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Removal of lead and sodium ions from aqueous media using natural wastes for desalination and water purification

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ABSTRACT

Sugarcane bagasse (SCB) and beet pulp (BP) are promising low cost natural wastes with cellulose–lignin polymeric structure. Their adsorption properties for the removal of Pb(II) and Na(I) under variable conditions of solution pH, time of equilibrium, weight of adsorbent, and metal ion concentration were investigated. These two adsorbents were characterized using Fourier transform infrared spectra, Scanning electron microscope (SEM), and X-ray diffraction. SCB and BP showed high percentage of extraction of Pb(II) (100.0 ± 1.0% and 100.0 ± 0.5%) and Na(I) (97.5 ± 0.1% and 98.9 ± 0.1%), respectively. The adsorption isotherm data for Pb(II) and Na(I) ions by the two adsorbents were modeled using Langmuir and Freundlich equations. Furthermore, the adsorption kinetics data were best fitted with the pseudo-second-order type. Finally, the proposed method has been successfully applied for removal of Pb(II) from environmental water samples. Adapting batch condition, this application revealed high efficiency and good precision as indicated by recovery values 95.2–103.2% and RSD% = 0.339–1.333%. Moreover, SCB and BP were used to reduce sodium ion concentrations from irrigation water for improvement of plants production.

Keywords: Sugarcane bagasse; Beet pulp; Heavy metals; Removal; Water samples; Desalination

1. Introduction

Heavy metals are continual pollutants due to their toxic, non-biodegradable, and accumulative characteristics. Because of the rapid increase of the industrial and mining activities which are responsible for the growing metal content in surface and groundwater (GW), heavy metal pollution of water bodies has become a serious problem in the world [1]. Some heavy metals at trace concentrations are essential for human metabolism. However, at high concentrations, most of these metals may be toxic [2]. From the perspective of environmental toxicology, lead is a very dangerous heavy metal since it finds its way into air and water through various sources such as lead smelter, battery manufacture, and paper industry. In addition, natural sources of the environmental lead contamination may include forest fires, volcanic eruptions, mineral breakdown, translocation, and sedimentation from dust storms [3,4]. In fact, lead as a poisonous metal can cause severe health problems for humans. It can attack almost all organs and systems in the human body, especially the nervous system in young children as well as blood and brain disorders [5]. Furthermore, the presence of such heavy metal in water resources represents a major concern due to its extreme toxicity toward aquatic system and environment [6]. On the other hand, sodium as one of the alkali metals is an essential element for human, animals, and plants, and has an electrolytic significance [7]. So, it has received more attention than other elements in the alkali metals group. However, excessive sodium salt concentration acts as an environmental stress that reduces plant's growth. All crop plants have physiological limits to salt concentration. Concentration above a certain threshold may reduce crop yields or cause death of plant cells [8–10]. For instance, high sodium concentration (salinity) in seed cells may induce changes in protein activity by affecting the hydration of nuclear contents, causing an inhibition of enzyme activity [11–13]. Therefore, the choice of an efficient technique for removal of such metal ions from water and wastewater (WW) is very important. For this purpose, several methods have been adapted including chemical precipitation, ion exchange, solvent extraction, reverse osmosis, and solid phase extraction (SPE) [14–17]. In fact, SPE has been known as a powerful tool for separation and removal of various inorganic and organic analytes. Recently, research efforts have been intensified and focused on the beneficial utilization of environmentally friendly solid phase extractors. In this respect, low cost natural polymeric wastes have received much attention on metal ions removal from contaminated water [18,19]. The most popular adsorbents among them are agricultural wastes [20]. They are available in large quantities at a low price such as sugarcane bagasse (SCB) [15,16,20], sugar beet pulp (BP) [21], and other low cost adsorbents [22]. SCB and BP are mainly composed of cellulose and lignin (Fig. 1) with a capacity for binding metal cations due to the occurrence of hydroxyl, carboxylic, and phenolic groups in their structures [15,16].

As the water is the main artery of human life, animals, and plants, it has been necessary to find a method to purify water and to reduce the salinity of water used for irrigation. So, the main goal of the current study is to apply simple and direct SPE technique utilizing SCB and BP as environment-friendly adsorbents for the removal of Pb(II) ions from water samples using batch mode. The efficiency of the same adsorbents to reduce Na(I) concentrations from irrigation water is also aimed to be explored for improving the productivity of zea maize and wheat as ones of the most popular cultivars in Egypt.

