Removal of Zn(II) and Hg(II) from aqueous solution on a carbonaceous sorbent chemically prepared from rice husk

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ABSTRACT

A carbonaceous sorbent was prepared from rice husk via sulfuric acid treatment. Sorption of Zn(II) and Hg(II) from aqueous solution was studied varying time, pH, metal concentration, temperature and sorbent status (wet and dry). Zn(II) sorption was found fast reaching equilibrium within ∼2 h while Hg(II) sorption was slow reaching equilibrium within ∼120 h with better performance for the wet sorbent than for the dry. Kinetics data for both metals were found to follow pseudo-second order model. Sorption rate of both metals was enhanced with temperature rise. Activation energy, E_a, for Zn(II) sorption, was ∼13.0 kJ/mol indicating a diffusion-controlled process ion exchange process, however, for Hg(II) sorption, E_a was ∼54 kJ/mol indicating a chemically controlled process. Sorption of both metals was low at low pH and increased with pH increase. Sorption was much higher for Hg(II) than for Zn(II) with higher uptake for both metals by rising the temperature. Hg(II) was reduced to Hg(I) on the sorbent surface. This was confirmed from the identification of Hg_2Cl_2 deposits on the sorbent surface by scanning electron microscopy and X-ray diffraction. However, no redox processes were observed in Zn(II) sorption. Sorption mechanism is discussed.

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1. Introduction

The presence of heavy metals in waste and surface waters is becoming a severe environmental problem and because of their non-biodegradability, they can accumulate in the food chain posing a significant danger to human health. Traditional methods for the removal of heavy metals from water include hydrometallurgical technologies, ion exchange, electrodialysis, reverse osmosis, precipitation and adsorption.

Zinc can be found in wastewater from metallurgical processes, galvanizing plants, stabilizers, thermoplastics, pigment formation, alloys and battery manufacturing in addition to the discharges of municipal wastewater treatment plants [1,2]. Mercury can also be found in wastewater because of the discharges of industrial wastewater from chlor-alkali, paper and pulp, oil refinery, paint, fossil fuel burning, metallurgical processes, pharmaceutical and battery manufacturing [3].

Zinc is an essential trace element in small quantities for humans taking role in electron transfer in many enzymatic reactions [4]. However, its prolonged and excessive intake may lead to toxic

effects such as carcinogenesis, mutagenesis and teratogenesis as a result of its bioaccumulation [5]. Mercury is a very toxic non-essential element and poses a potential threat to human health even at very low concentrations. It can cause brain damage, dysfunction of liver, kidney, gastrointestinal tract and central nervous system [6]. Inorganic mercury is the most prevalent form of mercury in aquatic ecosystems. However, its biochemical conversion into a more toxic form (methylmercury) by microorganisms is kinetically feasible both in water and soil [7]. Based on the Omani regulations that agree with the WHO standards [8,9], the maximum contaminant levels for zinc and mercury in wastewater are 5.0 and 0.001 mg/l, respectively.

Rice which is cultivated in more than 75 countries in the world is the essential food for over half the world's population. The worldwide annual rice husk output is about 80 million tones and over 97% of the husk is generated in the developing countries [10]. Unmodified rice husk has been evaluated for their ability to bind zinc (II) and other metal ions [11,12]. Various modifications on rice husk have been reported in order to enhance sorption capacities for metal ions and other pollutants [13,14]. Zn(II) was also removed from water using different sorbents including activated carbon [15], modified flax shive [16], rice husk ash [17], waste biomass [2], waste activated sludge [2] and lignite [18].

Different sorbents were used to remove mercury from aqueous solutions including peat [19], lignite [20], unmodified rice husks

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[21], rice-husk ash [22], modified flax shive [23], tea leaves [24], coffee beans [24] and activated carbon [25].

In this paper, rice husk was treated with sulfuric acid to produce a carbonaceous sorbent. The capability of the produced sorbent to remove Zn(II) and Hg(II) from aqueous solution was tested and removal mechanism was investigated.

2. Experimental

2.1. Sorbent preparation

Rice husk was received from a rice mill and washed with a stream of distilled water through a sieve of 16 mesh (Tyler Standard Screen Scale) to remove dirt, dust and any superficial impurities. The husk was put in trays and left to dry in open air at room temperature to constant weight. The sorbent was prepared as follows [26]: Clean air-dried rice husk (20 g) was weighed in a clean dry beaker of capacity 500 ml. 100 ml of 13 M sulfuric acid were added to the rice husk and the mixture was heated to 175–180 °C in 20 min with occasional stirring. The temperature was kept in that range of temperature for 20 min. The resulting black mixture was allowed to cool, and then filtered using a Buchner funnel under vacuum. The black spent sulfuric acid was filtered off and the carbonized material was washed several times with distilled water and was stored under dilute acidic conditions (dilute sulfuric acid, pH 1.5–2) to avoid any bacterial growth. Before use for metal sorption, a sample of the carbonized product was washed in Gooch crucible until the wash water did not show a change of methyl orange color and did not show a precipitate with barium chloride solution. The sample was washed again with a stream of distilled water between two sieves of 16 and 60 mesh (Tyler Standard Screen Scale) to remove fine particulates and to select a suitable size range for the experiments. The sample was transferred to a Gooch crucible and left under suction for 30 min. Suitable samples of the carbonaceous sorbent were then used in sorption experiments and a sample of 1 g was separated to measure the moisture content by oven drying at 120 °C to constant weight. For work under dry conditions, the carbonized wet product (acid-free) was dried in an oven at 120 °C to constant weight, transferred to a desiccator to cool and finally stored in a dry, clean and well-closed polyethylene jar. The sorbent was ground and the size range between two sieves of 16 and 60 mesh (Tyler Standard Screen Scale) were selected for the sorption experiments.

2.2. Metal sorption

All the chemicals used were of analytical grade. Stock solutions, 1000 mg/l of Zn(II) and 2000 mg/l of Hg(II), were prepared in distilled water using zinc chloride ($ZnCl_2$) and mercury(II) chloride ($HgCl_2$), respectively. All the working solutions were prepared by diluting the stock solution in distilled water.

In the kinetic experiments, for Zn(II) sorption, 0.1 g of the dry sorbent (or the equivalent weight of the wet sorbent) were mixed with 50 mg/l (100 ml) of Zn(II) at pH 6. For mercury sorption, 0.075 g of the dry sorbent (or the equivalent weight of the wet sorbent) were mixed with 200 mg/l (100 ml) of Hg(II) at pH 6. pH 6 was found optimal for the sorption of both metals, as shown later. At different periods of time, aliquot of supernatant was withdrawn for metal analysis. Batch experiments, were carried out by mixing 50 ml of metal solution of desired concentration, pH and temperature, with 0.1 g and 0.075 g of the dry sorbent (or the equivalent weight of the wet sorbent) for Zn(II) and Hg(II) sorption, respectively in a shaking water bath (100 rpm) until equilibrium was reached. The effect of pH on metal sorption was studied for metal concentration (100 mg/l for Zn(II) and 300 mg/l for Hg(II)) at dif-

ferent pH values (pH 1.5–6). The pH was adjusted by adding few drops of 0.1 M hydrochloric acid or 0.1 M sodium hydroxide before the addition of the pre-weighed sorbent. The isotherm studies were carried out using wet and dry sorbents at initial pH 6 in metal concentration range of 25–300 mg/l for Zn(II) and 100–1500 mg/l for Hg(II), at different temperature (25–45 °C). After the equilibrium time was reached, aliquot of supernatant was withdrawn and metal concentration was measured.

