intra-particle diffusion models were considered as given below (Odoemelam *et al*., 2011; Sonde & Odoemelam, 2012).

The external mass transfer diffusion model (Sag & Aktay, 2000):

$$\frac{C_t}{C_0} = -\beta_L St \quad ...(7)$$

where C_t and C_0 are metal ion concentration of the solution at time t and at t = 0, respectively, β_L is the liquid-solid mass transfer coefficient and S is the specific surface area for mass transfer.

McKay and Poots intra-particle diffusion model:

$$q_t = X_i + k't^{0.5} \quad ...(8)$$

where q_t is the adsorbed amount at time t, k' is the intraparticle diffusion rate constant and X_i is the boundary layer thickness.

Weber and Morris intra-particle diffusion model:

$$\log R = \log k_{id} + n\log(t) \quad ...(9)$$

where R is the percentage adsorption of a heavy metal, n is the gradient of linear plots and k_{id} is the intra-particle diffusion rate constant.

The actual slow step of the reaction can be predicted by the application of the Boyd model for the above data according to the equation (Nethaji *et al*., 2013),

$$F = 1 - \frac{6}{\pi}\exp(-B_t) \quad ...(10)$$

and

$$F = \frac{q_t}{q_e} \quad ...(11)$$

where q_e is the amount of adsorbate adsorbed at equilibrium (mg g^{-1}) and q_t represents the amount of adsorbate adsorbed at any time t (min), F represents the fraction of solute adsorbed at any time t, and B_t is a mathematical function of F.

The rearranged equation,

$$B_t = -0.4977 - \ln(1 - F) \qquad \text{...(12)}$$

explains the variation of B_t values with respect to the fraction of solute adsorbed.

RESULTS AND DISCUSSION

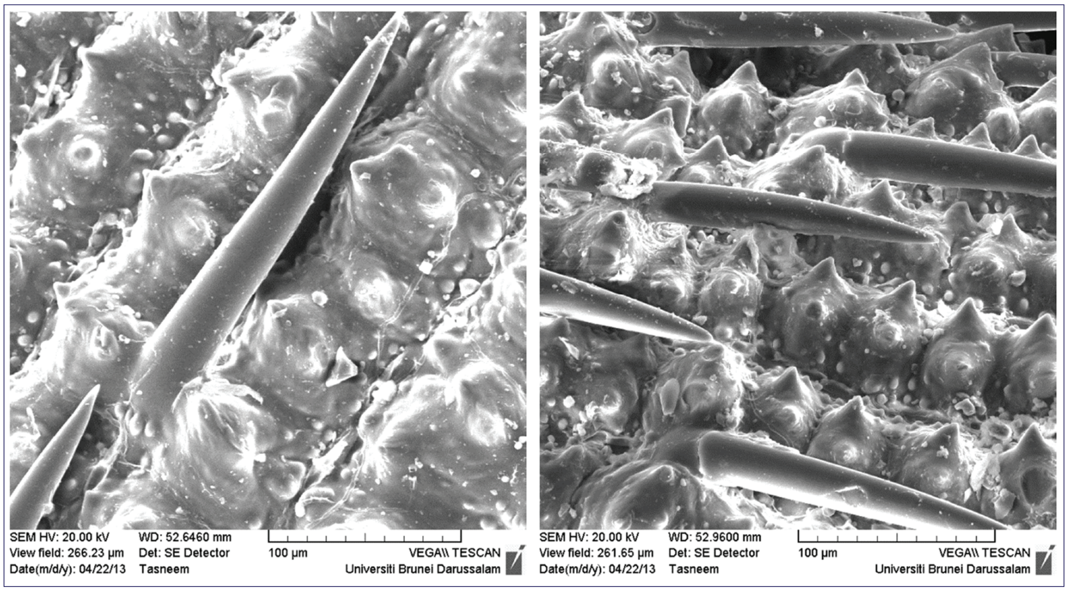
Effect of experimental/process parameters on removal of heavy metal ions from aqueous solutions

Determination of the extent of removal of each metal ion by the adsorbent monitored by changing the parameter of interest within a broad range, while keeping the other parameters constant leads to 10 minutes optimum shaking time and 10 minutes optimum settling time for the removal of each heavy metal ion under investigation. The percentage removal of heavy metal ions determined using pre-heated rice husk samples with different metal ion solutions of 10.0 mg L^{-1}, increased with the increase in firing temperature up to 100 ºC, and then decreased up to 200 ºC. The treatment temperature at which the maximum removal was observed remained unchanged with the change in the initial concentration. Therefore, 100 ºC was taken as the optimum temperature of treatment of the adsorbent, rice husk. More importantly, rice husk samples heated at this temperature shows more than 90 % removal as compared to raw rice husk, which shows about 65 % removal for all the metal ions investigated (Priyantha *et al.*, 2015). At the temperature employed for treatment, moisture would be evaporated, pores would be expanded, and more new pores could be created. However, no chemical reaction would be expected at this temperature.

Since the extent of removal of heavy metal ions using rice husks is increased with heat treatment, SEM images were taken to study surface changes and morphology of rice husk samples heated at different temperatures. Figure 1 clearly indicates the availability of more adsorption sites after heat treatment supporting the previous observation.

Effect of pH

The extent of adsorption of metal ions is controlled by the solution pH as both the solution properties and chemistry of the adsorbent depend on pH. The percentage removal *vs* pH investigated from an initial pH of 1.0 up to a value at which the corresponding hydroxide precipitation starts based on solubility product calculations for 10.0 mg L^{-1} concentration of each metal ion, is shown in Figure 2.



(a) (b)