2. Experimental

2.1. Chemicals and materials

All chemicals, metal salts, and other reagents used were of analytical grade and were purchased from Merck, Germany. SCB and BP were obtained from Abou-Korkas Sugar Factory, El-Minia, Egypt. WW was collected from Abou-Korkas Sugar Factory, El-Minia, Egypt. Drinking tap water (DTW), GW, zea maize, and wheat seeds were collected from El-Minia governorate, Egypt. Doubly distilled water (DDW) and mineral water (MW) were obtained from our lab and a local company for natural water, respectively.

2.2. Instrumentation

Mechanical shaker (Model 75) manufactured by Burrell Corp. Pittsburgh, PA, USA was used for the shaking process. The Fourier transform infrared (FT-IR) analyses of the adsorbents before and after metal-ion adsorption were obtained from KBr pellets by using FT-IR (Model 410) JASCO, Japan. Scan electron microscopy analysis (SEM) was obtained using JSM-5400 LV JEOL, Japan. X-ray diffraction (XRD) was carried out by Philips X-ray diffractometer PW 1370, Co. with Ni filtered Cu Kα radiation (1.5406 Å). A Fisher Scientific Accumet pH-meter (Model 825), Germany, calibrated against two standard buffer solutions at pH 4.0 and 9.2 were used for all pH measurements. Atomic absorption measurements of Pb(II) ion were performed with Perkin Elmer 2380 spectrometry, England. A flame photometer (Corning 410, Corning Science Products, Halstead, Essex, England) was used for measurements of Na(I) ion concentrations.

2.3. Development of SCB and BP adsorbents

SCB and BP were first washed thoroughly with distilled water to remove the dust particles, then soaked overnight in 0.1 N NaOH solution and washed with DDW. Then, they were soaked in 0.1 N CH_3COOH for 2–3 h to remove the traces of NaOH [23]. Finally, the produced adsorbents were washed with DDW and then filtered, well dried, powdered, and sieved before use. The average particle size was 0.75 mm for SCB and 0.5 mm for BP.

2.4. Adsorption measurements using batch equilibrium technique

The percentage of extraction of Pb(II) and Na(I) ions using SCB and BP were determined in triplicate under static conditions by the batch equilibrium technique. 4.0 and 2.0 g each of SCB and BP, respectively, was added to a mixture of 1.0 and 0.1 mL of 0.1 M each of Pb(II) and Na(I), respectively, and solution of pH 2.0–6.0 for Pb(II) and 2.0–10.0 for Na(I) (solutions of 0.1 M HCl and 0.1 M NaOH were used for pH adjustment); the total volume was completed to 50 ml by DDW in a 100 mL measuring flask. This mixture was mechanically shaken for 60 min at room temperature to attain equilibrium [16]. The SCB and BP were separated by filtration, washed with DDW, and the unretained metal ions in the filtrate were determined by complexometric EDTA titration for Pb(II) and flame photometry for Na(I). The equation of metal extraction could be obtained as follows:

$$\text{Percentage of extraction} = (C_o - C_f/C_o)\times 100 \tag{1}$$

where C_o refers to the initial concentration of metal ion in mol L^{-1}, C_f equals concentration of the unsorbed metal ion in the filtrate in mol L^{-1}. Moreover, the effect of contact time on Pb(II) and Na(I) uptake was determined under the same batch conditions, but at different shaking periods (10, 30, 45, 60, 90, and 120 min) and at the optimum pH for Pb(II) and Na(I). The effect of Pb(II) and Na(I) concentrations (2×10^{-4}–2×10^{-3} M) and weight of adsorbent (0.1–5.0 g) on their uptake efficiency by SCB and BP were also systematically investigated.

3. Results and discussion

3.1. FT-IR analysis

SCB and BP as lignocellulosic compounds are generally considered as structures built by cellulose molecules, organized in microfibrils and surrounded by hemicellulosic materials (xylans, mannans, glucomannans, galactans, and arabogalactans), lignin, and pectin along with small amounts of protein [24], Fig. 1. The FT-IR spectra of SCB and BP before and after adsorption of Pb(II) and Na(I) were performed to determine the vibration frequency changes in their functional groups within the range of 4,000–400 cm^{-1} as shown in Figs. 2(A), 2(B) and Table 1. The spectral measurements supported the complex nature of the examined adsorbents. FT-IR spectra of SCB and BP before Pb(II) and Na(I) adsorption were similar and showed as follows: an absorption peak around 3,428.81 cm^{-1} indicated the existence of free and intermolecular bonded hydroxyl groups (–OH). The other peaks observed for SCB and BP at 2,923.56 and 2,927.41 cm^{-1}, respectively, can be assigned to –C–H stretching vibration. The presence of strong C–O band

