

Sorption of Cd(II) and Se(IV) from aqueous solution using modified rice husk

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Abstract

A carbonaceous sorbent was prepared from rice husk via sulfuric acid treatment. Removal of Cd(II) and Se(IV) from aqueous solution was studied varying time, pH, metal concentration, temperature and sorbent status (wet and dry). Cd(II) sorption was found fast reaching equilibrium within ~2 h while Se(IV) sorption was slow reaching equilibrium within ~200 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. Cd(II) sorption was low at low pH values and increased with pH increase, however, Se(IV) sorption was high at low pH values, and decreased with the rise in initial pH until pH 7. A fall in the final pH was noticed with Cd(II) sorption due to the release of protons indicating an ion exchange mechanism. However, for Se(IV) sorption, a rise in the final pH was observed due to protons consumption in the process. For both metals, sorption fit well the Langmuir equation with higher uptake by rising the temperature.

Analysis by scanning electron microscope and X-ray powder diffraction for the sorbent after the reaction with acidified Se(IV) confirmed the availability of elemental selenium, Se(0), as particles on the sorbent surface. The reduction process of acidified Se(IV) to Se(0) is accompanied by surface oxidation. Physicochemical tests showed an increase in sorbent acidity, cation exchange capacity and surface functionality after the reaction with acidified Se(IV) indicating that oxidation processes took place on the sorbent surface. On the other hand, no changes in physicochemical tests were found after Cd(II) sorption indicating the absence of redox processes between Cd(II) and the sorbent.

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1. Introduction

The presence of heavy metals in waste and surface waters is becoming a severe environmental and public health problem. Various methods such as hydrometallurgical technologies, ion exchange, electrodialysis, reverse osmosis, precipitation and adsorption have been used for heavy metal removal from environmental aqueous solution [1].

The removal of cadmium and selenium from water has an increasing concern because of their involvement in many industries. Effluents from metallurgical and chemical industries, ceramics, electrogalvanization and textile industries are potential sources of water pollution by Cd(II) ions [2]. Selenium is found in the effluents in the form of selenate (SeO_4^{2-}) and selenite (SeO_3^{2-}) from thermal power stations, oil refineries

and smelting plants in addition to the industries of glass production, pigments, solar batteries and semiconductors [3,4]. Cd(II) ions cause serious cases of acute toxicity and diseases such as lung cancer and kidney failure. Selenium is an essential nutrient for animals and for human health in the range of 0.8–1.7 $\mu\text{mol/l}$, but toxic above this value [5].

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 tonnes and over 97% of the husk is generated in the developing countries [6]. Rice husk has been used, either plain (untreated) or modified, for the removal of cadmium and other heavy metals from water [7–11]. In addition, it has been used as a precursor material for activated carbon production that is used for pollution control [12,13]. Cd(II) was also removed from water using different sorbents including activated carbon [14], carbonaceous sorbents from flax shive [15], sugar beet pulp [14], peat and lignite [16], corncobs [14], Pine Park [14] and green coco-nut shell powder [17]. Se(IV) was removed via different sorbents includ-

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ing goethite [18], hematite [19], alluvial soil [20] and bacteria [21].

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

2. Experimental

2.1. Sorbent preparation

Rice husk was received from a local 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 [22]: clean air-dried rice husk (20 g) was weighed in a clean dry beaker of capacity 500 ml. One hundred milliliters 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 this range (175–180 °C) 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 (black liquor) 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.

Rice husk, as a precursor material, possesses cellulose, hemicelluloses and lignin as main components in addition to ash [6]. Concentrated sulfuric acid behaves as an extremely strong dehydrating agent [23]. In addition, it acts as a strong oxidizing agent because of its tendency to lose an atom of oxygen to form sulfurous acid, H₂SO₃, which readily decomposes to sulfur dioxide and water [24]. 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 [25] resulting in a carbonaceous material loaded with function groups on the surface. The effect of hot sulfuric acid on an agricultural material (flax shive) producing

a carbonaceous sorbent was studied and published earlier [25]. The moisture content of the prepared wet sorbent, in the current study, is 85%.

2.2. Physicochemical characterization of the carbonaceous sorbent

Physico-chemical tests were measured for the dry sorbent before and after the reaction with metal ions. ASTM standard methods were used to measure the cation exchange capacity (CEC) [26], ash content [27] and sorbent acidity (sorbent pH) [22].

Base neutralization capacity was measured by Boehm titrations [28]. Neutralization of 0.1 M sodium bicarbonate and sodium hydroxide, and 0.05 M sodium carbonate, by the dry sorbent was studied by mixing 0.25 g sorbent portions with 50 ml of the respective solution in 100 ml Quickfit polyethylene bottles. The suspensions were flushed with nitrogen gas to remove oxygen present [29]. This step was essential to avoid the possibility of base-catalyzed auto-oxidation of the carbonaceous sorbents in the presence of oxygen [30]. The suspensions were shaken mechanically for 72 h covering the equilibrium time. The fall in concentration of each solution was determined by titration of an aliquot of the supernatant liquid against 0.1 M HCl.

2.3. Sorption procedure

All the chemicals used were of analytical grade. Stock solutions (1000 mg/l) of Cd(II) and Se(IV) were prepared in distilled water using cadmium sulfate (3CdSO₄·8H₂O) and selenium dioxide (SeO₂), respectively. All the working solutions were prepared by diluting the stock solution in distilled water.

In the kinetic experiments, 0.1 g of the dry sorbent (or the equivalent weight of the wet sorbent) were mixed with 50 mg/l (100 ml) of either Cd(II) at pH 6 or Se(IV) at pH 1.5. pH 6 and 1.5 were found optimal for the sorption of Cd(II) and Se(IV), respectively, 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 of the dry sorbent (or the equivalent weight of the wet sorbent) 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) at different pH values (pH 1.5–7). The pH was adjusted by adding few drops of 0.1 M sulfuric 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 in metal concentration range of 25–250 mg/l at pH 6 for Cd(II) and pH 1.5 for Se(IV) at different temperature (25–45 °C). After the equilibrium time was reached, aliquot of supernatant was withdrawn and metal concentration was measured.