Figure 1: SEM images of rice husk samples (a) unfired; (b) heated at 100 ºC

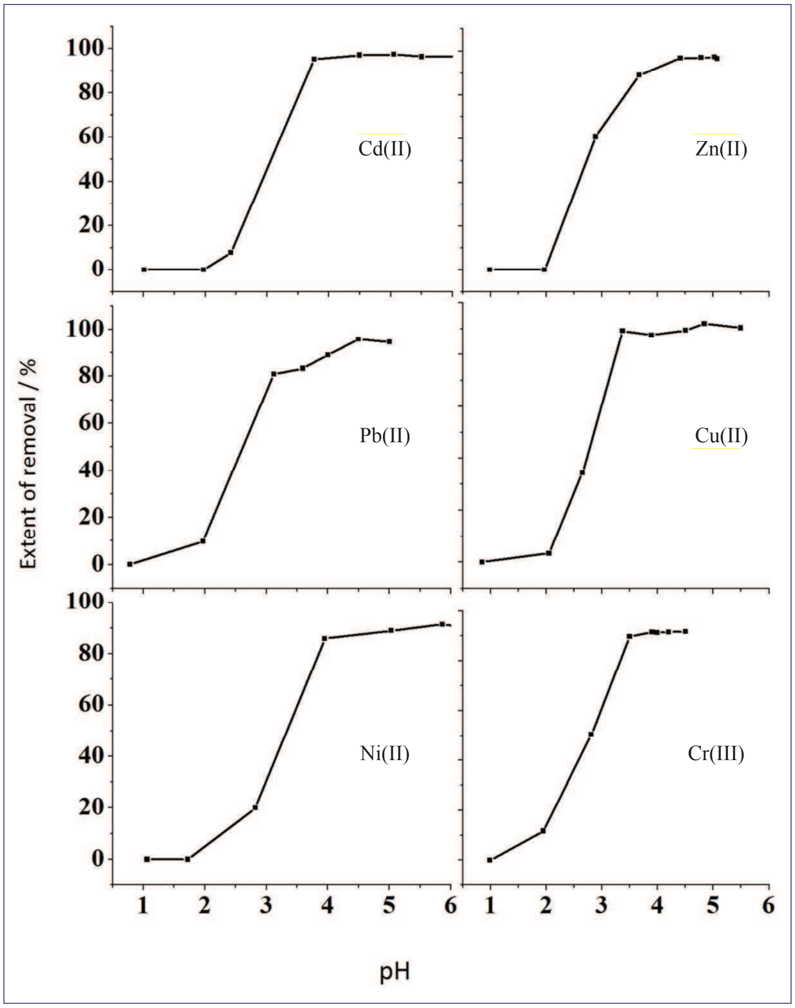


Figure 2: Variation of the extent of removal with initial pH (50.0 cm^3 of 10.0 mg L^{-1} concentration of individual metal ion solutions treated with 2.50 g of rice husk samples heated at 100 ºC)

According to the observations in Figure 2, the percentage removal is lower at low pH values, which is due to the competition of metal ions with H_3O^+ ions present in the solution for a limited number of surface –OH and –COOH sites in the adsorbent as evident by FTIR spectra. The extent of removal of each metal ion then increases with increase in pH up to a certain value, beyond which metal ions tend to precipitate as hydroxides. The increase in the extent of adsorption of metal ions can be attributed to the decrease in H_3O^+ concentration, and increase in the concentration of anionic forms of –OH and –COOH groups promoting stronger affinity towards metal ions. The lowest pH that leads to the most effective removal of metal ions was determined to be between 4.0 and 5.0, and thus, all the experiments were carried out by adjusting the initial pH to be within this range. Adsorption of metal ions, in general, increases with increasing pH up to a value of 4 and remains unchanged thereafter up to about pH 6.

Physico-chemical characteristics of rice husk

Characterisation of rice husk samples was conducted using XRD, XRF and FTIR analyses. The raw rice husk samples were analysed directly by scanning in the range of diffraction angle from 5º to 100º. Figure 3 illustrates the diffraction pattern obtained for an amorphous rice husk sample, which shows a broad peak within a wide angle of 2θ corresponding to silica present in the sample (Sonde & Odoemelam, 2012). Although XRD provides information on the crystalline nature and minerals present, the composition of individual elements (metals)

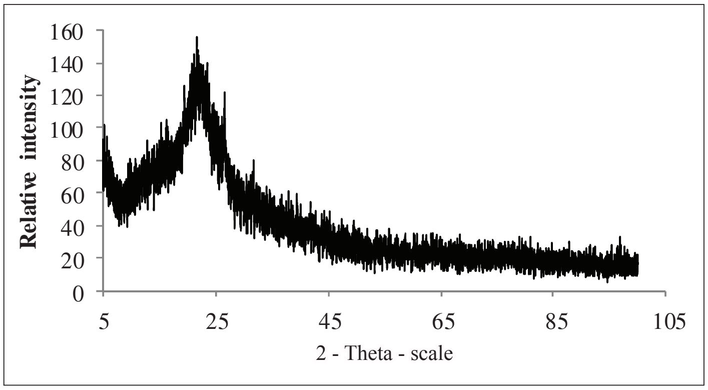


Figure 3: XRD pattern of a raw rice husk sample

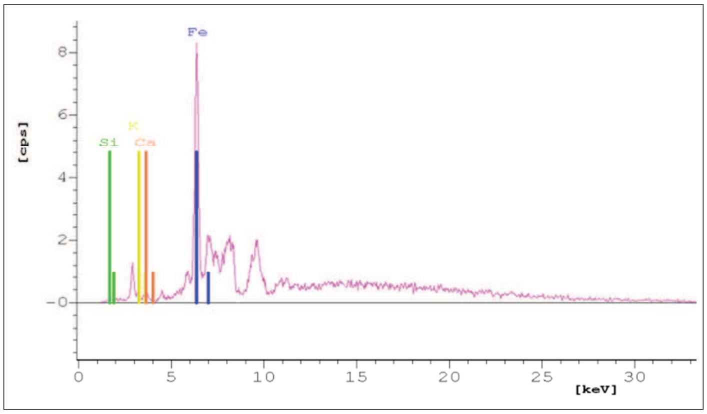


Figure 4: XRF spectrum of a raw rice husk sample

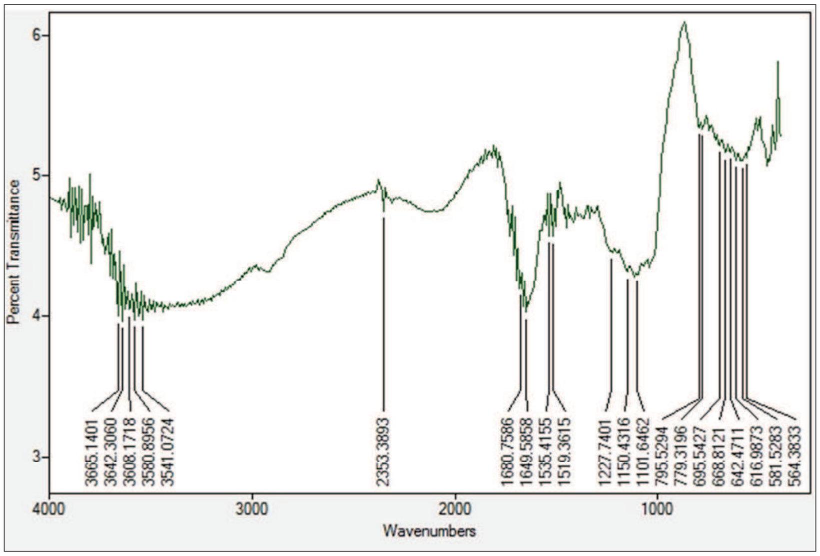


Figure 5: FTIR spectrum of a raw rice husk sample

cannot be obtained. On the other hand, XRF is useful in obtaining the composition of metallic elements, while FTIR provides information on organic functional groups.