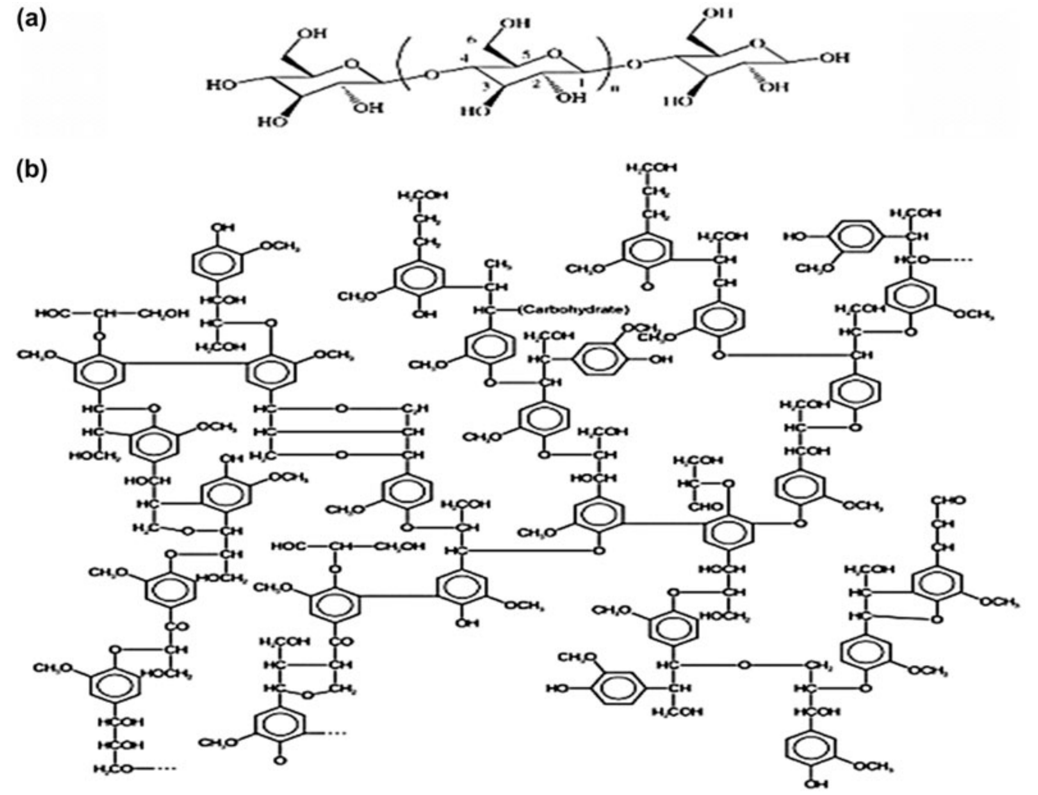


Fig. 1. Chemical structure of (a) cellulose and (b) lignin in SCB and BP molecules.