2.3. Sorbent acidity and cation exchange capacity

Sorbent acidity, or sorbent pH, was measured as follows [27,28]: a sample of the sorbent (0.1 g) was mixed with distilled decarbonated water (20 ml) and two drops of acetone, to facilitate wetting of the sample, and refluxed for 15 min. After cooling, the pH of the sludge was obtained using a pH meter and combined pH electrode. Cation exchange capacity was measured using ASTM standard method [29].

2.4. Metal analysis

Zn(II) was determined via Varian Spectra AA 220 FS atomic absorption spectrophotometer. Mercury content was analyzed spectrophotometrically (Varian Cary 50 Conc UV/Vis Spectrophotometer) at 488 nm, following a procedure adapted by Ahmed and Alam using dithizone [30]. Experiments and analysis have been carried out three times and maximum analytical error was found to be less than 5%.

### 2.5. Scanning electron microscope and X-ray powder diffraction

Scanning electron microscope (SEM) analysis was carried out using a Goel JSM 840-A scanning electron microscope. X-ray powder diffraction was carried out using a Philips PW 1830 generator with a Philips PW 1050 powder goniometer. Copper Kα was used as the incident radiation.

3. Results and discussion

Rice husk possesses cellulose, hemicelluloses and lignin as main components in addition to ash [10]. Concentrated sulfuric acid behaves as an extremely strong dehydrating agent [31]. It acts also as a strong oxidizing agent because of its tendency to lose an atom of oxygen to form sulfurous acid, H_2SO_3, which readily decomposes to sulfur dioxide and water [32]. Under the preparation conditions of the sorbent, carbonization with partial oxidation took place to the cellulose and hemicelluloses in addition to partial fragmentation to the lignin components [33] resulting in a carbonaceous material loaded with function groups on the surface such as –OH and –COOH [26]. The effect of hot sulfuric acid on an agricultural material (flax shive) producing a carbonaceous sorbent was studied and published earlier [33]. The surface area of the dry sorbent, measured by nitrogen adsorption, is 66 m^2/g. Low surface area was also observed for carbons prepared from flax shive with sulfuric acid dehydration (19 m^2/g) [33]. This could be related to the presence of carbon–oxygen species that occupy a large fraction of the sorbent surface [34]. Sorbent pH and cation exchange capacity were measured to be 1.34 meq/g and 2.65, respectively. The moisture content of the prepared wet sorbent, in the current study, was 85% and ash content 17.7%.

3.1. Effect of pH

In the pH range 1.5–2, sorption of both divalent metal ions was extremely low, and with the rise in the initial pH, metal uptake increased (Fig. 1). For Zn(II) uptake, almost no significant change
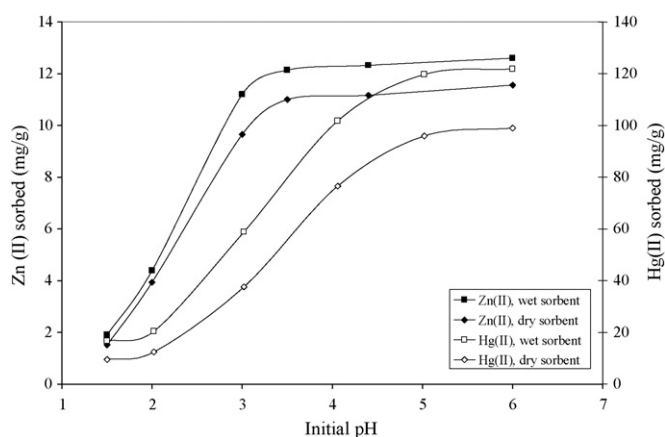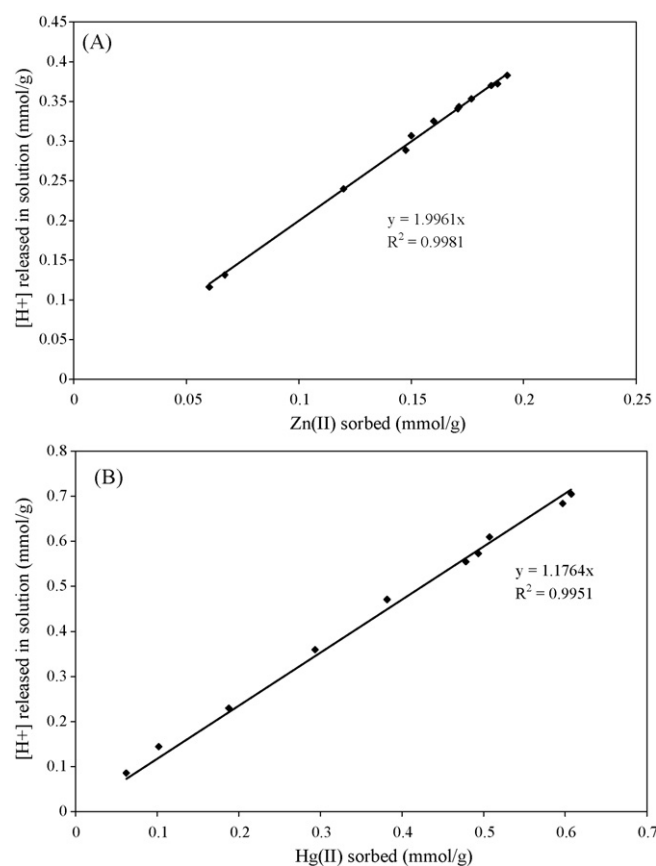
Fig. 1. Sorption of Zn(II) and Hg(II) at different initial pH values and 25 °C. (Initial concentration 100 mg/l for Zn(II) and 300 mg/l for Hg(II), volume of metal solution 50 ml, shaking speed 100 rpm.)
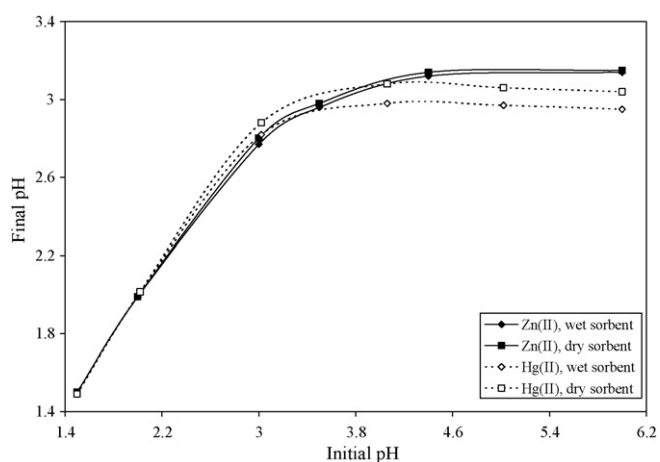
Fig. 2. A plot of initial and final pH for Zn(II) and Hg(II) sorption.