The inorganic chemical composition determined using XRF spectrum indicates the presence of mainly Si, Fe, Ca and K in rice husk (Figure 4). Among the constituents detected, Si showed the highest percentage at 94 %, which is supported by previous studies (Omatola & Onojah, 2009; Ramezanianpour *et al.*, 2009).

FTIR spectrum for a raw rice husk sample is shown in Figure 5. The broad band observed within the region from 3000 cm^{-1} to 4000 cm^{-1} can be attributed to C-H, Si-O-H and O-H groups. The broad intense band centered at 1600 cm^{-1} corresponds to –C=O and –C-OH stretching of aldehydes and ketones (Ahmad *et al.*, 2011). Both peaks are ascribed to stretching of hydrogen bonds and bending of hydroxyl (OH) groups bound to the cellulose structure (Johar *et al.*, 2012). The peak at 2353 cm^{-1} indicates N-H stretching, while peaks at 1266 – 1200 cm^{-1} correspond to bending of C-H, O-H or CH_2, and the bands at 1150 and 1101 cm^{-1} are assigned to C-O stretching of tertiary, secondary and primary hydroxyl groups (Malik *et al.*, 2006; Elizalde-gonzalez *et al.*, 2007). The presence of these polar groups on the surface of rice husk is likely to result in a considerable cation exchange capacity to the adsorbent in order to adsorb metal ions.

According to the results, neither XRD patterns nor FTIR spectra provide sufficient information on chemical/physical changes that would occur during heat treatment. The results obtained for both thermogravimetric analysis (TGA) and differential scanning colourimetry (DSC) curves (Priyantha *et al.*, 2015) correspond to the mass loss of the sample upon continuous heating up to 600 ºC. An initial mass loss of rice husk that occurs below 100 ºC is associated with the vapourisation of water due to hydrophilic character of the lignocellulose fibres. This mainly depends on the initial moisture content of the sample. The sharper mass loss observed beyond 300 ºC is due to the presence of hemicellulose, lignin and pectin in rice husk as such components have a lower decomposition temperature as compared to cellulose. The mass fraction remained after heating above 400 ºC includes ash and silica (Johar *et al.*, 2012). The exothermic nature of combustion is evident by observing positive energy release values at firing temperatures beyond 100 ºC as reported earlier (Priyantha *et al.*, 2015).

The point of zero charge (PZC) of the adsorbent was determined in order to understand the mechanism of adsorption. Adsorption of cations is favoured at $pH > pH_{PZC}$, while the adsorption of anions is favoured at $pH < pH_{PZC}$. Surface charge of the sorbent was determined to be highly dependent on the pH of the medium for different ionic strengths. The point of zero charge, estimated by considering the point of intersection of curves obtained for different ionic strengths, is at pH 4.0 for rice husk samples heated at 100 ºC (Priyantha *et al.*, 2015). The influence of the pH of metal ion solution on adsorption on rice husk samples observed in Figure 2 supports the pH dependence of the surface charge of rice husk.

Surface area determination

Methylene blue (MB) test (Yukselen & Kaya, 2008) was performed with rice husk samples heated at 100 ºC to calculate the surface area of rice husks using equation (13),

$$S_s = m_{MB} A_v A_{MB} / m_s M \qquad ...(13)$$

where S_s is the surface area of rice husk ($m^2\ g^{-1}$), m_{MB} is the mass of MB adsorbed at the point of complete cation replacement (g), A_v is the Avogadro constant, A_{MB} is the area covered by a MB molecule ($1.30\times10^{-18}\ m^2$) (Johar *et al.*, 2012), m_s is the mass of the rice husk sample, and M is the molar mass of MB (319.87 g mol^{-1}).

This method has been used to determine the surface charge of natural adsorbents (Ramezanianpour *et al.*, 2009; Johar *et al.*, 2012). Figure 6 shows the variation

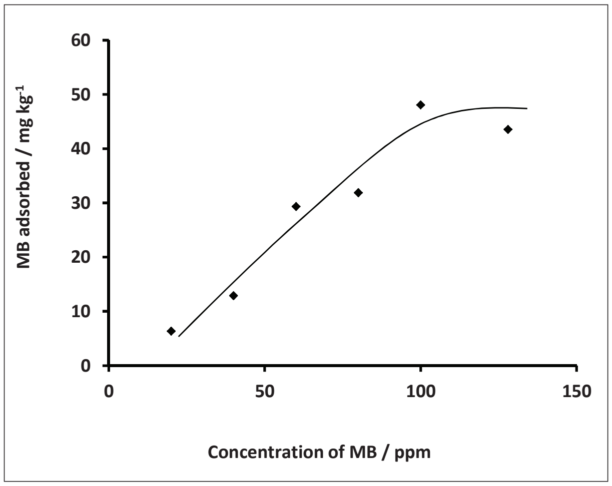


Figure 6: Variation of the amount of methylene blue adsorbed on rice husk heated at 100 ºC with the initial methylene blue concentration (0.100 g of rice husk, 100 cm^3 solution, 2.0 h shaking time, 12.0 h settling time)

of the amount of MB adsorbed on the rice husk surface with the initial amount of MB added to the solution. According to the figure, the amount adsorbed is levelled off with the increase in the concentration of MB. The surface area determined based on the saturation point at the concentration of 100 mg L^{-1} is 110.13 $m^2 g^{-1}$, which is comparably higher among other adsorbents demonstrating the usefulness of rice husk for the removal of pollutants using adsorption. The surface area determined using the same method for avocado kernel seed in its natural form is 53 $m^2 g^{-1}$, while it has decreased to 23 $m^2 g^{-1}$ with its activation with peroxide (Ramezanianpour *et al.*, 2009). On the other hand, the surface area of different soils differs from 50 $m^2 g^{-1}$ to 900 $m^2 g^{-1}$, as reported earlier (Johar *et al.*, 2012).

The adsorption capacity is greater for materials of higher surface area (larger pore size) due to increased pore volumes. When compared to surface areas of natural substances reported, heated rice husk shows comparable values indicating that it can be used as an effective adsorbent (Bhattacharyya & Gupta, 2006).

Characterisation of metal-treated adsorbent

SEM images can be used to compare the porosity and the texture of a biosorbent before and after adsorption of metal ions. With the treatment of metal ions with rice husk pre-heated at 100 ºC, the adsorbent surface appears to be smoothened (Figure 7).