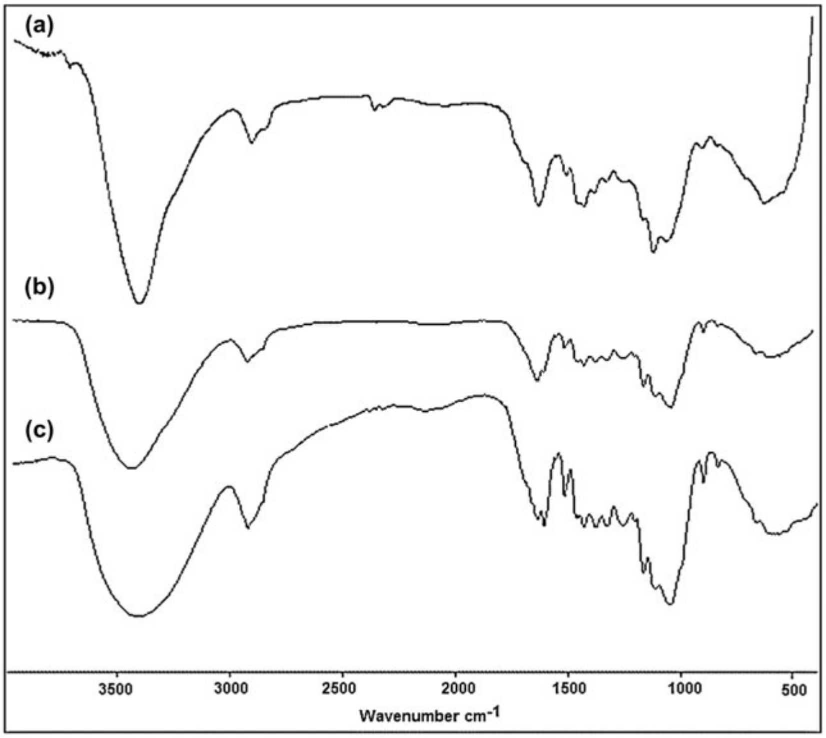


Fig. 2A. FT-IR spectra of (a) SCB, (b) SCB-Pb(II), and (c) SCB-Na(I) phases.

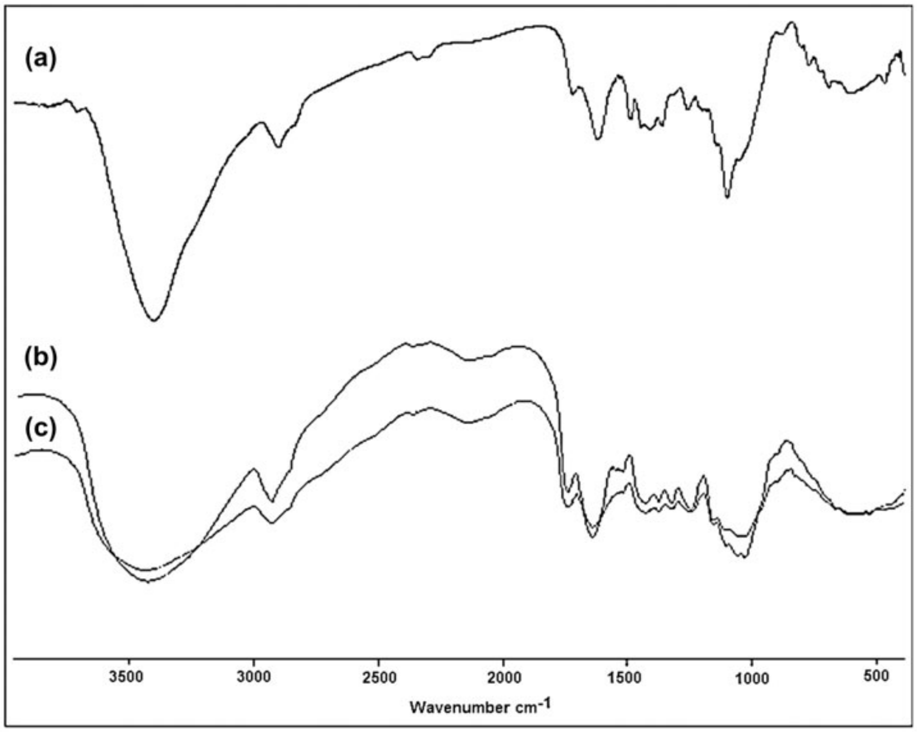


Fig. 2B. FT-IR spectra of (a) BP, (b) BP-Pb(II), and (c) BP-Na(I) phases.

Table 1
List of absorption frequencies of FT-IR spectra of SCB and BP before and after adsorption of Pb(II) and Na(I)

Absorption frequencies before metal sorption (cm$^{-1)}$			Absorption frequencies after metal sorption using SCB, (cm^{-1})		Absorption frequencies after metal sorption using BP, (cm^{-1})	
Groups	SCB	BP	Pb(II)	Na(I)	Pb(II)	Na(I)
–OH	3,428.81	3,428.81	3,417.11	3,442.06	3,423.17	3,424.16
–CH	2,923.56	2,927.41	2,917.71	2,919.67	2,924.74	2,925.93
–OCH_3	1,113.69	1,113.69	1,110.21	1,111.81	1,030.88	1,031.43
	1,054.87	–	1,039.94	1,038.94	–	–
Lignin structure	896.73	624.82	897.60	897.73	–	–
	611.32	–	663.52	663.71	559.95	560.91
–COOH	1,628.59	1,636.30	1,631.96	1,632.80	1,738.17	1,738.70
	1,509.03	1,506.13	1,604.65	1,514.00	1,641.74	1,641.07
	1,428.03	1,426.10	1,461,046	1,426.87	1,426.63	1,426.08