Fig. 3. A plot of [H$^+$] released in solution against (A) Zn(II) sorbed and (B) Hg(II) sorbed at 25 °C.

appeared between pH 3.5 and 6, while maximum Hg(II) uptake took place at pH 5–6. Higher initial pH values were avoided to prevent possible precipitation as hydroxides [35]. Metal sorption was accompanied by a decrease in the final pH (Fig. 2) indicating protons release in solution and suggesting an ion exchange mechanism. Similar results showed an increase in the uptake of Zn(II) [2,12,14,16,36] and Hg(II) [3,7,23,35] with the increase in the initial pH of sorption solution on different sorbents. Plotting [H$^+$] released in solution against Zn(II) and Hg(II) uptake would give a straight line of slope ∼2, if the ion exchange process is dominating the metal uptake. The slopes of [H$^+$] released/[metal] sorbed were 2.00 and 1.18 for Zn(II) and Hg(II) sorption, respec-

tively (Fig. 3). This suggests that an ion exchange process is the dominating mechanism for Zn(II) removal, however, for Hg(II) removal, there may be other processes involved in addition to ion exchange.
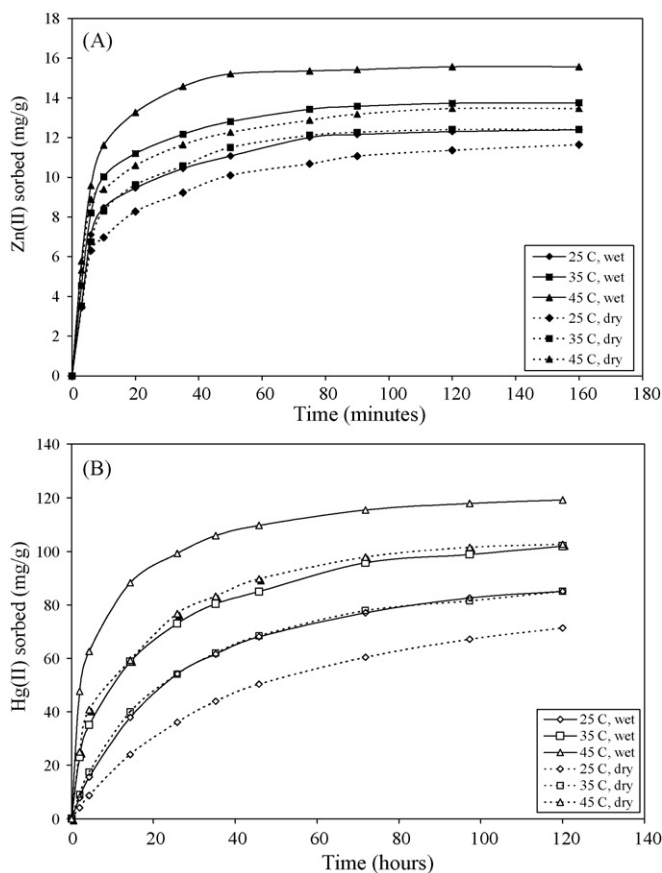
Wet sorbents behave similarly to the dry ones with an increase in metal uptake for the former. The wet sorbent has wider pores and, probably, more access for metal ions for sorption sites than the dry sorbent [23]. Hg(II) uptake is obviously higher than Zn(II) uptake by the wet and dry sorbents.

3.2. Kinetics of metal sorption

Based on the results of the pH experiments, Zn(II) and Hg(II) were sorbed best at pH 6. Accordingly, pH 6 was chosen for the studies of sorption kinetics and temperature effect for both metals. Equilibrium was reached within ∼2 h for Zn(II) sorption (Fig. 4A), however, for Hg(II) sorption, approximate equilibrium was reached

Table 1
Pseudo-second order rate constants of the kinetics of Zn(II) and Hg(II) sorption.

Sorbent status	Temperature (°C)	Zn(II) sorption					Hg(II) sorption		
		Rate constant, k		Initial adsorption rate, h		Correlation value, R^2	Rate constant, k (g mg^{-1} h^{-1})	Initial adsorption rate, h (mg g^{-1} h^{-1})	Correlation value, R^2
		(g mg^{-1} min^{-1})	(g mg^{-1} h^{-1})	(mg g^{-1} min^{-1})	(mg g^{-1} h^{-1})				
Wet sorbent	25	0.0114	0.684	1.91	114.8	0.9994	0.000415	4.32	0.9998
	35	0.0134	0.807	2.74	164.2	0.9998	0.000818	9.88	0.9976
	45	0.0158	0.948	4.07	244.2	0.9998	0.00160	24.4	0.9994
Dry sorbent	25	0.0097	0.582	1.43	85.78	0.9990	0.00023	2.21	0.9997
	35	0.0116	0.698	1.97	118.3	0.9996	0.00049	4.80	0.9997
	45	0.0135	0.807	2.60	156.1	0.9995	0.00092	11.3	0.9979

Fig. 4. Sorption of (A) Zn(II) and (B) Hg(II) on the carbonaceous sorbent against time at different temperature. (Initial pH 6.0, volume of metal solution 50 ml, shaking speed 100 rpm, initial concentration 50 mg/l for Zn(II) and 200 mg/l for Hg(II).)

Fig. 5. Pseudo-second order kinetics for the sorption of (A) Zn(II) and (B) Hg(II) at pH 6.0 at 25 °C.

within ∼120 h (Fig. 4B). Evidently, Zn(II) sorption shows a much faster kinetics, however, with less metal uptake than Hg(II).
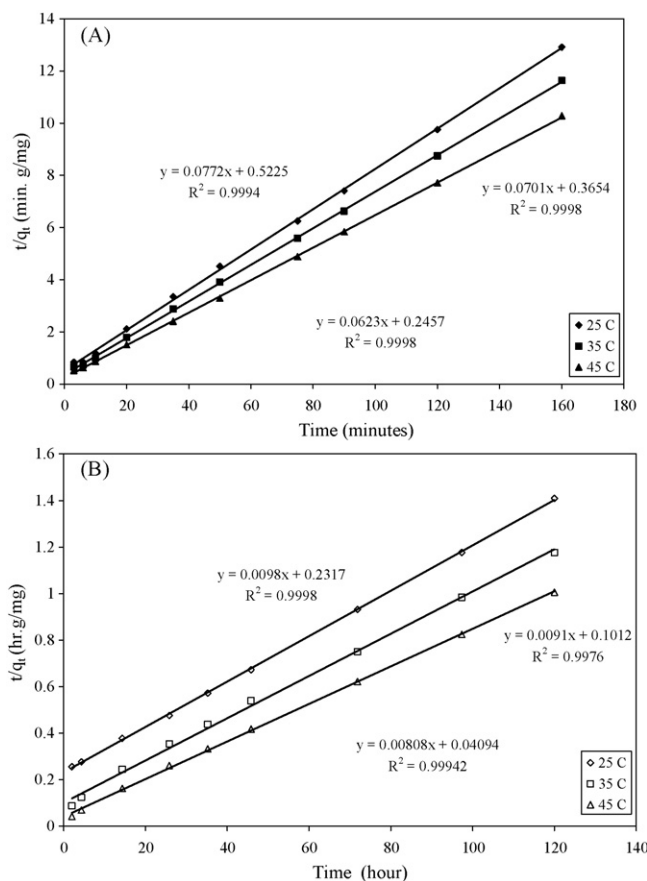
Sorption of Zn(II) and Hg(II) follows pseudo-second order kinetic model [37], Eq. (1).

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{t}{q_e} \qquad (1)$$

where k (g mg^{-1} h^{-1}) is the rate constant of the pseudo-second order model. q_e and q_t are the amount of metal sorbed at equilibrium and at time t per unit weight of the sorbent (mg/g), respectively. The initial sorption rate, $h = kq_e^2$.

The linear plots of t/q_t versus t for the pseudo-second order model of Eq. (1) (Fig. 5A and B) show a good fitting with high correlation coefficient values, R^2, Table 1. This indicates that the sorption of Zn(II) and Hg(II) complies very well with pseudo-second order kinetic reaction which agreed with chemisorption as the rate-limiting mechanism through sharing or exchange of electron between sorbent and sorbate [37,38]. Both of the rate constant, k, and the initial adsorption rate, h, are slightly higher for the wet sorbent than for the dry (Table 1) and this could be related to the shrinkage and compaction of the sorbent as a result of drying, giving narrower pores for the diffusion of metal ions [23,26].