2.4. Metal analysis

Cd(II) was determined via Perkin-Elmer 2380 atomic absorption spectrophotometer. Se(IV) was analyzed spectrophotometrically using 3,3'-diaminobenzidine reagent (DAB)

[31,32]. This technique is based on the measurement of the yellow colored compound formed when DAB reagent reacts with Se(IV) in 2 M hydrochloric acid. The selenium complex, after neutralization with concentrated ammonium hydroxide to pH 7–8, was extracted in toluene and its absorbance was measured at 420 nm [32] using Unicam UV/VIS spectrophotometer UV2 5000. Experiments and analysis have been carried out three times and the relative standard deviation was $\pm 4.1\%$.

2.5. Scanning electron microscope and X-ray powder diffraction

Scanning electron microscope (SEM) analysis was carried out using a Leo Stereoscan 440 Scanning Electron Microscope. Electron probe microanalysis was carried out using SEM facilities for different precipitated particles on the sorbent surface. X-ray powder diffraction was carried out using a Philips PW 1830 generator with a Philips PW 1050 powder goniometer. Cu K α was used as the incident radiation.

3. Results and discussion

3.1. Effect of pH

In the pH range 1.5–2, Cd(II) sorption was extremely low, and with the rise in the initial pH, Cd(II) uptake increased (Fig. 1). Between pH 4 and 7, the sorption of Cd(II) almost showed no significant change. Cd(II) sorption was accompanied by a decrease in the final pH (Fig. 2) indicating protons release into solution and suggesting ion exchange mechanism. Rice husk could exhibit a hydration shell at lower pH positively charged by the hydronium ion in the solution. This restricted the uptake of Cd(II) ions. Adsorption capacity increases with increasing pH values as shown by Roy et al. [9]. In another study [15], Cd(II) sorption on a carbonaceous sorbent, prepared from flax shive via sulfuric acid treatment, was very low at pH 2 and increased with pH increase showing almost no change in Cd(II) uptake in the pH range 3–7. In that study, Cd(II) sorption was accompanied

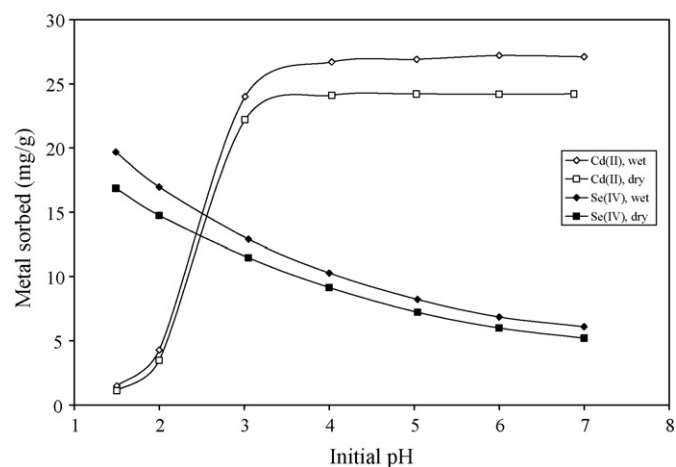


Fig. 1. Sorption of Cd(II) and Se(IV) at different initial pH values at 25 °C (initial concentration 100 mg/l, volume of metal solution 50 ml, shaking speed 100 rpm).

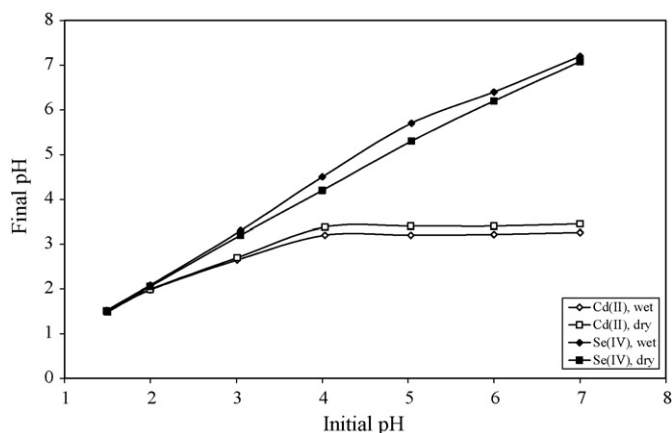


Fig. 2. A plot of initial and final pH for Cd(II) and Se(IV) sorption at 25 °C (initial metal concentration 100 mg/l).

by a decrease in the final pH due to proton release in the solution indicating ion exchange process [15].

Se(IV) species in aqueous solution include selenious acid (H_2SeO_3), biselenite (HSeO_3^-) and selenite (SeO_3^{2-}). Between pH 3.5 and 9.0 biselenite ion is the predominant ion in water. Above pH 9.0 selenite species dominate and as pH decreases below pH 3.5, selenious acid dominates [33]. In the present work, Se(IV) sorption was high at pH 1.5, the lowest pH applied, and sorption decreased with the initial pH increase (Fig. 1). Se(IV) sorption was accompanied by a slight rise in the final pH due to protons consumption in the Se(IV) sorption process (Fig. 2) indicating a reduction process of Se(IV). 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 [34].

3.2. Kinetics of metal sorption

Based on the pH experiments, shown above, Cd(II) was sorbed best in the pH range 4–7 and Se(IV) at pH 1.5, the lowest pH applied. Accordingly, pH 6 and 1.5 were chosen for the studies of sorption kinetics and temperature effect for Cd(II) and Se(IV), respectively. Kinetics of Cd(II) sorption was investigated at pH 6.0 and equilibrium was reached within ~ 2 h (Fig. 3A), however, for Se(IV) sorption, at pH 1.5, approximate equilibrium was reached within ~ 200 h (Fig. 3B). Obviously, Cd(II) sorption shows a much faster kinetics than Se(IV) sorption.

Sorption kinetics of Cd(II) and Se(IV) were tested using non-linear and linear pseudo-second order equations [35,36], Eqs. (1) and (2).