Further confirmation of the involvement of ion exchange process in the uptake of metal ions on heated rice husk surface was obtained by energy dispersive X-ray (EDX) analysis (Figure 8). The typical EDX spectrum of untreated rice husk samples clearly indicates that they contain Si, O, S, Fe, Al, Mg and C in its natural form [Figure 8(a)], which does not show any characteristic peak for the heavy metal ions considered. The EDX spectrum of Ni(II)-treated rice husk clearly indicates the presence of Ni(II) in their sample together with decreased intensities of Mg, Fe and Al. Adsorption of Cd(II) and Cu(II) also shows a similar trend. These observations indicate the involvement of an ion exchange mechanism for the removal of metal ions by rice husks,

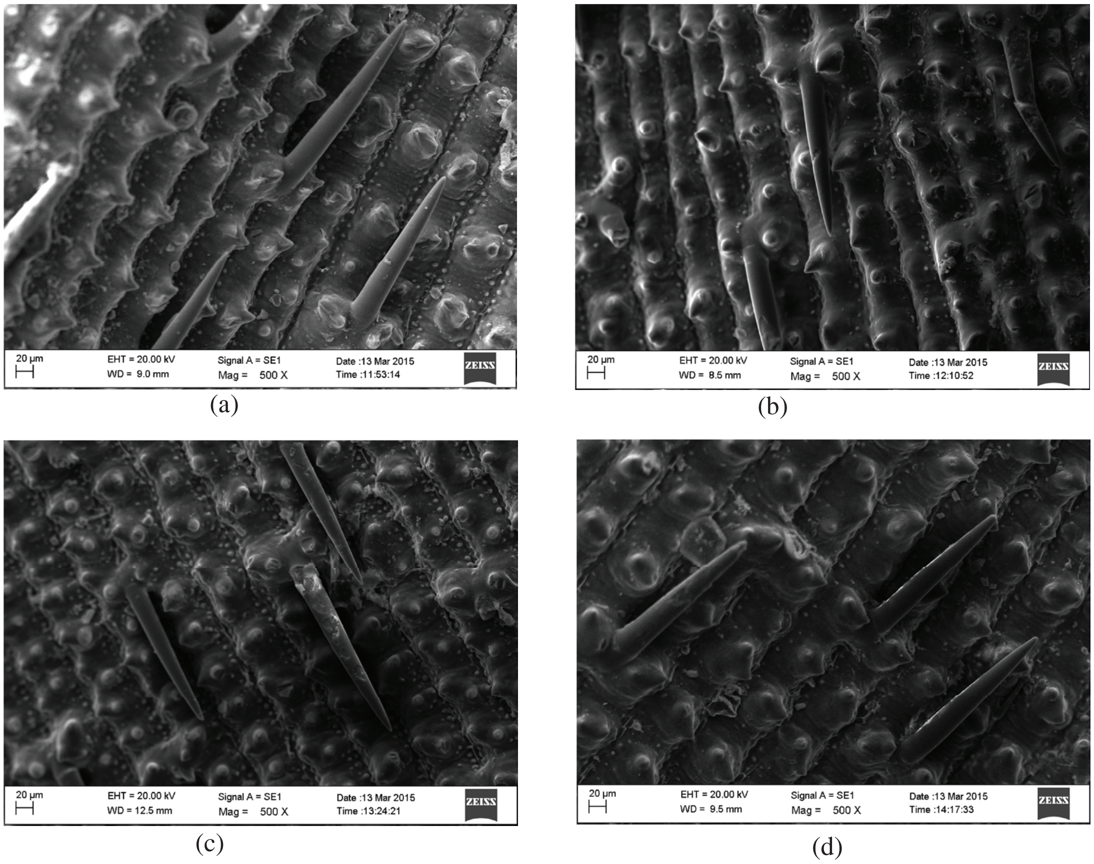
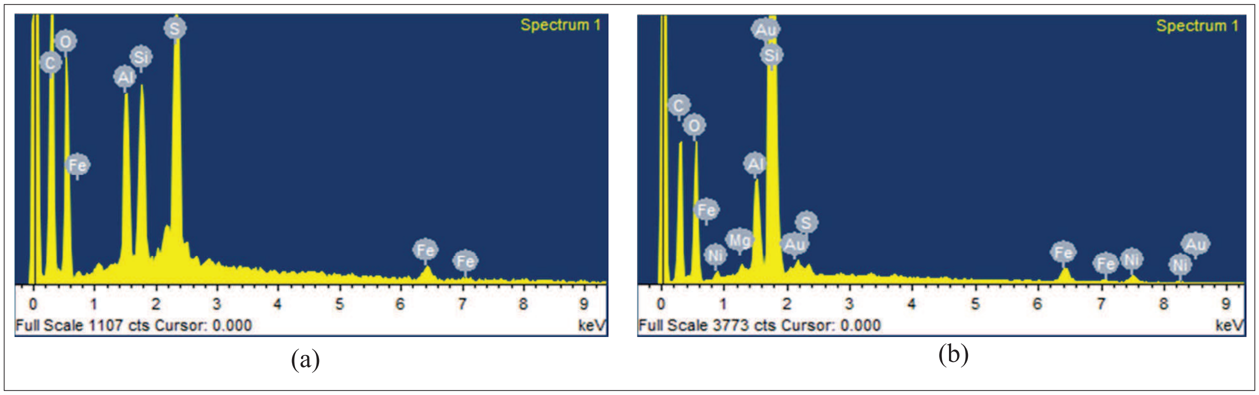
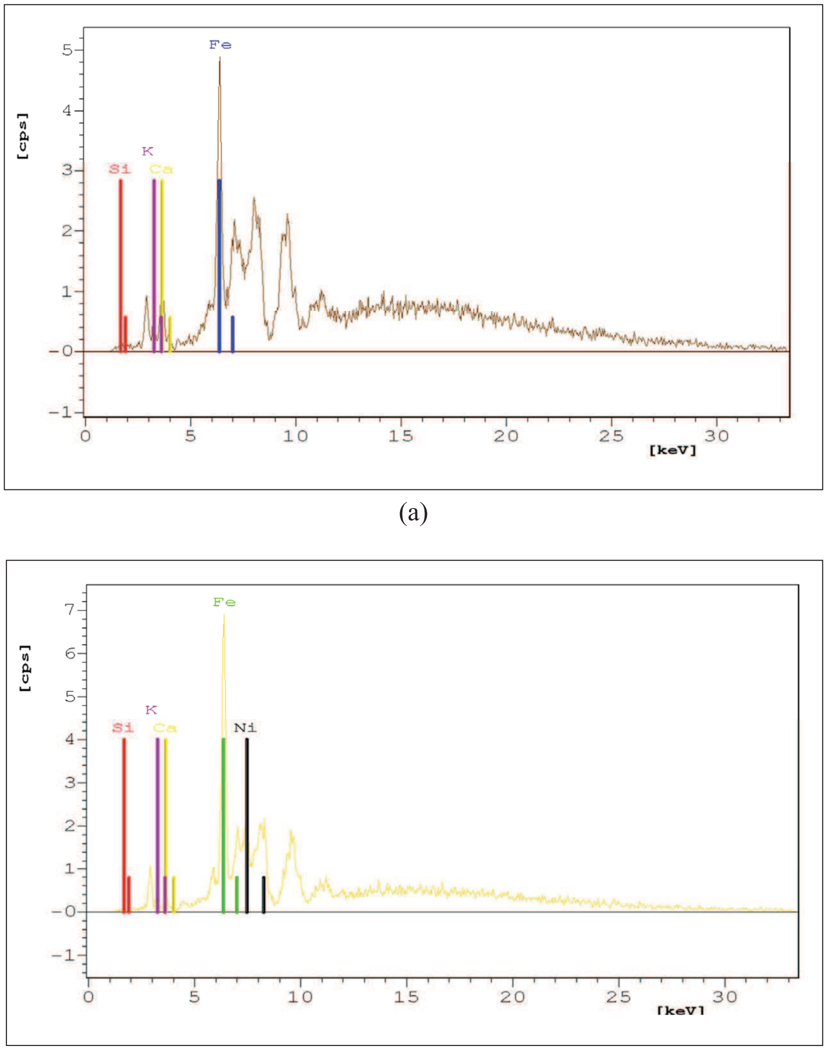