at 1,113.69 and 1,054.87 cm^{-1} due to –OCH_3 group in addition to the peaks at 896.73, 624.82, and 611.32 cm^{-1} related to bending modes of aromatic compounds confirm the presence of lignin structure incorporated SCB and BP [25]. Moreover, a weak intensity band located at 1,628.59, 1,509.03, 1,428.03, and 1,636.30, 1,506.13, 1,426.10 cm^{-1} was argued to –COOH stretching vibration of galacturonic acid [26] (Figs. 2A(a) and 2B(a)). Generally, the binding of metal ions to adsorbents may proceed via complexation with functional groups, ionic exchange, surface precipitations, and chemical reaction with surface sites [27]. Regarding FT-IR for SCB and BP after Pb(II) and Na(I) adsorption, it was found that oxygen containing functional groups vis, methoxy –OCH_3, carboxy –COOH and phenolic –OH groups are affected after uptake process. This was judging from changes in shapes or band intensities and shifting in their positions from 1,054.87 and 1,113.69 cm^{-1} to 1,039.94 and

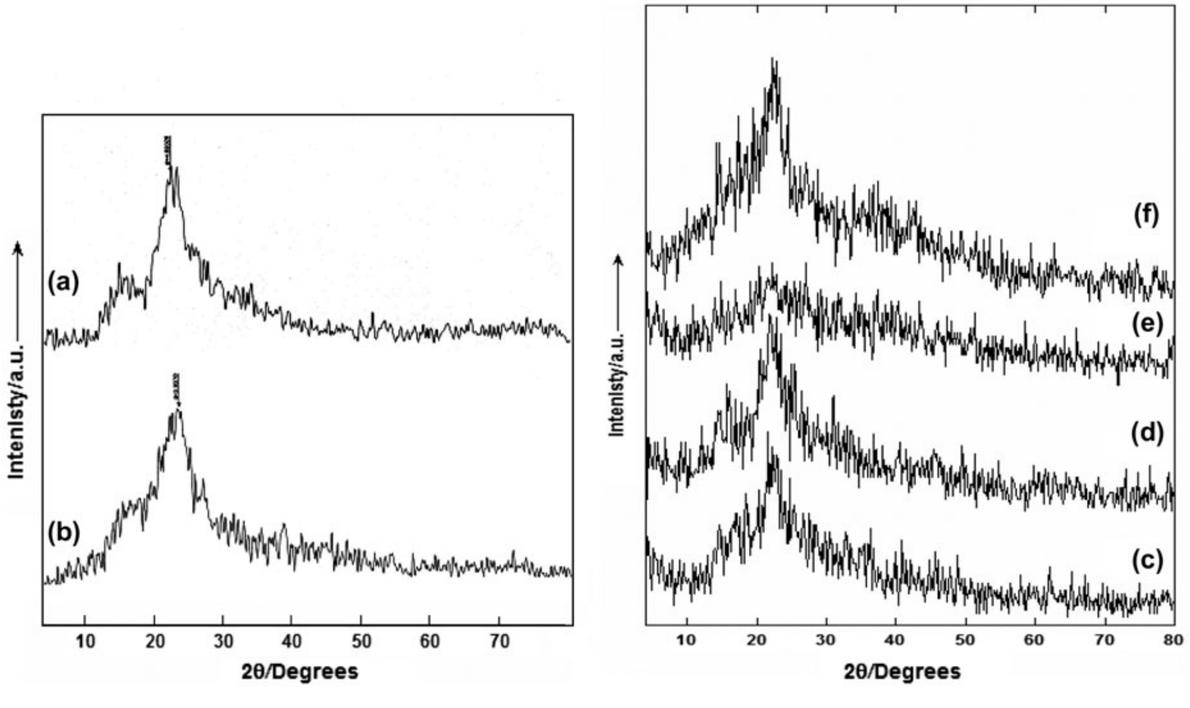


Fig. 3. XRD of (a) SCB, (b) BP, (c) SCB-Pb(II), (d) SCB-Na(I), (e) BP-Pb(II), and (f) BP-Na(I) phases.