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

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

where k 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

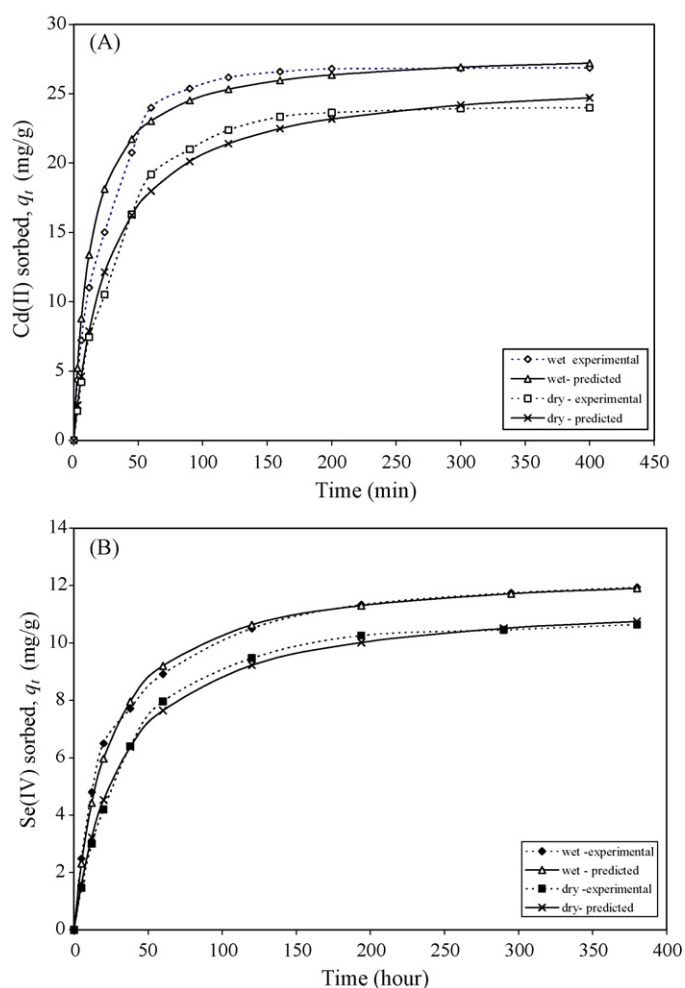


Fig. 3. Pseudo-second order kinetics by non-linear method and experimental kinetics for the sorption of: (A) Cd(II) at pH 6 and (B) Se(IV) at pH 1.5 on the carbonaceous sorbent at 25 °C (initial concentration 50 mg/l, volume of metal solution 100 ml, shaking speed 100 rpm).

the pseudo-second order model of Eq. (2) (Fig. 4A and B) show a good fitting with high values of the coefficient of determination, r^2 (Table 1). This showed that the sorption process followed the pseudo-second order kinetic, which agreed with chemisorption as the rate-limiting mechanism through sharing or exchange of electron between sorbent and sorbate [36,37]. 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

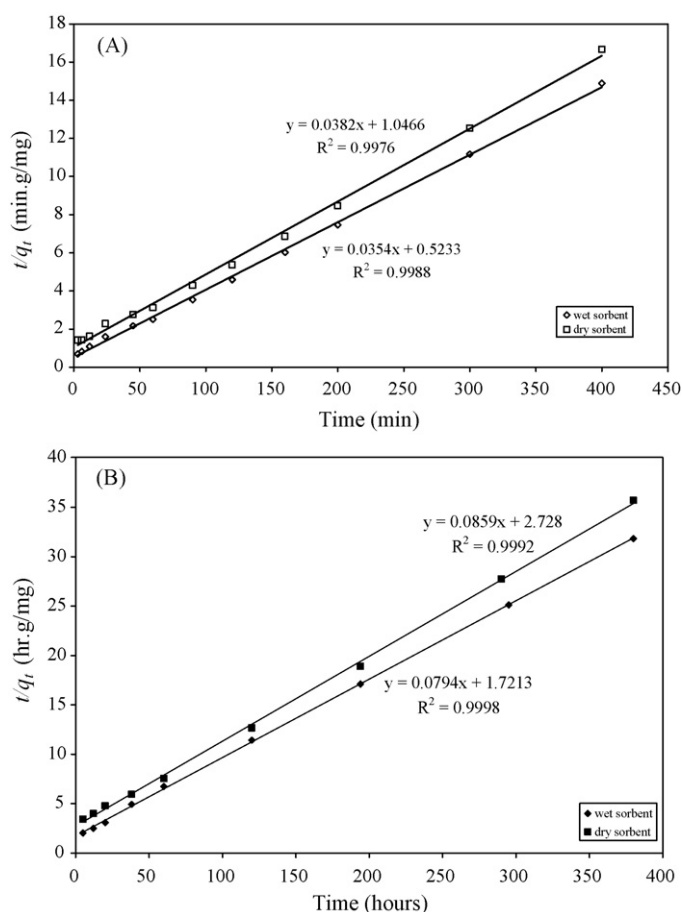


Fig. 4. Pseudo-second order kinetics by linear method for the sorption of: (A) Cd(II) at pH 6 and (B) Se(IV) at pH 1.5 at 25 °C (initial concentration 50 mg/l, volume of metal solution 100 ml, shaking speed 100 rpm).

of drying giving narrower pores for the diffusion of metal ions [22,34].

Rate constant, k , and initial adsorption rate, h , for Cd(II) sorption were much higher than that for Se(IV) sorption in the units of (g/mg/h) and (mg/g/h), respectively (Table 1). The decrease in the values of k and h for Se(IV) sorption, due to its slow sorption kinetics, reflects a different mechanism from that for Cd(II) sorption. In a previous study [38], 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 [38].

Table 1

Pseudo-second order rate constants of the sorption kinetics of Cd(II) at pH 6 and Se(IV) at pH 1.5, at 25 °C, by linear and non-linear regression methods

Regression method	Sorbent status	Cd(II) sorption						Se(IV) sorption			
		k (g/mg/min)	k (g/mg/h)	q , predicted (mg/g)	h (mg/g/min)	h (mg/g/h)	r^2	k (g/mg/h)	q , predicted (mg/g)	h (mg/g/h)	r^2
Linear	Wet sorbent	0.00239	0.1434	28.249	1.9110	114.66	0.99883	0.00366	12.594	0.5809	0.99995
	Dry sorbent	0.00139	0.0834	26.171	0.9554	57.324	0.99759	0.00271	11.637	0.3666	0.99922
Non-linear	Wet sorbent	0.00270	0.1619	28.102	2.1311	127.87	0.98379	0.00358	12.600	0.5682	0.99533
	Dry sorbent	0.00133	0.0801	26.461	0.9345	56.070	0.99150	0.00274	11.640	0.3710	0.99698

For the non-linear method, a trial and error procedure, which is applicable to computer operation, was used to determine the kinetic parameters by minimizing the respective coefficient of determination (r^2) between experimental data and kinetics using the solver add-in with Microsoft's spreadsheet, Microsoft Excel as detailed by Vasanth Kumar and Sivanesan [39]. Fig. 3A and B shows the experimental kinetic data and the predicted kinetics of pseudo-second order using non-linear method [35]. The difference in r^2 values obtained by linear and non-linear method for the same kinetic expression are due to the error alterations while transforming the data that represents a non-linear kinetics to a linearized form [39].