Figure 7: SEM images of rice husk samples (a) untreated; (b) Cd-treated; (c) Cr-treated; (d) Cu-treated



(a) (b)

Figure 8: Energy-dispersive X-ray spectroscopy (EDX) spectra of rice husk samples (a) untreated; (b) treated with 1000 mg L^{-1} Ni(II) solution



(a)

(b)

Figure 9: XRF spectra of rice husk samples (a) raw sample; (b) Ni-treated sample

which is also supported by the XRF spectrum obtained for the same metal ion (Figure 9). Adsorption of Pb(II) on mango peel waste has described the same phenomenon of replacement of Ca^{2+} and K^+ with Pb(II) through EDX spectra (Iqbal *et al*., 2009).

Adsorption isotherms

The adsorption patterns of all the metal ions investigated qualify Type I isotherm with different saturation concentrations according to IUPAC classification (Thommes *et al.*, 2015). Surface changes of rice husk after metal ion adsorption suggest that rice husk shows microporous characteristics for adsorption (Priyantha *et al.*, 2015). According to the data obtained, the Langmuir adsorption isotherm model, having regression coefficients (R^2) close to unity for all six metal ions, is suited to explain adsorption characteristics of metal ions on rice husk samples heated at 100 ºC. This model assumes monolayer adsorption, which occurs on specific sites, and is independent of the amount of material adsorbed (Dada *et al.*, 2012; Priyantha *et al.*, 2015).

Investigation of kinetics

The efficiency of the adsorption process mainly depends on the mechanism. Figure 10 illustrates the variation of the extent of adsorption with contact time for different metal ions, when an aqueous solution of each metal ion was individually treated with rice husk samples heated at the optimum temperature. The extent of removal of heavy metal ions by rice husks determined after the system reaches equilibrium follows the order, Cr(III) < Ni(II) < Cu(II) < Cd(II) < Zn(II) < Pb(II) according to the figure. On the other hand, the rate at which the rice husk-metal ion solution reaches equilibrium is different for each ion. The adsorption of Pb(II) has reached equilibrium almost instantly followed by Zn(II), Cd(II) and Cu(II). Adsorption of Ni(II) and Cr(III) takes the longest time to reach equilibrium. Kinetics modelling for the adsorption