Rate constant, k, and initial adsorption rate, h, for Zn(II) sorption were much higher than that for Hg(II) sorption in the units of (g mg^{-1} h^{-1}) and (mg g^{-1} h^{-1}), respectively (Table 1). The decrease in the values of k and h for Hg(II) sorption, due to its slow sorption kinetics, reflects a different mechanism from that for Zn(II) sorption. In previous studies [16,23], Cd(II) was sorbed much faster than Hg(II) on a carbonaceous sorbent prepared from flax shive via sulfuric acid treatment and Cd(II) uptake was related to ion exchange

mechanism, however, sorption reduction processes were involved in Hg(II) uptake by the sorbent.

A larger increase in rate constants, k, and initial adsorption rates, h, was observed with temperature rise for Hg(II) than for Zn(II) sorption (Table 1). By rising the temperature from 25 to 45 °C, an increase in k and h, for Zn(II) sorption, to 1.39 and 2.1 folds for the wet sorbent and to 1.39 and 1.8 folds for dry sorbent, respectively. However, for Hg(II) sorption, k and h showed an increase to 4.0 and 5.8 folds for the wet sorbent and 4.1 and 5.2 for the dry sorbent, respectively.

The Arhenius equation (Eq. (2)) was applied to calculate E_a for the sorption processes.

$$k = Ae^{-E_a/RT} \qquad (2)$$

k refers to the pseudo-second order rate constant (g mg^{-1} h^{-1}), and E_a is the activation energy of metal sorption (kJ/mol). A is the pre-exponential factor (frequency factor), R is the gas constant (8.314 J/mol K) and T is the solution temperature (K).

From the linear relationships between the logarithm of rate constants and the reciprocal of the Kelvin temperature, Fig. 6A and B, E_a for Zn(II) sorption was 12.83 and 12.86 kJ/mol using the wet and dry sorbents, respectively, indicating an ion exchange diffusion-controlled mechanism [36]. However, for Hg(II) sorption, E_a values were 53.1 and 54.5 kJ/mol using the wet and dry sorbent, respectively, indicating that the rate-limiting process was evidently a chemical process. Low E_a values (<42 kJ/mol) indicate diffusion-controlled processes, whereas higher E_a values (>42 kJ/mol) indicate chemically controlled processes [39,40].
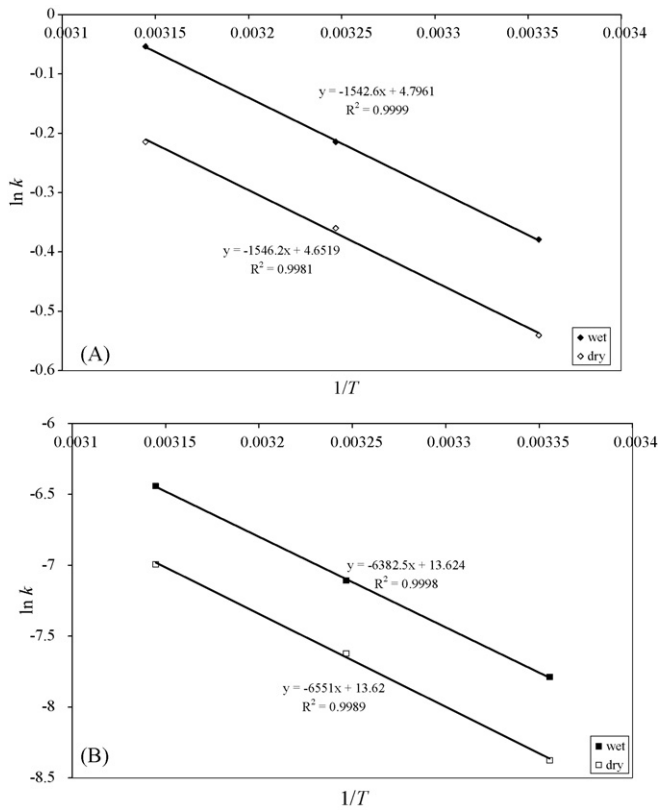
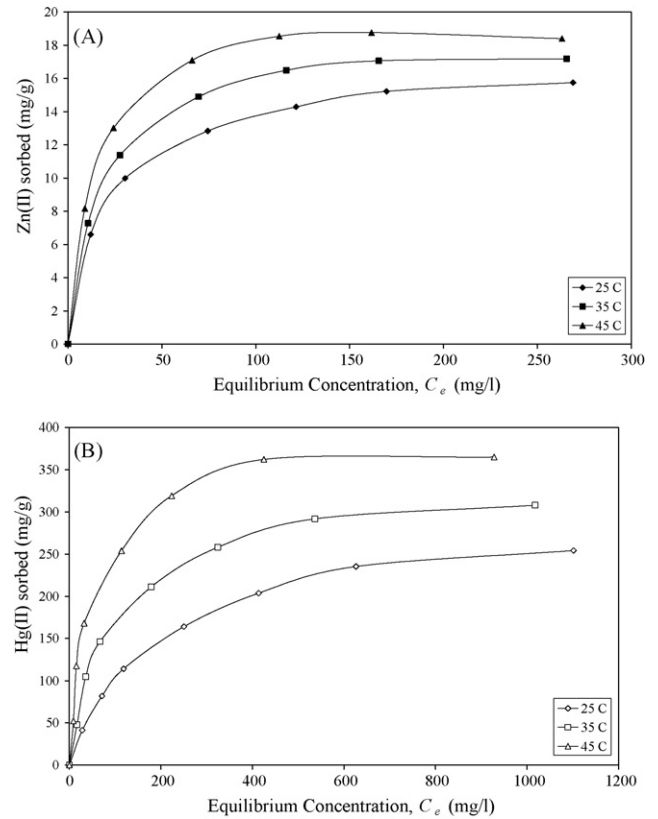**Fig. 6.** Plots of ln k against $1/T$ for the sorption of (A) Zn(II) and (B) Hg(II) at different temperature.

Fig. 7. Sorption of (A) Zn(II) and (B) Hg(II) at pH 6 on the wet sorbent at different temperatures.

3.3. Sorption capacity and temperature effect

Sorption of Zn(II) and Hg(II) on the wet and dry sorbents follows an "L- type" adsorption isotherm, with increased uptake as temperature rises. Fig. 7A and B represents the sorption of Zn(II) and Hg(II) at different temperature on the wet sorbent. The experimental isotherm data fit well the Langmuir equation [14], Eq. (3), for both metals on the wet and dry sorbents (Table 2). Freundlich equation [14], Eq. (4), was also tested for the sorption equilibrium data (Table 2). The Langmuir and Freundlich isotherms for Zn(II) and Hg(II) sorption, on the wet sorbent, are shown in Figs. 8 and 9, respectively.

$$\frac{C_e}{q_e} = \frac{1}{bq} + \frac{C_e}{q} \tag{3}$$

C_e, equilibrium metal concentration; q, and b are the Langmuir constants related to maximum adsorption capacity (mg/g), and the relative energy of adsorption (l/mg), respectively.

$$\log q_e = \frac{1}{n} \log C_e + \log K \tag{4}$$

where K (l$^{1/n}$ mg$^{1-1/n}$ g^{-1}) and $1/n$ are the constants, which are considered to be the relative indicators of adsorption capacity and adsorption intensity. The values of $1/n$ that vary between 0.1 and 1.0 indicate the favorable adsorption of heavy metals [41].