1,110.21 cm^{-1} for –OCH$_3$, from 1,628.59, 1,509.03, and 1,428.03 cm^{-1} to 1,631.96, 1,604.65, and 1,461.46 cm^{-1} for –COOH, and from 3,428.81 to 3,417.11 cm^{-1} for –OH after adsorption of Pb(II) and shifted to 1,038.94 and 1,111.81 cm^{-1}, to 1,632.80, 1,514.0, and 1,426.87 cm^{-1} and to 3,442.06 cm^{-1} after adsorption of Na(I) using SCB, respectively. On the other hand, for the BP adsorbent the bands are shifted after Pb(II) adsorption to 1,030.88 cm^{-1}, to 1,738.17, 1,641.74, and 1,426.63 cm^{-1} and 3,423.17 cm^{-1} and after Na(I) adsorption to 1,031.43 cm^{-1}, to 1,738.70, 1,641.07, and 1,426.08 cm^{-1} and 3,423.16 cm^{-1} for –OCH$_3$, –COOH and –OH, respectively. In addition to the peaks at 896.73, 624.82, and 611.32 cm^{-1} of lignin structure of the two adsorbents shifted to 897.60, 663.52, and 897.73, 663.71 cm^{-1} using SCB and to 559.95 and 560.91 cm^{-1} using BP for adsorption of Pb(II) and Na(I), respectively. These results indicated the participation of –OCH$_3$, –COOH, and –OH via oxygen atom for Pb (II) and Na(I) binding to SCB and BP (Fig. 2A(b, c) and 2B(b, c)). This is in agreement with Person principal for hard–soft acids and bases [28].

3.2. X-ray diffraction

The crystallinity of SCB and BP could significantly influence the adsorption properties by controlling the accessibility to adsorption sites. Fig. 3(a) and (b) shows the smooth shape of XRD pattern of SCB and BP. There are two strong peaks in their diffractogram at $2\theta = 4.02^\circ$ and 3.94°, respectively. XRD patterns of SCB and BP after adsorption with Pb(II) and Na(I) in Fig. 3(c)–(f) mainly showed a slight shift and change in intensity compared to the parent peaks of SCB and BP patterns, indicating and emphasizing the adsorption process [29].

3.3. Scan electron microscope

The surface morphology of SCB and BP were analyzed using a SEM before and after Pb(II) and Na(I) ions adsorption, Figs. 4A and 4B. The microphotographs before metal ions adsorption revealed clearly dense and rough surface with narrow thickness between fibers which facilitated the mass transfer rate of metal ions