The good fit of experimental data in both the linearized and non-linear forms of the pseudo-second order expression suggests that non-linear and the linearized forms proposed by Ho and McKay [35] can be used to predict the kinetic parameters involved in the kinetic expression [39].

3.3. Sorption capacity and temperature effect

Sorption of Cd(II) and Se(IV) on the wet and dry sorbents follows an "L-type" adsorption isotherm, with increased uptake as temperature rises. Fig. 5A and B represents the sorption of Cd(II) and Se(IV) at different temperature on the wet sorbent. The experimental isotherm data fit well the Langmuir equation [40], Eq. (3), for both metals on the wet and dry sorbents (Table 2). Freundlich equation [11], Eq. (4), was also tested for the sorption equilibrium data, Table 2. The Langmuir and Freundlich isotherms for Cd(II) and Se(IV) sorption, on the wet sorbent, are shown in Figs. 6A and B and 7A and B, respectively.

$$\frac{C_e}{q_e} = \frac{1}{bq} + \frac{C_e}{q} \quad (3)$$

where C_e is the equilibrium metal concentration, q the amount of metal sorbed per unit weight of the sorbent (on dry basis) for monolayer coverage of the surface (monolayer capacity) and b is the sorption equilibrium constant which is temperature

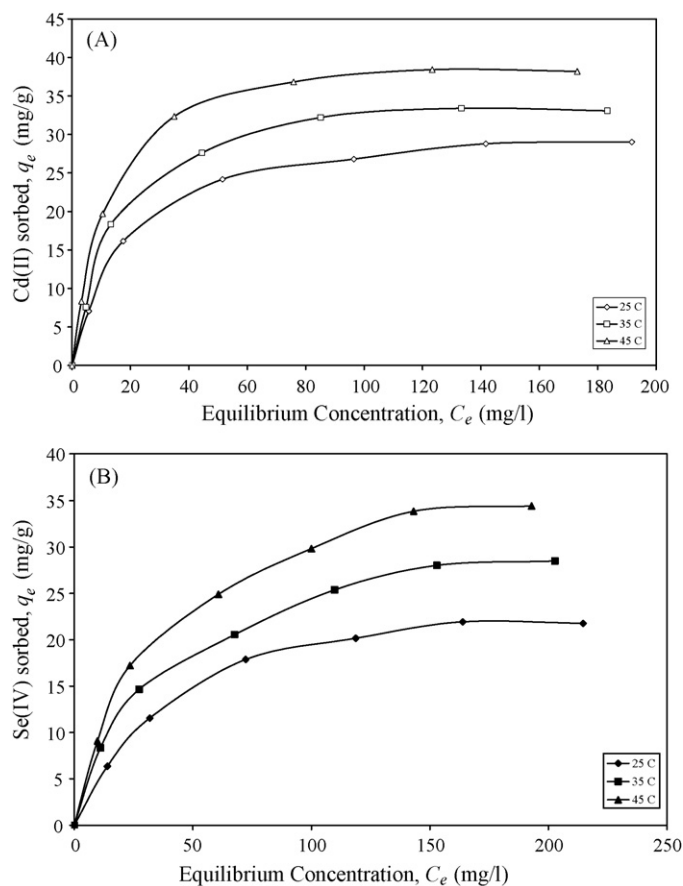


Fig. 5. Sorption of: (A) Cd(II) at pH 6 and (B) Se(IV) at pH 1.5 on the wet sorbent at different temperatures (volume of metal solution 50 ml, shaking speed 100 rpm).

dependent and related to the heat of sorption [40].

$$\log q_e = \frac{1}{n} \log C_e + \log K \quad (4)$$

where K and $1/n$ are the constants, which are considered to be the relative indicators of adsorption capacity and adsorption inten-

Table 2
Langmuir and Freundlich parameters for the sorption Cd(II) at pH 6 and Se(IV) at pH 1.5 at different temperatures

Metal	Sorbent	Sorption temperature (°C)	Langmuir constants		r^2	Freundlich constants		r^2
			q (mg/g)	b (l/mg)		$1/n$	K	
Cd(II)	Wet	25	32.05	0.0551	0.999	0.248	8.777	0.940
		35	36.23	0.0710	0.998	0.234	10.650	0.923
		45	41.15	0.0931	0.999	0.238	12.297	0.889
	Dry	25	31.15	0.0632	0.999	0.214	9.736	0.943
		35	34.13	0.0705	0.999	0.217	10.775	0.937
		45	38.76	0.0869	0.998	0.233	11.725	0.916
Se(IV)	Wet	25	26.46	0.0253	0.996	0.454	2.191	0.940
		35	33.88	0.0272	0.997	0.425	3.278	0.974
		45	40.92	0.0287	0.998	0.442	3.754	0.962
	Dry	25	25.51	0.019	0.999	0.483	1.688	0.979
		35	29.41	0.0203	0.997	0.4679	2.183	0.974
		45	34.13	0.0232	0.997	0.4638	2.653	0.985