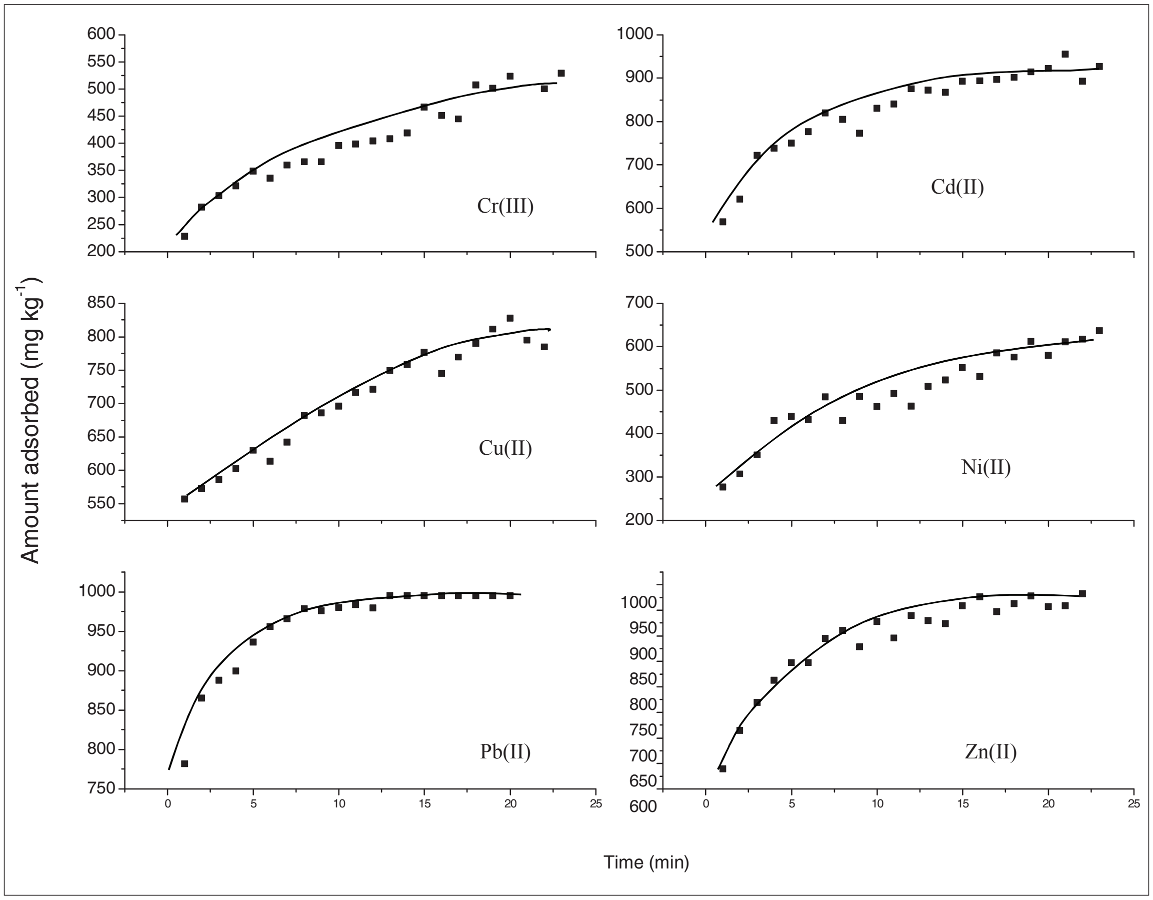


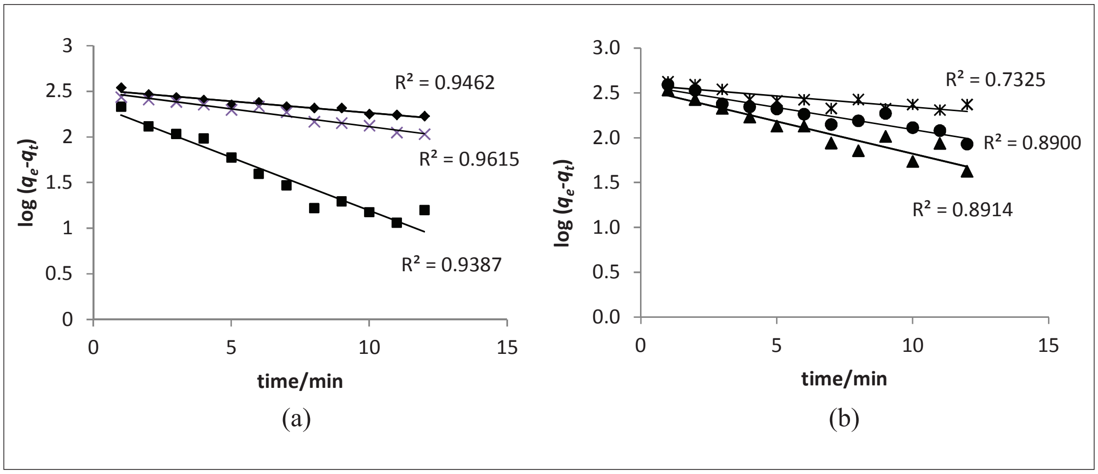
Figure 10: Variation of the amount of metal ions adsorbed with contact time (1000 cm^3 of 10.0 mg L^{-1} metal ion solution, 10.0 g heated rice husk)

of metal ions was applied within the time period before the systems have reached equilibrium according to the observations (Figure 10).

The order of adsorbate-adsorbent interactions is defined using kinetics models. Application of adsorption data of metal ions for the linearised pseudo first order model [equation (3)] is shown in Figure 11. The regression coefficients determined from each linear plot are not favourable, suggesting that the calculated q_e values for metal ions would not represent the actual adsorption system. Therefore, the determination of kinetics parameters based on the pseudo first order model was not attempted. The application of the pseudo second

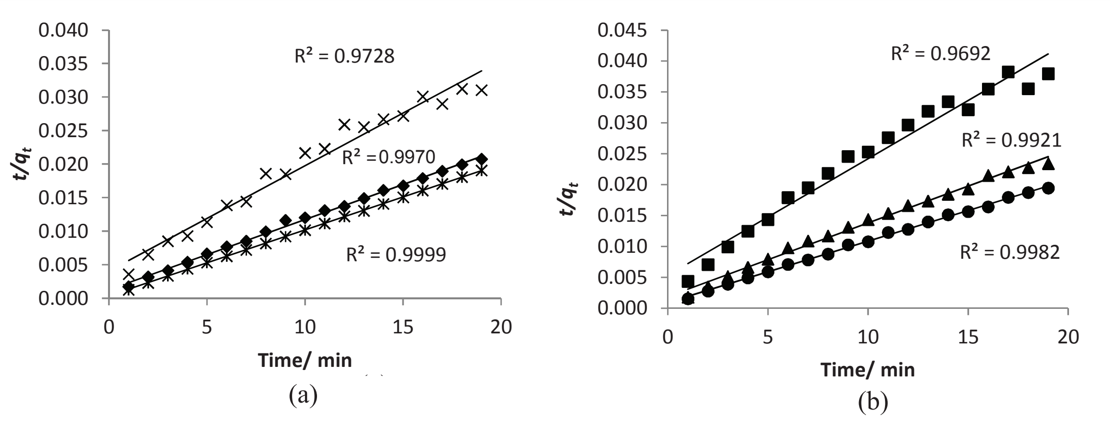
Table 1: Kinetics parameters from the pseudo second order model for adsorption of heavy metal ions (initial concentration 10 mg L^{-1}) on rice husk

Metal ion	q_e /mg kg^{-1}	$k'\times10^4$ /kg mg^{-1} min^{-1}	$h_0\times10^{-2}$ /mg kg^{-1} min^{-1}
Cd(II)	1000	8.0	7.69
Cr(III)	526	7.0	1.88
Cu(II)	833	8.0	5.26
Ni(II)	625	6.0	2.44
Pb(II)	1000	25.0	25.0
Zn(II)	1000	11.0	11.1



(a) (b)

Figure 11: Plots of linearised pseudo first order kinetics model for adsorption of metal ions on heated rice husk (a): Pb(II) (■), Cr(III) (♦) and Cu(II) (×); (b): Zn(II) (▲), Ni(II) ( ) and Cd(II) (•) (1000 cm^3 of 10.0 mg L^{-1} metal ion solution, 10.0 g heated rice husk)



(a) (b)

Figure 12: Plots of linearised pseudo second order kinetics model for adsorption of metal ions on heated rice husk; (a): Cd(II) (♦), Ni(II) (×) and Pb(II) (*); (b): Cr(III) (■), Cu(II) (▲) and Zn(II) (•) (1000 cm^3 of 10.0 mg L^{-1} metal ion solution, 10.0 g heated rice husk)

order kinetics model [equation (4)] shows a much better agreement of experimental data for the heavy metal ions, according to regression coefficients (R^2) being close to 1.00 (Figure 12). Table 1 shows the adsorption capacity at equilibrium (q_e), pseudo second order rate constant (k') and initial adsorption rate (h_0) determined from the pseudo second order kinetics model.