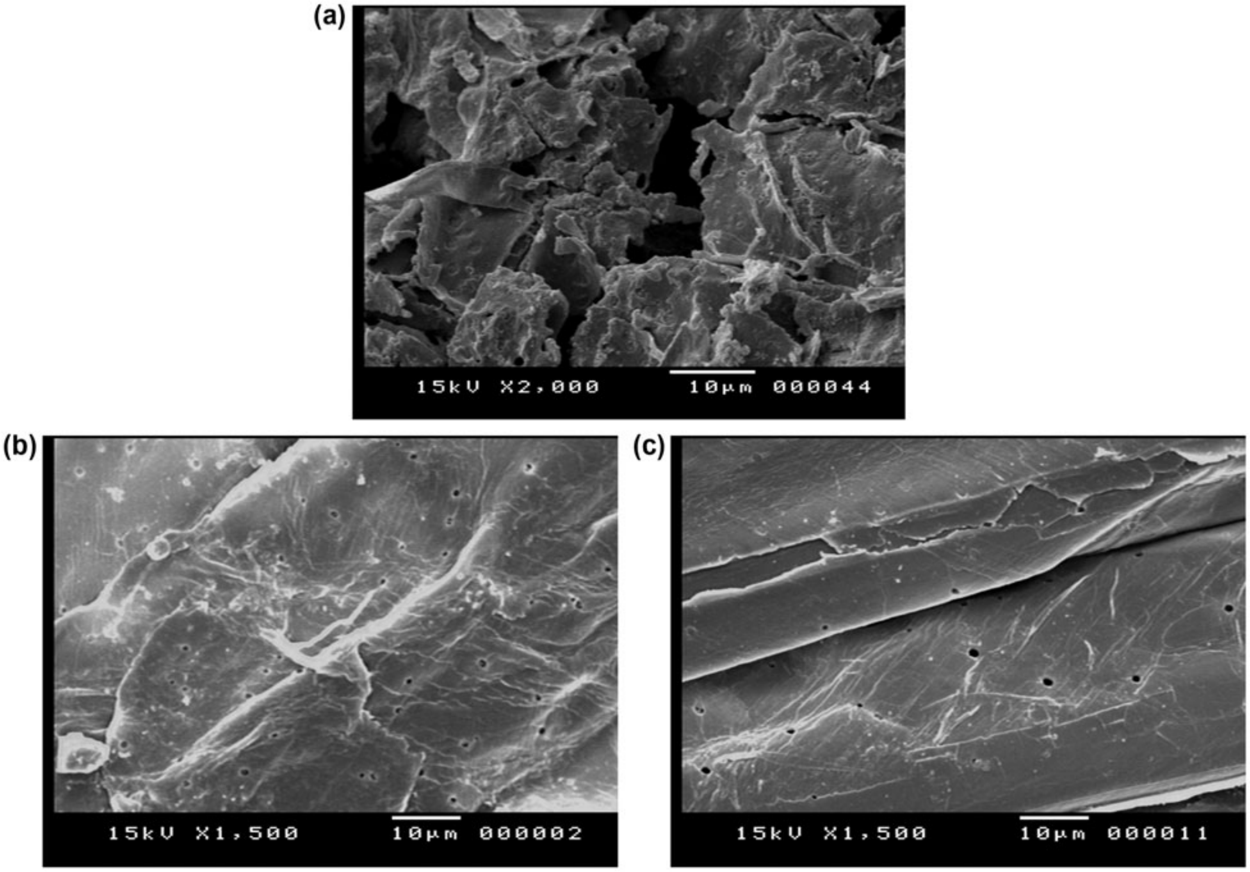


Fig. 4A. SEM images of (a) SCB (b) SCB with Pb(II), and (c) SCB with Na(I).

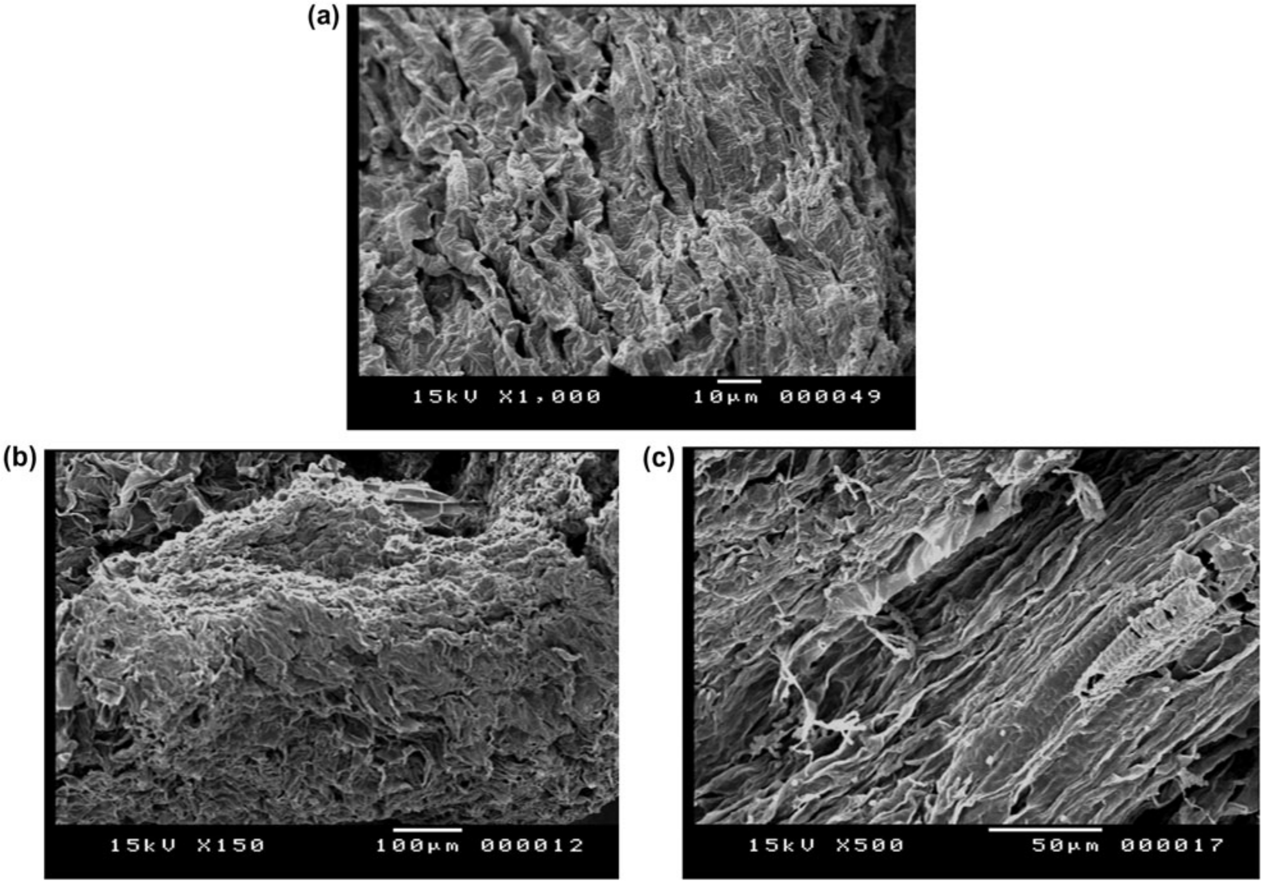


Fig. 4B. SEM images of (a) BP (b) BP with Pb(II), and (c) BP with Na(I).