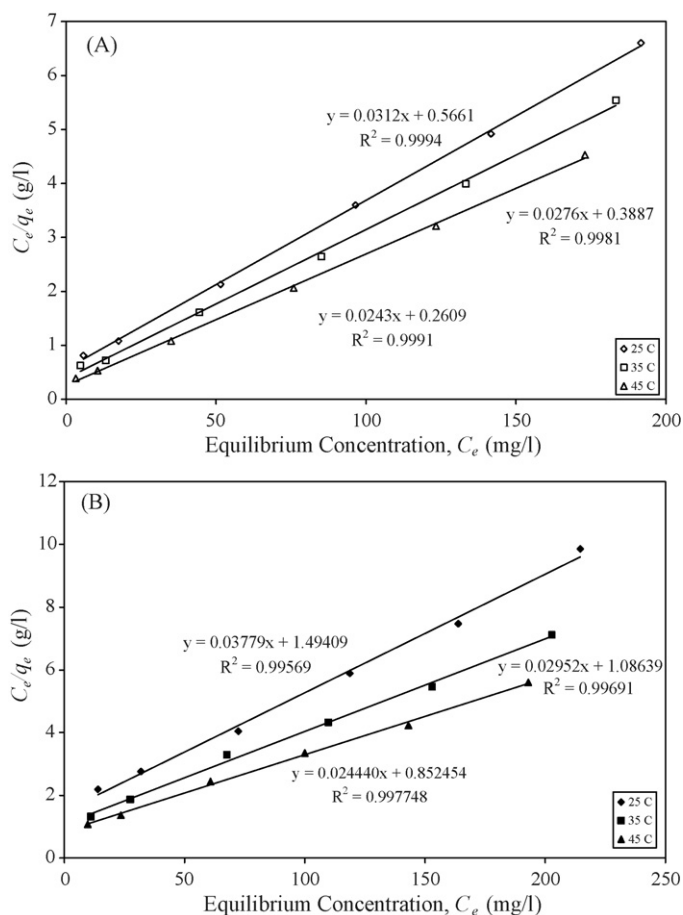


Fig. 6. Langmuir isotherms for the sorption of: (A) Cd(II) at pH 6 and (B) Se(IV) at pH 1.5 on the wet sorbent at different temperatures.

sity. 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), calculated from the Langmuir equation, was slightly higher for the wet sorbent than for the dry (Table 2). 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. 5A and B and Table 2). This could be due to some swelling of the carbon and a consequent increase in ion exchange sites as found earlier for Cd(II) and Hg(II) sorption on a carbon sorbent prepared from flax shive via sulfuric acid treatment [15,34,38]. 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 evident that the produced sorbent, in the present study, has high sorption capacity for Cd(II) and Se(IV).

Comparatively the obtained r^2 values are more satisfactory for Langmuir isotherm than for Freundlich isotherm (Table 2). The basic assumption of Langmuir adsorption isotherm is based on monolayer coverage of the adsorbate on the surface of adsorbent [46,47] which is an indication of the fact that the sorption of Cd(II) or Se(IV) on to the investigated sorbents generates monolayer formation.

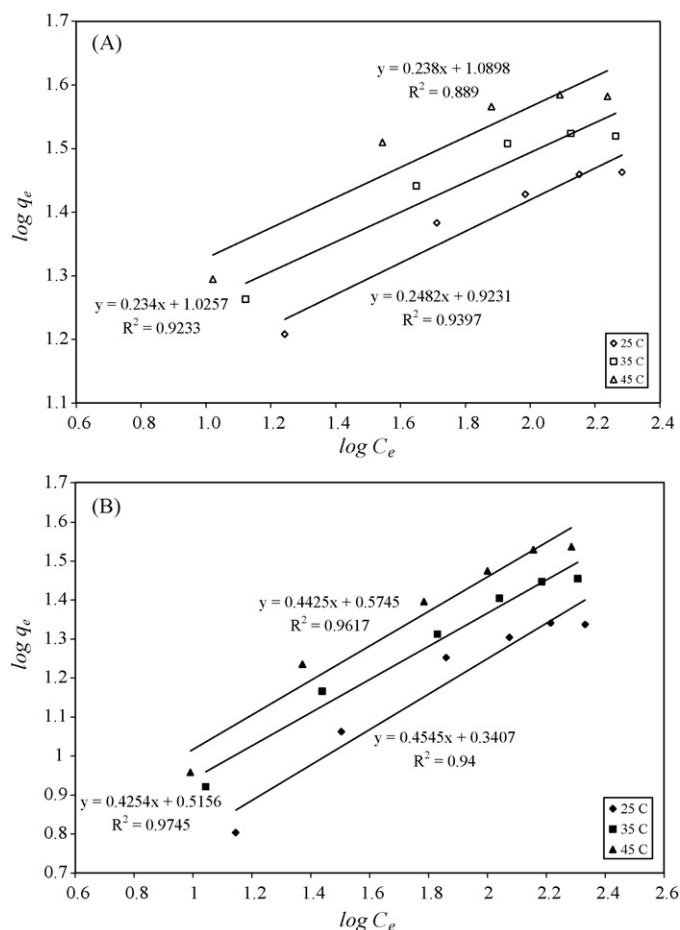


Fig. 7. Freundlich isotherms for the sorption of: (A) Cd(II) at pH 6 and (B) Se(IV) at pH 1.5 on the wet sorbent at different temperatures.

3.4. SEM and X-ray powder diffraction

Wet sorbent samples, after the equilibrium contact with 250 mg/l of Cd(II) at pH 6.0 or Se(IV) at pH 1.5 at 45 °C, were separated, dried at 120 °C and then used for SEM and X-ray analysis. Particles of elemental selenium on the sorbent surface are clearly identified on SEM photograph (Fig. 8). Elemental selenium was also identified by examining the surface by electron probe microanalysis, using the scanning electron microscope facilities. X-ray powder diffraction pattern confirmed the identification of elemental selenium on the sorbent with the interplanar spacing (d) and relative line intensities (I) agreeing with those recorded (Table 4). This indicates that a reduction process of Se(IV) to Se(0) took place on the sorbent surface. The sorbent under investigation showed a reduction capability of Cr(VI) to Cr(III) in a previous study [22]. In other studies [34,38], Hg(II) was reduced to Hg(I) and Hg(0) on the surface of a carbonaceous sorbent prepared from flax shive via sulfuric acid treatment. On the other hand, SEM analysis and X-ray powder diffraction did not show any change on the sorbent surface after Cd(II) sorption.