The data reported in Table 1 indicates that h_o of metal ions under investigation follows the order, Pb(II) > Zn(II) > Cd(II) > Cu(II) > Ni(II) > Cr(III), which is a measure of how fast the adsorption reaction proceeds. This could be partly explained by the variation of the ionic radius, which follows the order Pb(II) > Cd(II) > Zn(II) > Cu(II) > Ni(II) > Cr(III). Table 2 gives previous results reported for the adsorbed amount at equilibrium for different adsorbents for different metal ions in different initial concentrations. According to the results obtained, it is much higher for higher initial concentrations as reported. The order of variation of the adsorption rate determined based on kinetics, which depends on the path to reach equilibrium, is not in agreement with the order of variation of the extent of removal of metal ions determined when the system has reached equilibrium, due to the fact that kinetics and equilibrium aspects are not inter-dependent. The pseudo second order model, the best fitted model for the data describes that the rate limiting step of this sorption system suggests chemisorption that involves sharing or exchange of electrons between the adsorbate and the adsorbent.

Five adsorption kinetics models, whose linear relationships [equations (6) – (10)] result in satisfactory regression coefficients are shown in Table 3. Among these, Weber and Morris intra-particle model, which provides R^2 values close to unity, is the most satisfactory model to explain the adsorption of the heavy metal ions selected on rice husk.

Table 2: Previous results obtained for adsorbed amount at equilibrium (q_e) for different adsorbents

Metal ion	Adsorbent	Initial concentration /mg L^{-1}	$q_e \times 10^4$ /mg kg^{-1}	Reference
Cd (II)	Green coconut shell powder	80	1.53	Pino *et al*., 2006
	Tree fern	100	1.22	Ho, 2006
Zn(II)	Natural clay	20	0.36	Veli & Aly, 2007
Cu(II)	Natural clay	20	0.44	Veli & Aly, 2007
	Meranti saw dust	100	1.86	Rafatullah *et al*., 2009
Cr(III)	Meranti saw dust	100	1.93	Rafatullah *et al*., 2009
Ni(II)	Meranti saw dust	100	1.85	Rafatullah *et al*., 2009
Pb(II)	Meranti saw dust	100	2.00	Rafatullah *et al*., 2009
	Peat	10	0.41	Zehra *et al*., 2015
	Vegetable waste	50	0.20	Gill *et al*., 2014

Table 3: Regression coefficients obtained for heavy metal ion adsorption on rice husk according to adsorption kinetics models

Metal ion	Elovich model	External mass transfer diffusion model	Mckay and Poots intra-particle diffusion model	Weber and Morris intra-particle diffusion model	Boyd model
Cd(II)	0.948	0.858	0.928	0.964	0.890
Cr(III)	0.975	0.950	0.953	0.954	0.946
Cu(II)	0.868	0.950	0.967	0.910	0.961
Ni(II)	0.882	0.933	0.915	0.932	0.732
Pb(II)	0.967	0.788	0.818	0.927	0.939
Zn(II)	0.967	0.826	0.900	0.961	0.891

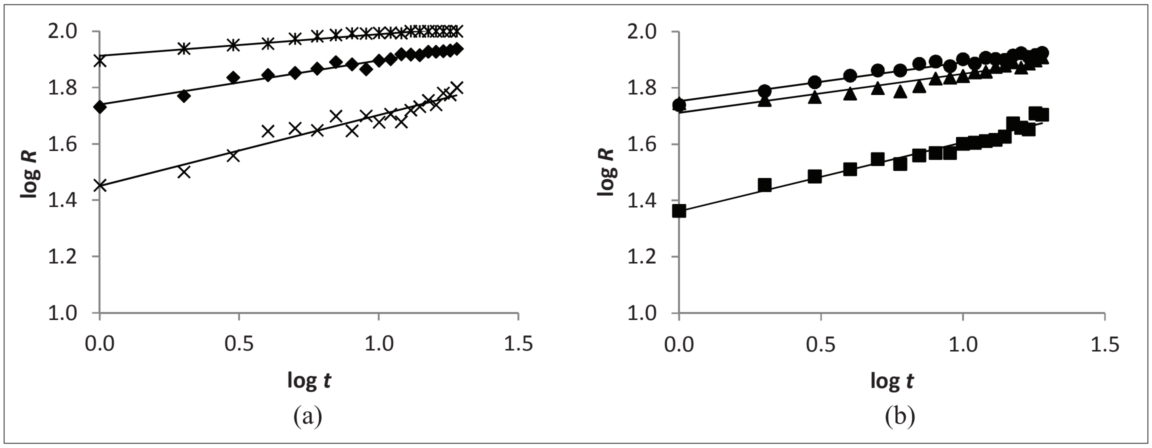


Figure 13: Weber and Morris intra-particle diffusion model for sorption of heavy metals on heated rice husk plotted according to equation (9). (a): Pb(II) (∗), Cd(III) (♦) and Ni(II) (×); (b): Zn(II) (•), Cu(II) (▲) and Cr(III) (■)

Figure 13 shows the linearised plots of log *R* *vs* log *t* according to the Weber and Morris intra-particle diffusion model. Satisfactory agreement of experimental data with this model indicates that the adsorption process is controlled by either particle-diffusion or intra-particle mass transfer as the rate determining step (Odoemelam *et al.*, 2011). The gradient of plots (*n*) and intra-particle diffusion rate constant (k_{id}) determined from the slope and the intercept of each linear plot, respectively, are given in Table 4.

The value k_{id} can be taken as a rate factor, which increases in the order of, Pb(II) > Zn(II) > Cd(II) > Cu(II) > Ni(II) > Cr(III), where higher values of k_{id} show an improvement in the rate of adsorption. The increasing order of the intra-particle diffusion rate constant (k_{id}) determined from the Weber and Morris model and that of the pseudo second order rate constant *(k′*) obtained by the simple kinetics model follow the same trend, demonstrating the validity of the two models to describe the adsorption of heavy metal ions investigated on rice husk. Further, larger *n* values show strong adsorption indicating strong bonding between the metal ion and the adsorbent (Odoemelam *et al.*, 2011). The adsorption of these metal ions on rice husk shows much strong bonding when compared with the previous reports on adsorption of Cu(II), Cd(II) and Pb(II) on different adsorbents (Table 5).

Table 4: Intra-particle diffusion model parameters for heavy metal ions investigated, determined by Weber and Morris model.

Metal ion	*n*	k_{id} (min^{-1})
Cd(II)	0.16	54.97
Cr(III)	0.24	23.00
Cu(II)	0.14	51.42
Ni(II)	0.25	28.25
Pb(II)	0.08	81.79
Zn(II)	0.14	56.72

Table 5: Previous results obtained for *n* and k_{id} parameters for different adsorbents

Metal ion	Adsorbent	Unmodified		Modified		Reference
		n	k_{id} (min^{-1})	*n*	k_{id} (min^{-1})	
Cu(II)		0.0009	97.01	0.0125	90.30	Odoemelam *et al.*, 2011
Cd(II)	Cocoa pod husk	0.0004	98.58	0.0068	94.58	
Pb(II)		0.00002	99.93	0.0048	96.14	
Cu(II)		0.005	94.86	0.0035	97.79	Sonde & Odoemelam, 2012
Cd(II)	Breadfruit seed hull	0.0015	97.86	0.0019	98.76	
Pb(II)		0.0001	99.88	0.0014	99.13	

The Boyd model predicts the actual slow step involved in the adsorption process. The graph of B_t against t indicates that the slowest step in the adsorption process is the internal diffusion if it does pass through the origin. The Boyd plots obtained from experimental data of the metal ions investigated (Figure 14) do not go through the origin, suggesting that the film diffusion mainly governs the rate of the reaction for all the adsorbates. The regression coefficient associated with each line is shown in the graph.