The monolayer capacity, q (mg/g), for Zn(II) sorption, was slightly higher for the wet sorbent than for the dry (Table 2), however this increase was significant for Hg(II) sorption. The drying process causes the pores to become narrower and some sorption sites to be hidden or inaccessible to metal ions. Rising the temperature has increased the sorption of both metals, Fig. 7A and B and

Table 2
Langmuir parameters for the sorption Zn(II) and Hg(II) at pH 6 at different temperature.

Metal	Sorbent	Sorption temp. (°C)	Langmuir constants		Correlation value, R^2	Freundlich constants		Correlation value, R^2
			q (mg/g)	b (l/mg)		$1/n$	K (l$^{1/n}$ mg$^{1-1/n}$ g^{-1})	
Zn(II)	Wet	25 °C	16.978	0.0469	0.9996	0.2158	4.925	0.9627
		35 °C	18.349	0.0642	0.9995	0.1893	6.371	0.9033
		45 °C	19.380	0.1044	0.9984	0.1527	8.488	0.8207
	Dry	25 °C	16.026	0.0450	0.9986	0.2210	4.485	0.9761
		35 °C	17.889	0.0558	0.9997	0.1884	6.129	0.9270
		45 °C	18.939	0.0763	0.9994	0.1630	7.612	0.9276
Hg(II)	Wet	25 °C	303.03	0.00522	0.9990	0.5579	7.137	0.9812
		35 °C	336.70	0.0107	0.9992	0.3767	28.71	0.9867
		45 °C	384.62	0.0219	0.9988	0.3407	48.87	0.9863
	Dry	25 °C	227.27	0.0052	0.9991	0.4607	8.712	0.9523
		35 °C	270.27	0.0088	0.9998	0.4281	15.03	0.9278
		45 °C	303.03	0.0129	0.9993	0.4484	18.13	0.9593
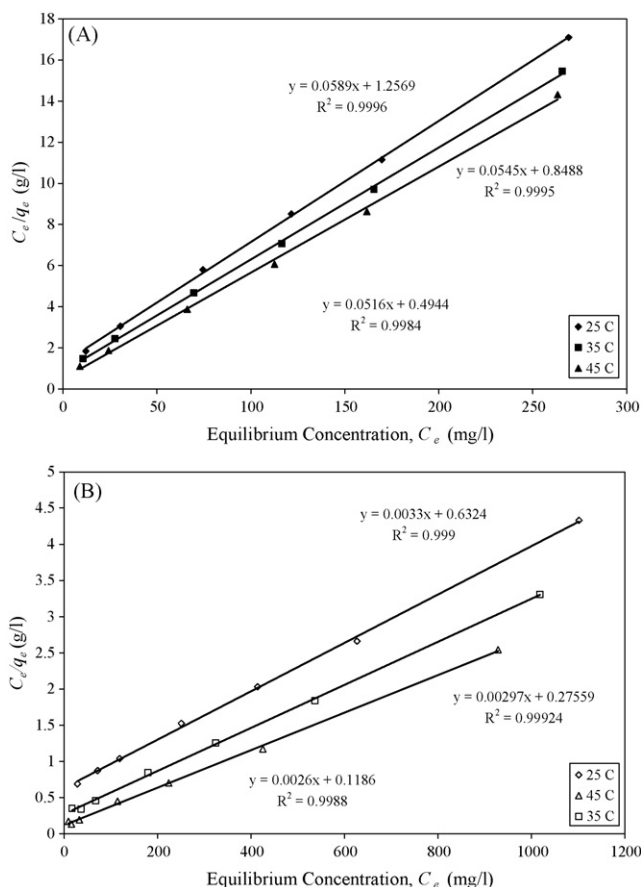
Fig. 8. Langmuir isotherms for the sorption of (A) Zn(II) and (B) Hg(II) at pH 6.0 on the wet sorbent at different temperatures.
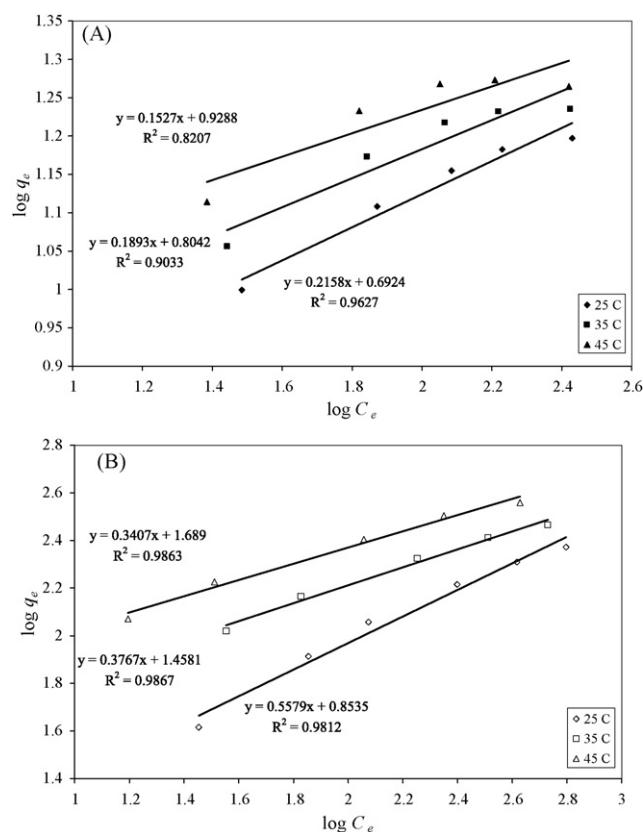

Fig. 9. Freundlich isotherms for the sorption of (A) Zn(II) and (B) Hg(II) at pH 6.0 on the wet sorbent at different temperatures.

Table 2. This could be due to some swelling of the carbon and a consequent increase in sorption sites as found earlier for Cd(II) and Hg(II) sorption on carbon sorbents prepared from flax shive via sulfuric acid treatment [16,23]. Sorption capacities from the present study (Table 2) were compared with rice husk, modified rice husk

and other adsorbents from other studies in Table 3. It is obvious that carbonized sorbents, prepared via sulfuric acid treatment from rice husk (the present study) or flax shive (a previous study [23]), show larger sorption capacities for Hg(II) than other known adsorbents (Table 3). The sorbent, in the present study, in addition of being cheap, shows also a comparable sorption capacity to other sorbents for Zn(II) sorption (Table 3).
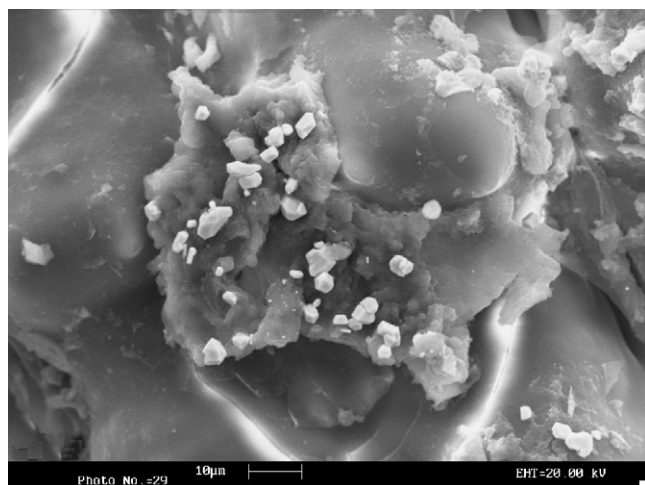
Table 3
Maximum sorption capacities of Zn(II) and Hg(II) on different sorbents.