3.5. Physicochemical tests

Wet sorbents, after the contact with 250 mg/l of Cd(II) at pH 6.0 or Se(IV) at pH 1.5, at 45 °C until the equilibrium was

Table 3
Maximum sorption capacities of Cd(II) and Se(IV) on different sorbents

Metal ion	Material	Maximum sorption (mg/g)	Reference	
Cd(II)	Rice husk	8.58	[7]	
	Rice husk	4.00	[8]	
	Rice husk	21.36	[9]	
	Rice husk	0.16	[10]	
	Epichlorohydrin treated rice husk	11.12	[7]	
	Sodium hydroxide treated rice husk	20.24	[7]	
	Sodium hydroxide treated rice husk	7.00	[8]	
	Sodium carbonate treated rice husk	16.18	[7]	
	Sugar beet pulp	17.2	[14]	
	Powdered activated carbon	3.7	[14]	
	Granular activated carbon	3.7	[14]	
	Corncobs	8.89	[14]	
	Pine Park	14.16	[14]	
	Amberlite 200	224.8	[14]	
	Duolite GT-73	105.66	[14]	
	Sulfuric acid treated rice husk (wet sorbent)	41.15 (pH 6, 45 °C)	Present study	
	Sulfuric acid treated rice husk (dry sorbent)	38.76 (pH 6, 45 °C)	Present study	
	Se(IV)	Zn–Al-layered double hydroxides	125	[42]
		Mg–Al-layered double hydroxides	152	[42]
Mercapto-silica		7.5	[43]	
Aluminum oxide coated sand		1.08 (pH 4.8)	[44]	
Iron oxide coated sand		1.34	[45]	
Sulfuric acid treated rice husk (wet sorbent)		40.92 (pH 1.5, 45 °C)	Present study	
Sulfuric acid treated rice husk (dry sorbent)		34.13 (pH 1.5, 45 °C)	Present study	

reached, were separated and washed with 0.1 M H₂SO₄, to strip metal ions from the sorbent. The sorbent samples were then washed by distilled water to become acid-free, dried at 120 °C and then used to carry out the physicochemical tests [26]. These tests before and after the reaction with Cd(II) and Se(IV) are shown in Table 5. 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 acidified Se(IV). The pH of the sorbent is mainly related to the concentration of carboxylic groups [48]. CEC which is a measurement of

the total amount of exchangeable cations that can be held by a sorbent, was found to increase after the reaction with acidified Se(IV) indicating the presence of more acidic groups on the sorbent surface, such as –COOH, Table 5. The differences in surface functionalities developed by the preparation method and further surface oxidation after the reaction with acidified Se(IV) were determined by Boehm titrations [28,29]. The three bases used in titration are considered as approximate probes for acidic functionalities: NaHCO₃ (carboxylic), Na₂CO₃ (carboxylic and lactonic), NaOH (carboxylic, lactonic and phenolic). As shown in Table 5, an increase in the concentration of carboxylic, lactonic and phenolic groups on the sorbent surface was found after the reaction with acidified Se(IV). In general, the increase in sorbent acidity, cation exchange capacity and

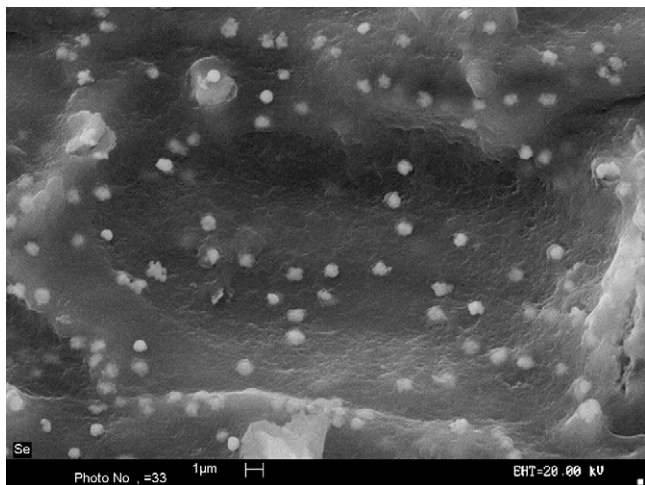


Fig. 8. SEM photograph for elemental selenium precipitated on the sorbent surface.

Table 4
X-ray powder diffraction after Se(IV) loading confirms the presence of elemental selenium

Observed		Literature	
<i>d</i> (Å)	Intensity (<i>I</i>)	<i>d</i> (Å) ^a	Intensity (<i>I</i>) ^a
3.783	61	3.78	55
3.007	100	3.005	100
2.183	20	2.184	16
2.072	36	2.072	35
1.999	27	1.998	20
1.765	28	1.766	20
1.638	26	1.637	12

^a Data from JCPDS-ICDD copyright © 1994 PDF-2 Sets 1-44 database (26-312).

Table 5
Physico-chemical properties of the sorbent before and after the interaction with metals

Dry sorbent ^a	Sorbent pH	CEC (meq/g)	Surface acidic functionalities based on weight (meq/g)		
			Carboxyl ^b	Lactone ^b	Phenol ^b
Before reaction	2.65	1.34	2.18	0.42	2.02
After interaction with Cd(II), pH 6	2.64	1.34	2.18	0.43	2.02
After reaction with Se(IV), pH 1.5	2.51	1.49	2.33	0.86	2.15

^a Surface area of the dry sorbent measured by nitrogen adsorption 66 m²/g, ash content 17.7%.

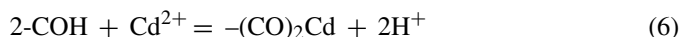
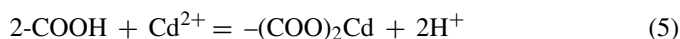
^b NaHCO₃ (carboxyl), Na₂CO₃ (carboxyl and lactone), NaOH (carboxyl, lactone and phenolic).

base neutralization capacities, for the sorbent, after the reaction with acidified Se(IV) indicates the oxidation processes taking place on the surface of the carbon sorbent. However, no change was noticed for the physicochemical tests after Cd(II) sorption (Table 5).

3.6. Mechanism of sorption

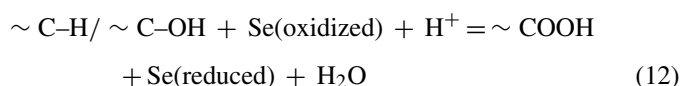
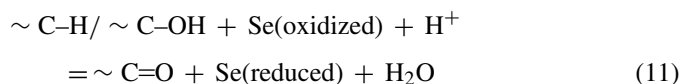
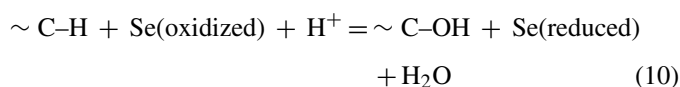
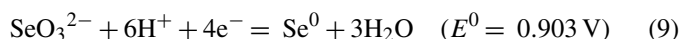
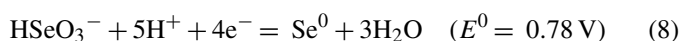
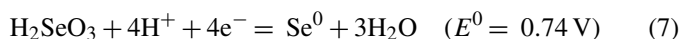
Natural adsorbents such as rice husk have the ability to adsorb metal ions due to different functional groups present on their macromolecules, which include polysaccharides, lignin and others via complexation or ion-exchange [8,49].