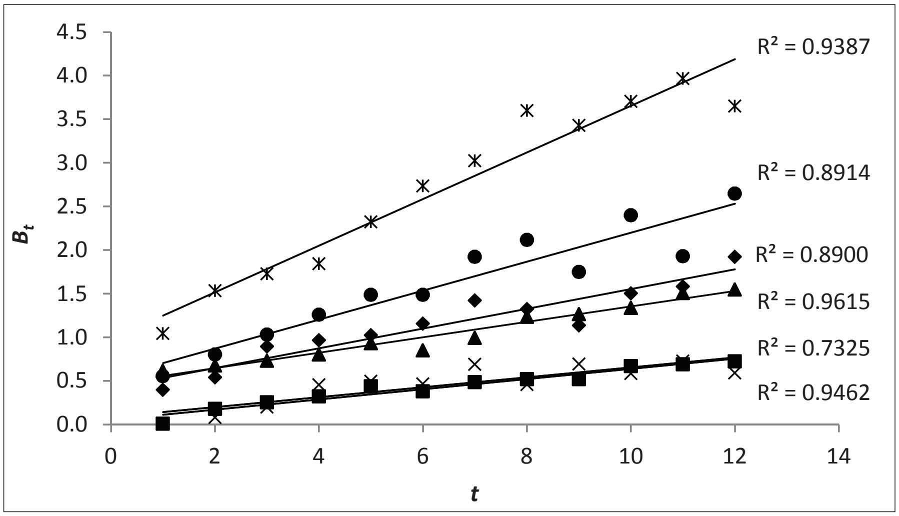


Figure 14: Boyd model for sorption of heavy metals on heated rice husk plotted according to equation (12). Pb(II) (∗), Cd(III) (♦), Ni(II) (×), Zn(II) (•), Cu(II) (▲) and Cr(III) (■)

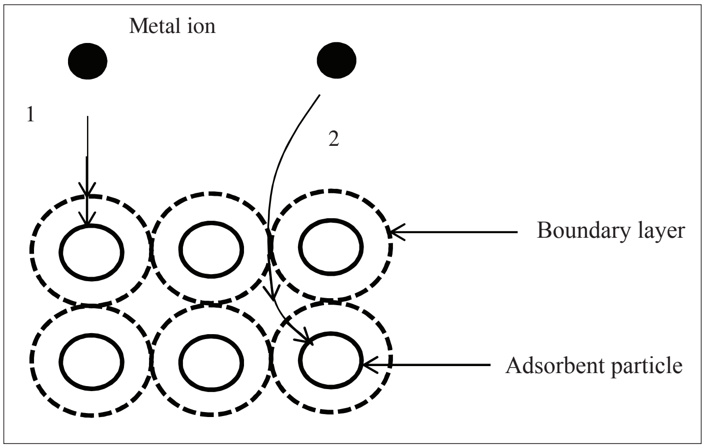


Figure 15: Schematic diagram of the mechanism of the adsorption of metal ions on rice husk

Considering the findings of all models, it is suggested that adsorption of Cd(II), Cr(III), Cu(II), Ni(II), Pb(II) and Zn(II) might be a chemisorption process whose rate is controlled by two species. Further, the mass transfer of heavy metal ions to the adsorbent phase is controlled by particle diffusion or intra-particle mass transfer, which involves film diffusion. Therefore, the rate limiting step may be the combination of the processes as illustrated in Figure 15 (Chakraborty *et al.*, 2011; Lim *et al.*, 2015).

1. Transfer of metal ions from the bulk solution on to the boundary film and then on to the surface of the adsorbent
2. Adsorbate transfer from the sorbent surface to the interparticle areas and then migrate to intraparticle active sites

Adsorption mechanism

According to the overall observation, as silica is a major constituent of rice husk, the sorption of metal ions would take place by the cation exchange reaction through the substitution of protons attached to silanol groups on the surface by the metal ions (M) from the solution as follows (Srivastava *et al*., 2006);

$$m(\text{- SiOH}) \rightleftharpoons m(\text{ -SiO}^-) + m\text{H+}$$

$$\text{M}^{n+} + m(\text{- SiO}^-) \rightleftharpoons \text{M(OSi-)}_m^{(n-m)+}$$

The overall reaction can thus be represented as:

$$\text{M}^{n+} + m(\text{- SiOH}) \rightleftharpoons \text{M(OSi-)}_m^{(n-m)+} + m\text{ H+}$$

In addition to the silanol groups, metal ion removal would also be contributed by organic compounds present in rice husk through complexation and/or ion exchange reactions. However, the relative contribution of each component present in rice husk to the overall removal process is yet to be investigated.

CONCLUSION

Adsorption of Cd(II), Cr(III), Cu(II), Ni(II), Pb(II) and Zn(II) on rice husk heated at 100 °C reaches equilibrium within a short time period and follows pseudo second order kinetics with high correlation coefficients ($R^2 > 0.900$) according to the linearised kinetics equation. The initial adsorption rates (h_o) of the heavy metal ions determined from the second order kinetics model in mg kg^{-1} min^{-1}, are 2500, 188, 526, 1111, 244 and 769 for Pb(II), Cr(III), Cu(II), Zn(II), Ni(II) and Cd(II), respectively, and these values vary in the order of Pb(II) > Zn(II) > Cd(II) > Cu(II) > Ni(II) > Cr(III). Among the diffusion models, namely, the external mass transfer diffusion model, the Weber and Morris intra-particle diffusion model, the Mckay and Poots intra-particle diffusion model and the Boyd model, the Weber and Morris model is in good agreement for the metal ion removal process according to the regression coefficient values obtained based on their linear forms. The rate constants of particle diffusion according to the Weber and Morris intra-particle diffusion model, in minutes, are 54.97, 23.00, 51.42, 28.25, 81.79 and 56.72 for Cd(II), Cr(III), Cu(II), Ni(II), Pb(II) and Zn(II), respectively, and it increases in the same order as observed in initial adsorption rate measurements (h_o).

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