Metal ion	Sorbent material	Maximum sorption (mg/g)	Reference
Zn(II)	Activated carbon from lemon peel	0.262 (30 °C, pH 5.9)	[15]
	Activated carbon from date nuts	0.426 (30 °C, pH 5.9)	[15]
	Chabazite (natural zeolite)	5.23 (20 °C, pH 5)	[2]
	Rice husk ash	6.4 (30 °C, pH 6.5)	[17]
	Biomatrix from rice husk	8.14 (32.0 °C, pH 6.0)	[14]
	Lignite	10.72 (25 °C, pH 4–5)	[18]
	Sulfuric acid treated rice husk (dry sorbent)	18.94 (45 °C, pH 6.0)	Present study
	Sulfuric acid treated rice husk (wet sorbent)	19.38 (45 °C, pH 6.0)	Present study
	Mycelial waste biomass	21.58 (20 °C, pH 5)	[2]
	Unmodified rice husk	30.8 (50 °C, pH 6.2)	[42]
	Sulfuric acid treated flax shive (C200)	32.47 (25 °C, pH 4.2)	[16]
	Waste activated sludge biosolid	36.88 (20 °C, pH 4)	[2]
Hg(II)	Unmodified rice husk	1.28 (50 °C, pH 6)	[21]
	Biomatrix from rice husk	36.1 (32.0 °C, pH 5.5)	[14]
	Extracellular biopolymer poly(c-glutamic acid)	96.79 (30 °C, pH 6.0)	[7]
	Activated carbon from fruit shell of *Terminalia catappa*	184.0 (60 °C, pH 5.0)	[36]
	Steam activated carbon (SA-C)	208.3 (60 °C, pH 6.0)	[3]
	Steam activated carbon in presence of H_2S (SA-H_2S-C)	217.4 (60 °C, pH 6.0)	[3]
	Steam activated carbon in presence of SO_2 (SA-SO_2-C)	222.2 (60 °C, pH 6.0)	[3]
	Steam activated carbon in presence of H_2S and SO_2 (SA-SO_2-H_2S-C)	227.3 (60 °C, pH 6.0)	[3]
	Sulfuric acid treated rice husk (dry sorbent)	303.03 (45 °C, pH 6.0)	Present study
	Sulfuric acid treated rice husk (wet sorbent)	384.62 (45 °C, pH 6.0)	Present study
	Sulfuric acid treated flax shive (dry sorbent)	385 (45 °C, pH 6.5)	[23]
	Sulfuric acid treated flax shive (wet sorbent)	526 (45 °C, pH 6.5)	[23]

Fig. 10. SEM photograph of loaded sorbent with mercury(I) chloride.

Comparatively, the obtained R^2 values are more satisfactory for the Langmuir isotherm than for the Freundlich isotherm (Table 2). The basic assumption of the Langmuir adsorption isotherm is based on monolayer coverage of the adsorbate on the surface of adsorbent [43,44] which is an indication of the fact that the sorption of Zn(II) or Hg(II) on to the investigated sorbents generates monolayer formation.

3.4. SEM and X-ray powder diffraction

Wet sorbent samples, after the equilibrium contact with 300 mg/l of Zn(II) or 1500 mg/l of Hg(II) at pH 6 and 45 °C, were separated, left to dry at room temperature and then used for SEM and X-ray analysis. Crystals of mercury(I) chloride on the sorbent surface are clearly identified on SEM photograph, Fig. 10. X-ray powder diffraction pattern confirmed the identification of mercury(I) chloride, calomel type, on the sorbent surface with the interplanar spacing (d) and relative line intensities (I) agreeing with those recorded (Fig. 11 and Table 4). This indicates that a reduction process of Hg(II) to Hg(I) took place on the sorbent surface. Hg(I) cations interacted with chloride ions in solution forming the crystals of Hg₂Cl₂. In previous studies, the sorbent under investigation showed a reduction capability of Cr(VI) to Cr(III) [26] and Se(IV) to elemental selenium [46]. In other studies [23], Hg(II) was reduced
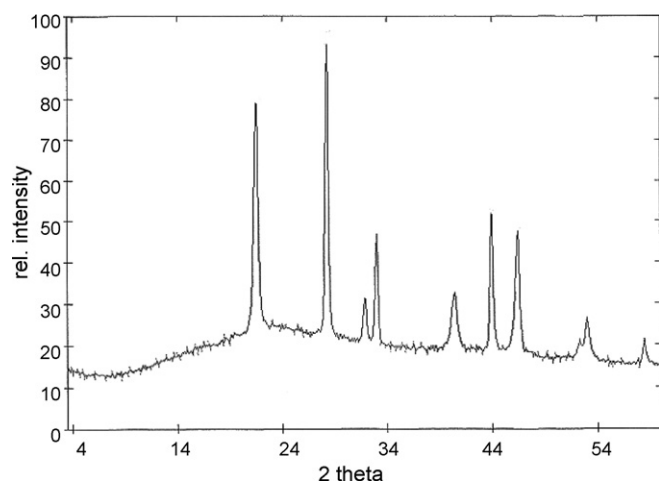

Fig. 11. X-ray diffraction pattern for the carbonaceous sorbent after mercury(II) loading.

Table 4
X-ray powder diffraction after mercury(II) chloride loading confirming that the crystals available are of mercury(I) chloride.

Observed		Literature [45]	
d (Å)	Intensity (I)	d (Å)	Intensity (I)
4.156	75	4.15	75
3.174	100	3.17	100
2.837	12	2.824	12
2.733	36	2.727	30
2.242	14	2.240	14
2.070	43	2.067	40
1.975	30	1.97	16
1.755	3.7	1.756	4
1.735	10.7	1.732	12
1.585	5.4	1.5841	6

to Hg(I) and Hg(0) on the surface of a carbonaceous sorbent prepared from flax shive via sulfuric acid treatment. In the present study, SEM analysis and X-ray powder diffraction did not show any changes on the sorbent surface after Zn(II) sorption indicating the absence of redox reactions between the sorbent and Zn(II).

3.5. Sorbent pH and cation exchange capacity

Wet sorbents, after the contact with 300 mg/l of Zn(II) or 1500 mg/l Hg(II) at pH 6.0, at 45 °C until the equilibrium was reached, were separated and washed with 0.1 M HCl, to strip metal ions from the sorbent surface. The sorbent samples were then washed by distilled water to become acid-free, dried at 105 °C and then used to carry out sorbent acidity and cation exchange capacity experiments. Sorbent acidity (the pH of the aqueous slurry of the carbonaceous sorbent) that provides a convenient indicator of the surface groups on the carbon sorbent has increased, or sorbent pH decreased, after the reaction with Hg(II). The pH of the sorbent is mainly related to the concentration of carboxylic groups [47]. Sorbent pH was found to decrease after the reaction with Hg(II) from 2.65 to 2.33. This indicates an increase in carbon–oxygen functional groups on the surface mainly –COOH [47]. Cation exchange capacity was also found to increase from 1.34 to 1.67 meq/g after the reaction with Hg(II), however, on the other hand, almost no change in sorbent acidity or cation exchange capacity of the sorbent after Zn(II) loading.

3.6. Mechanism of sorption

From the speciation diagram that has been reported by Carrott et al. [48], the predominant ionic species is Zn^{2+} at pH < 7, whereas Zn(II) is present mainly as Zn^{2+} and $Zn(OH)_2$, and in lesser quantity as $Zn(OH)^+$ at pH between 8 and 9 [49]. Since all the experiments were carried at a maximum pH of 6, the predominant Zn(II) species found in solution and adsorbed on the sorbent surface was Zn^{2+}.