Due to the increased Cd(II) sorption at high pH values until pH 7 with the release of protons, it can be concluded that Cd(II) was sorbed via ion exchange. The carbon possesses acidic functional groups on surface such as –COOH and –OH that are responsible for the cation exchange property as expressed in Eqs. (5) and (6).



The main species of Cd(II) is Cd²⁺ up to pH 8 and above pH 8 Cd(II) forms Cd(OH)⁺ [50]. In the present work, since pH 6 was applied for Cd(II) sorption at different temperature and the final pH was <6, it can be concluded that Cd(II) was sorbed in the present work as Cd²⁺ ions as in Eqs. (5) and (6). Due to the high silica content in rice husks, Cd(II) ions can also be sorbed via an ion-exchange reaction through the substitution of protons from silanol groups on the surface by the metal ions [8].

SeO₂ forms H₂SeO₃, HSeO₃[−] and SeO₃^{2−} on contact with water [33]. Sorption of Se(IV) on the carbon sorbent involves redox processes that include Se(IV) reduction to elemental selenium, Eqs. (7)–(9) [51,52] and carbon oxidation, Eqs. (10)–(12).



In the present work, since pH 1.5 was applied for Se(IV) sorption at different temperatures and the final pH was <3, it can be concluded that Se(IV) as selenious acid, that dominates at such low pH [33], was reduced to elemental selenium (Eq. (7)).

Surface oxidation, as shown in Eqs. (10)–(12), by the reaction with acidified Se(IV), has increased the surface functionality as shown in Table 5. Because of the insolubility of elemental selenium in aquatic systems, reduction of Se(VI) to Se(0) is considered to be a useful technique for removing selenium from Se-contaminated water [21].

The increased Se(IV) sorption at low pH values (Fig. 1), with the view of the redox processes can be explained. Se(IV) reduction to elemental selenium requires protons to take place (Eqs. (7)–(9)). The extent of reduction increases with protons sufficiency at low pH values and decreases with protons insufficiency at high pH values.

4. Conclusion

The carbonaceous sorbent produced via sulfuric acid treatment is loaded by surface functionality such as –COOH and –OH as a result of the preparation conditions. It possesses ion exchange and reduction properties. Cd(II) showed a faster sorption kinetics than Se(IV) following pseudo-second order model. Cd(II) sorption was extremely low at low pH values (pH 1.5–2) and increased with pH rising with a decrease in the final pH due to protons release indicating ion exchange mechanism. On the other hand, Se(IV) sorption was high at low pH and as the pH increased Se(IV) uptake decreased with a rise in the final pH due to protons consumption indicating reduction process of Se(IV). Sorption of Cd(II) and Se(IV) 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 Se(IV) to elemental selenium on the sorbent surface is confirmed by SEM analysis and X-ray powder diffraction.

Physicochemical tests after the reaction with acidified Se(IV) showed a rise in sorbent acidity, CEC and base neutralization capacities indicating surface oxidation. However, no changes in the SEM, X-ray analysis or the physicochemical tests were observed on the sorbent after Cd(II) sorption.

References

- [1] M.D. La Grega, P.L. Buckingham, J.C. Evans, Hazardous Waste Management, McGraw-Hill, New York, 1994, p. 859.
- [2] J. Hizal, R. Apak, Modeling of cadmium(II) adsorption on kaolinite-based clays in the absence and presence of humic acid, Appl. Clay Sci. 32 (3–4) (2006) 232–244.
- [3] S. Lawson, J.M. Macy, Bioremediation of selenite in oil refinery wastewater, Appl. Microbiol. Biotechnol. 43 (4) (1995) 762–765.
- [4] M. Kashiwa, S. Nishimoto, K. Takahashi, M. Ike, M. Fujita, Factors affecting soluble selenium removal by a selenate reducing bacterium *Bacillus* sp. SF-1, J. Biosci. Bioeng. 89 (6) (2000) 528–533.
- [5] M. Albert, C. Demesmay, J.L. Rocca, Analysis of organic and nonorganic arsenious or selenious compounds by capillary electrophoresis, Fresenius J. Anal. Chem. 351 (4–5) (1995) 426–432.
- [6] 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.
- [7] U. Kumar, M. Bandyopadhyay, Sorption of cadmium from aqueous solution using pretreated rice husk, Bioresour. Technol. 97 (1) (2006) 104–109.
- [8] C.R.T. Tarley, S.L.C. Ferreira, M.A.Z. Arruda, Use of modified rice husks as a natural solid adsorbent of trace metals: characterisation and development of an on-line preconcentration system for cadmium and lead determination by FAAS, Microchem. J. 77 (2) (2004) 163–175.
- [9] D. Roy, P.N.C. Greenlaw, B.S. Shane, Adsorption of heavy metals by green algae and ground rice hulls, J. Env. Sci. Health A28 (1993) 37–50.
- [10] E. Munafand, R. Zein, The use of rice husk for removal of toxic metals from waste water, Env. Technol. 18 (1997) 359–362.
- [11] U. Kumar, M. Bandyopadhyay, Fixed bed column study for Cd(II) removal from wastewater using treated rice husk, J. Hazard. Mater. B129 (2006) 253–259.
- [12] T.H. Usmani, T.W. Ahmed, S.Z. Ahmed, A.H.K. Yousufzai, Activated carbon from rice husk. Part I. Activating agent selection, Pak. J. Sci. Ind. Res. 36 (6–7) (1993) 236–239.
- [13] T.H. Usmani, T.W. Ahmed, S.Z. Ahmed, A.H.K. Yousufzai, Activated carbon from rice husk. Part II. Impregnation ratio, temperature and time influence, Pak. J. Sci. Ind. Res. 36 (6–7) (1993) 240–243.
- [14] R. Zacaria, C. Gerente, Y. Andres, P.L. Cloirec, Adsorption of several metal ions onto low-cost biosorbent: kinetic and equilibrium studies, Env. Sci. Technol. 36 (2002) 2067–2073.
- [15] 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. Tech. Biotechnol. 77 (4) (2002) 429–436.
- [16] P.A. Brown, The application of peat and lignite to the removal of heavy metals from industrial wastewater, Ph.D. Thesis, The Queen's University Belfast, Belfast, Northern Ireland, 1992.
- [17] G.H. Pino, L.M.S. de Mesquita, M.L. Torem, G.A.S. Pinto, Biosorption of cadmium by green coconut shell powder, Miner. Eng. 19 (5) (2006) 380–387.
- [18] L.S. Balistrieri, T.T. Chao, Selenium adsorption by goethite, Soil Sci. Soc. Am. J. 51 (1987) 1145–1151.
- [19] M. Duc, G. Lefevre, M. Fedoroff, Sorption of selenite ions on hematite, J. Colloid Interface Sci. 298 (2) (2006) 556–563.
- [20] R.H. Neal, G. Sposito, K.M. Holtzclaw, S.J. Tarina, Selenite adsorption on alluvial soils. I. Soil composition and pH effects, Soil Sci. Soc. Am. J. 51 (1987) 1161–1165.
- [21] Y. Zhang, W.T. Frankenberger Jr., Removal of selenium from river water by a microbial community enhanced with *Enterobacter taylorae* in organic carbon coated sand columns, Sci. Total Env. 346 (1–3) (2005) 280–285.
- [22] 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.
- [23] S.E. Manahan, Environmental Chemistry, fifth ed., Lewis Publishing, London, 1991.
- [24] McGraw-Hill Encyclopaedia of Science and Technology, vol. 7, eighth ed., McGraw-Hill, London, 1997, p. 161.
- [25] 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. Tech. Biotechnol. 74 (11) (1999) 1019–1029.
- [26] V.A. Thorpe, Collaborative study of the cation exchange capacity of peat materials, J. AOAC 56 (1) (1973) 154–156.
- [27] Annual Book of ASTM Standards, D 2866-94: Standard Test Method for Total Ash Content of Activated Carbon, vol. 15.01, 1996, p. 498.
- [28] H.P. Boehm, Chemical identification of surface groups, in: Advances in Catalysis, vol. 16, Academic Press, New York, 1996, p. 179.
- [29] O.P. Mahajan, A. Youssef, P.L. Walker Jr., Surface-treated activated carbon for removal of ammonia from water, Sep. Sci. Technol. 13 (6) (1978) 487–499.
- [30] D. Rivin, Use of lithium aluminium hydride in the study of surface chemistry of carbon black, Rubber Chem. Technol. 36 (1963) 729–739.
- [31] K.L. Cheng, Determination of traces of selenium 3,3'-diaminobenzidine as selenium(IV) organic reagent, Anal. Chem. 28 (1956) 1738–1742.
- [32] R. Yu, Toxicity comparison of selenium oxyanions with a proposed biomethylation intermediate dimethyl selenone in a minimal medium accompanied by selenium distribution analysis, M.Sc. Thesis, Sam Houston State University, Huntsville, Texas, 1996.
- [33] S.D. Faust, O.M. Aly, Chemistry of Natural Waters, Ann Arbor Science, Ann Arbor, MI, 1981, pp. 359–371.
- [34] 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. Tech. Biotechnol. 75 (6) (2000) 427–435.
- [35] Y.S. Ho, G. McKay, The kinetics of sorption of divalent metal ions onto sphagnum moss peat, Water Res. 34 (3) (2000) 735–742.
- [36] Y.S. Ho, G. McKay, Pseudo-second order model for sorption processes, Process Biochem. 34 (5) (1999) 451–465.
- [37] Y.S. Ho, G. McKay, Sorption of dye from aqueous solution by peat, Chem. Eng. J. 70 (1998) 115–124.
- [38] M. Cox, E.I. El-Shafey, A.A. Pichugin, Applications of a carbon sorbent for the recovery of heavy metals from waste waters, in: Proceeding of the REWAS'99, Global Symposium on Recycling, Waste Treatment and Clean Technology, vol. 3, San Sebastian, Spain, September 5–9, 1999, pp. 2087–2096.
- [39] K. Vasanth Kumar, S. Sivanesan, Pseudo-second order kinetic models for safranin onto rice husk: comparison of linear and non-linear regression analysis, Process Biochem. 41 (5) (2006) 1198–1202.
- [40] S.D. Faust, O.M. Aly, Adsorption Processes For Water Treatment, Butterworths, London, 1987.
- [41] M.R. Unnithan, 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] Y. You, G.F. Vance, H. Zhao, Selenium adsorption on Mg–Al and Zn–Al layered double hydroxides, Appl. Clay Sci. 20 (1–2) (2001) 13–25.
- [43] F. Sahin, M. Volkan, A.G. Howard, O.Y. Ataman, Selective preconcentration of selenite from aqueous samples using mercapto-silica, Talanta 60 (5) (2003) 1003–1009.
- [44] W. Kuan, S. Lo, M.K. Wang, C. Lin, Removal of se(IV) and SE(VI) from water by aluminum-oxide-coated sand, Water Res. 32 (3) (1998) 915–923.
- [45] S. Lo, T. Chen, Adsorption of Se(IV) and Se(VI) on an iron-coated sand from water, Chemosphere 45 (5) (1997) 919–930.
- [46] 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.

- [47] 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.* B138 (2006) 604–613.
- [48] K. Kinoshita, *Carbon: Electrochemical and Physicochemical Properties*, Wiley, New York, 1988, pp. 86–173.
- [49] S.M. Lee, P.D. Allen, Removal of Cu(II) and Cd(II) from aqueous solution by seafood processing waste sludge, *Water Res.* 35 (2) (2001) 534–540.
- [50] C.F. Baes Jr., R.E. Mesmer, *The Hydrolysis of Cations*, Wiley-Interscience, New York, 1976.
- [51] D.R. Lide, H.P.R. Frederikse, *CRC Handbook of Chemistry and Physics*, 77th ed., CRC Press, London, 1995, pp. 8–20: 8–30.
- [52] F. Seby, M. Potin-Gautier, E. Giffaut, G. Borge, O.F.X. Donard, A critical review of thermodynamic data for selenium species at 25 °C, *Chem. Geol.* 171 (3–4) (2001) 173–194.