Due to the increased Zn(II) sorption at high pH values until pH 6 with the release of protons with the ratio of $[H^+]$ release/$[Zn^{2+}]$ sorbed ~ 2, it can be concluded that Zn(II) was sorbed mostly via ion exchange. The carbon possesses acidic functional groups on surface such as –COOH and –OH [46] that are responsible for the cation exchange property as expressed in Eqs. (5) and (6).

$$2 -COOH + Zn^{2+} = -(COO)_2Zn + 2H^+ \tag{5}$$

$$2 -COH + Zn^{2+} = -(CO)_2Zn + 2H^+ \tag{6}$$
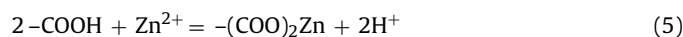
At low pH values, excess H^+ present in solution competes with Zn(II) ions for active sites leading to less Zn(II) removal. However, when the pH was increased the concentration of H^+ decreases, but the concentration of Zn(II) ions remains the same leading to increased uptake.
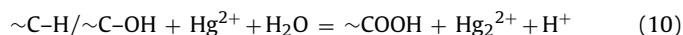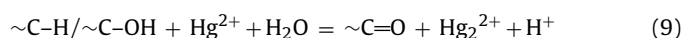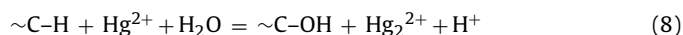
For Hg(II) sorption from chloride media at different pH values, according to stability constant calculations in the presence of Cl⁻, the predominant species at pH < 4.0 is $HgCl_2$ [3,35]. This should prevent mercury(II) from binding onto the sorbent at low pH, as chloride anions tend to form more stable complexes with mercury such as $HgCl_2$, $HgCl_3^-$ and $HgCl_4^{2-}$ [3]. Besides, the excess H^+ ions present in solution, at low pH values, competes with Hg(II) ions for active sites leading to less Hg(II) removal.

Hg(II) sorption shows a slower kinetic process with higher sorption capacity than Zn(II) sorption. In addition, E_a for Hg(II) sorption was higher than that of Zn(II) sorption indicating a chemically controlled process for the former and a diffusion-controlled process for the later. The difference in the behavior of Hg(II) sorption is directly related to Hg(II) reduction and related surface oxidation.

Presence of mercury(I) chloride crystals on the sorbent surface in addition to the increased surface acidity and cation exchange capacity after the reaction with Hg(II) chloride is an obvious evident for Hg(II) reduction to Hg(I). Hg(II) reduction is represented by Eq. (7).

$$2Hg^{2+} + 2e = Hg_2^{2+} \qquad E^0 = +0.92\,V\,[50] \tag{7}$$
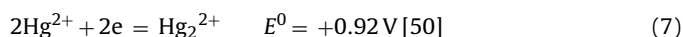
Possible surface oxidation, as shown in Eqs. (8)–(10), by the reaction with Hg(II), has increased the sorbent acidity and cation exchange capacity.

$$\sim\!C\text{–}H + Hg^{2+} + H_2O = \sim\!C\text{–}OH + Hg_2^{2+} + H^+ \tag{8}$$

$$\sim\!C\text{–}H/\!\sim\!C\text{–}OH + Hg^{2+} + H_2O = \sim\!C\!=\!O + Hg_2^{2+} + H^+ \tag{9}$$

$$\sim\!C\text{–}H/\!\sim\!C\text{–}OH + Hg^{2+} + H_2O = \sim\!COOH + Hg_2^{2+} + H^+ \tag{10}$$

Because Hg_2Cl_2 is sparingly soluble in aquatic systems, reduction of $HgCl_2$ to insoluble Hg_2Cl_2 seems a useful technique for the decontamination of mercury polluted water.

4. Conclusion

The carbonaceous sorbent prepared from rice husk, a cheap agricultural waste, via sulfuric acid treatment, possesses ion exchange and reduction properties. Zn(II) showed a faster sorption kinetics than Hg(II) following pseudo-second order model. Sorption of Zn(II) and Hg(II) was extremely low at low pH values and increased with pH rising with a decrease in the final pH due to protons release in solution. E_a was found to be ~13.0 kJ/mol for Zn(II) sorption indicating a diffusion-controlled ion exchange mechanism, however, for Hg(II) sorption, E_a was ~54 kJ/mol indicating a chemically controlled process. Sorption of Zn(II) and Hg(II) follows the Langmuir equation with an increase in metal uptake as temperature rises due to an expected increase in the swelling of the sorbent allowing more active sites to become available for metal ions.

Reduction of $HgCl_2$ to Hg_2Cl_2 crystals on the sorbent surface is confirmed by SEM analysis and X-ray powder diffraction. In addition, sorbent acidity and cation exchange capacity of the sorbent were increased after the reaction with Hg(II). However no changes in the SEM, X-ray analysis, sorbent acidity or cation exchange capacity were observed on the sorbent after Zn(II) sorption. The differences in the behavior of both metal ions Zn(II) and Hg(II) on the sorbent surface is directly related to Hg(II) reduction to Hg(I) on the sorbent surface.

References

[1] P.C. Mishra, R.K. Patel, Removal of lead and zinc ions from water by low cost adsorbents, J. Hazard. Mater. 168 (2009) 319–325.
[2] L. Norton, K. Baskaran, T. McKenzie, Biosorption of zinc from aqueous solutions using biosolids, Adv. Environ. Res. 8 (2004) 629–635.
[3] K.A. Krishnan, T.S. Anirudhan, Removal of mercury(II) from aqueous solutions and chlor-alkali industry effluent by steam activated and sulphurised activated carbons prepared from bagasse pith: kinetics and equilibrium studies, J. Hazard. Mater. 92 (2002) 161–183.
[4] A. Gül, M. Yilmaz, Z. Isilak, Acute toxicity of zinc sulphate (ZnSO₄·H₂O) to Guppies (Poecilia reticulata P., 1859), G.U. J. Sci. 22 (2009) 59–65.
[5] Agency for Toxic Compounds and Disease Registry (ATSDR), Toxicological Profile for Zinc, Public Health Service, U.S. Department of Health and Human Services, Atlanta, Georgia, 1993.
[6] C. Namasivayam, K. Kadirvelu, Uptake of mercury(II) from wastewater by activated carbon from an unwanted agricultural solid by-product: coirpith, Carbon 37 (1999) 79–84.
[7] B.S. Inbaraj, J.S. Wang, J.F. Lu, F.Y. Siao, B.H. Chen, Adsorption of toxic mercury(II) by an extracellular biopolymer poly(c-glutamic acid), Bioresour. Technol. 100 (2009) 200–207.
[8] Ministerial decision number 145/93, regulation for wastewater reuse and discharge, on 13th June 1993, Ministry of Regional Municipalities and Environment, Muscat, Sultanate of Oman.
[9] WHO Guidelines for Drinking-Water Quality, World Health Organisation, 2004.
[10] L. Armesto, A. Bahillo, K. Veijonen, A. Cabanillas, J. Otero, Combustion behaviour of rice husk in a bubbling fluidised bed, Biomass Bioenergy 23 (2002) 171–179.
[11] D. Roy, P.N. Greenla, B.S. Shane, Adsorption of heavy metals by green algae and ground rice husks, J. Environ. Sci. Health A 28 (1993) 37–50.
[12] E. Munaf, R. Zein, The use of rice husk for removal of toxic metals from wastewater, Environ. Technol. 18 (1997) 359–362.
[13] R. Suemitsu, R. Uenishi, I. Akashi, M. Nakano, The use of dyestuff-treated rice hulls for removal of heavy metal from wastewater, J. Appl. Polym. Sci. 31 (1986) 75–83.
[14] K.K. Krishnani, X. Meng, C. Christodoulatos, V.M. Bodduc, Biosorption mechanism of nine different heavy metals onto biomatrix from rice husk, J. Hazard. Mater. 153 (2008) 1222–1234.
[15] N. Kannan, T. Veemaraj, Adsorption behaviour of zinc (II) ions and zinc (II)-EDTA complex from aqueous solution onto lemon peel and dates nut carbons—a comparative study, EJEAFChe 8 (2009) 666–675.
[16] E.I. El-Shafey, M. Cox, A.A. Pichugin, Q. Appleton, Application of a carbon sorbent for the removal of cadmium and other heavy metal ions from aqueous solution, J. Chem. Technol. Biotechnol. 77 (2002) 429–436.
[17] V.C. Srivastava, I.D. Mall, I.M. Mishra, Characterization of mesoporous rice husk ash (RHA) and adsorption kinetics of metal ions from aqueous solution onto RHA, J. Hazard. Mater. 134 (2006) 257–267.
[18] D. Pentari, V. Perdikatsis, D. Katsimicha, A. Kanaki, Sorption properties of low calorific value Greek lignites: removal of lead, cadmium, zinc and copper ions from aqueous solutions, J. Hazard. Mater. 168 (2009) 1017–1021.
[19] M. Lodenius, A. Seppanen, A. Uusirauva, Sorption and mobilization of mercury in peat soil, Chemosphere 12 (1983) 1575–1581.
[20] C.A. Eligwe, N.B. Okolue, C.O. Nwambu, C.I.A. Nwoko, Adsorption thermodynamics and kinetics of mercury(II), cadmium(II) and lead(II) on lignite, Chem. Eng. Technol. 22 (1999) 45–49.
[21] N. Khalid, S. Ahmad, S.N. Kiani, J. Ahmed, Removal of mercury from aqueous solutions by adsorption to rice husks, Sep. Sci. Technol. 34 (1999) 3139–3153.
[22] D.P. Tiwari, D.K. Singh, D.N. Saksena, Hg(II) adsorption from aqueous solutions using rice-husk ash, J. Environ. Eng. 121 (1995) 479–481.
[23] M. Cox, E.I. El-Shafey, A.A. Pichugin, Q. Appleton, Removal of mercury(II) from aqueous solution on a carbonaceous sorbent prepared from flax shive, J. Chem. Technol. Biotechnol. 75 (2000) 427–435.
[24] T. Kiyohara, K. Anazawa, H. Sakamoto, T. Tomiyasu, Adsorption of mercury on used tea leaves and coffee beans, Bunseki Kagaku 52 (2003) 887–890.
[25] C. Namasivayam, K. Periasamy, Bicarbonate-treated peanut hull carbon for mercury(II) removal from aqueous solution, Water Res. 27 (1993) 1663–1668.
[26] E.I. El-Shafey, Behaviour of reduction–sorption of chromium (VI) from an aqueous solution on a modified sorbent from rice husk, Water Air Soil Pollut. 163 (2005) 81–102.
[27] Annual Book of ASTM Standards, Standard Test Methods for Carbon Black—pH value, D1512-95, 9.01 (1996) 293–296.
[28] Annual Book of ASTM Standards, Standard Test Method for pH of Activated Carbon, D3838-80, 15.01 (1996) 531–532.
[29] V.A. Thorpe, Collaborative study of the cation exchange capacity of peat materials, J. AOAC 56 (1973) 154–156.
[30] M.J. Ahmed, Md.S. Alam, A rapid spectrophotometric method for the determination of mercury in environmental, biological, soil and plant samples using diphenylthiocarbazone, Spectroscopy 17 (2003) 45–52.
[31] S.E Manahan, Environmental Chemistry, 5th ed., Lewis Publishing, London, 1991.
[32] , McGraw-Hill Encyclopaedia of Science & Technology, vol. 7, 8th ed., McGraw-Hill, London, 1997, p. 161.
[33] M. Cox, E.I. El-Shafey, A.A. Pichugin, Q. Appleton, Preparation and characterization of a carbon adsorbent from flax shive by dehydration with sulphuric acid, J. Chem. Technol. Biotechnol. 74 (1999) 1019–1029.
[34] A.M. Youssef, A.A. El-Khouly, A.I. Ahmed, E.I. El-Shafey, Changes in the adsorption properties of activated carbon due to partial oxidation of the surface, Adsorpt. Sci. Technol. 12 (1995) 211–219.
[35] B.S. Inbaraj, N. Sulochana, Mercury adsorption on a carbon sorbent derived from fruit shell of *Terminalia catappa*, J. Hazard. Mater. 133 (2006) 283–290.
[36] S.P. Mishra, G.R. Chaudhury, Kinetics of Zn²⁺ adsorption by *Penicillium* sp., Hydrometallurgy 40 (1996) 11–23.
[37] Y.S. Ho, G. Mckay, Pseudo-second order model for sorption processes, Process Biochem. 34 (1999) 451–465.

[38] Y.S. Ho, G. Mckay, Sorption of dye from aqueous solution by peat, Chem. Eng. J. 70 (1998) 115–124.
[39] D.L. Sparks, Kinetics of Soil Chemical Processes, Academic Press, New York, 1989.
[40] C. Liu, P.M. Huang, Kinetics of lead adsorption by iron oxides formed under the influence of citrate, Geochim. Cosmochim. Acta 67 (2003) 1045–1054.
[41] M.R. Unninathan, T.S. Anirudhan, The kinetics and thermodynamics of sorption of Cr(VI) onto the Fe(III) complex of a poly acrylamide-grafted saw dust, Ind. Eng. Chem. Res. 40 (2001) 2693–2701.
[42] S.P. Mishra, D. Tiwari, R.S. Dubey, The uptake behavior of rice (jaya) husk in the removal of Zn(II) ions: a radiotracer study, Appl. Radiat. lsot. 48 (1997) 877–882.
[43] K.K. Singh, A.K. Singh, S.H. Hasan, Low cost biosorbent 'wheat bran' for the removal of cadmium from wastewater: kinetic and equilibrium studies, Bioresour. Technol. 97 (2006) 994–1001.

[44] M. Nadeem, A. Mahmood, S.A. Shahid, S.S. Shah, A.M. Khalid, G. McKay, Sorption of lead from aqueous solution by chemically modified carbon adsorbents, J. Hazard. Mater. 138 (2006) 604–613.
[45] The Joint Committee of Powder Diffraction Standards (JCPDS-ICDD), PDF-2, 1994, Sets 1-44 database (26-312).
[46] E.I. El-Shafey, Sorption of Cd(II) and Se(IV) from aqueous solution using modified rice husk, J. Hazard. Mater. 147 (2007) 546–555.
[47] K. Kinoshita, Carbon: Electrochemical and Physicochemical Properties, Wiley, New York, 1988, pp. 86–173.
[48] P.J.M. Carrott, M.M.L.R. Carrott, J.M.V. Nabais, J.P.P. Ramalho, Influence of surface ionization on the adsorption of aqueous zinc species by activated carbons, Carbon 35 (1997) 403–410.
[49] K.L. Wasewar, M. Atif, B. Prasad, I.M. Mishra, Batch adsorption of zinc on tea factory waste, Desalination 244 (2009) 66–71.
[50] D.R. Lide, H.P.R. Frederikse, CRC Handbook of Chemistry and Physics, 77th ed., CRC Press, London, 1995, pp. 8-20: 8-30.