toward the adsorbent surface and consequently improving its adsorption capacity [30] (Figs. 4A(a) and 4B(a)). After Pb(II) and Na(I) adsorption, the micrographs revealed the presence of more smooth and even surface with wide thickness. These changes of the structure of the two adsorbents confirmed the presence of the selected metal ions on the surface of these adsorbents (Figs. 4A(b, c) and 4B(b, c)).

3.4. Effect of pH on metal ion removal using SCB and BP

In the SPE studies of metal ions, the influence of pH of an aqueous solution is one of the main factors for quantitative recoveries of the analytes. The predominant metal species at pH ≥ 2.0 are positively charged [M^{n+} and $M(OH)^{(n-1)+}$]; therefore, uptake of metals may proceed through M^{n+} exchange process with acidic sites H^{+}, complexing with functional groups, coordination, and/or chelation [31]. Due to this important point, the effect of pH was investigated in the pH ranges of 2.0–10.0 with the model solution, keeping the other parameters constant. As shown in Fig. 5, for the extraction of Pb(II) and Na(I) as a function of pH (2.0–10.0), it is noteworthy that a strong dependence of the percentage of extraction values on the pH of the tested metal ion solution is observed, which can be summarized by the significant increase in the percentage of extraction values ongoing from 2.0 to 6.0 for Pb(II) and from pH 2.0 to 10.0 for Na(I) using SCB and BP. The optimum pH value was chosen to be 5.0 for Pb(II) using SCB and BP, 6.0 and 10.0 for Na(I) using SCB and BP, respectively. However, the two adsorbents showed low efficiency toward the extraction of these two metal ions from aqueous solutions at low pH values. At lower pH value, the H^{+} ions compete with metal cation for the exchange sites in the system, thereby partially releasing the latter. At high pH values, the adsorbent surface becomes more negatively charged, increasing the attraction between the metal ions and adsorbent, until a maximum is reached at around optimum pH [2]. In this context, it was found that with increase in pH of the solution, the extent of extraction was found to range from 45.0% to 100.0 ± 1.0% and from 55.0% to 100.0 ± 0.5%

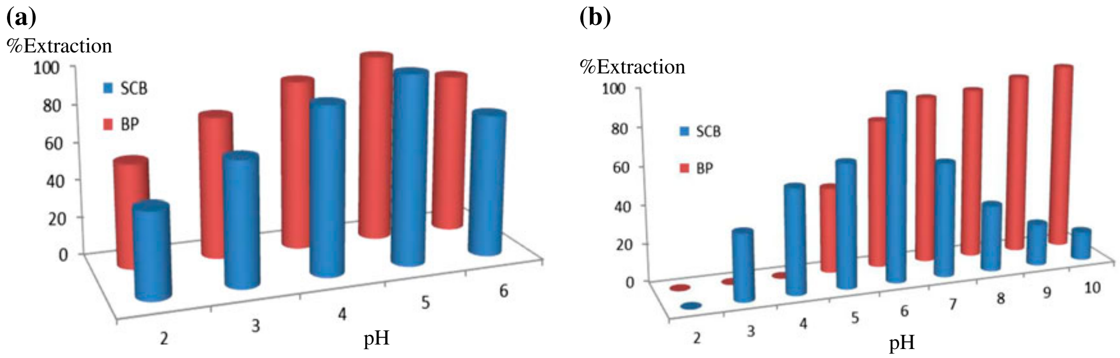


Fig. 5. Percentage extraction of (a) Pb(II) and (b) Na(I) as a function of pH using SCB and BP.

for Pb(II) at pH 2.0–5.0 and from 35.0% to 97.5 ± 0.1% and from 0.0% to 98.9 ± 0.1% for Na(I) at pH 3.0–10.0 with SCB and BP, respectively. SCB and BP mainly contain cellulose, hemi-cellulose, and lignin, but they differ in their percentages. The percentages of cellulose were 50% and 20–30% and of lignin were 23 and 10% for SCB and BP, respectively [24,26]. This variety of chemical composition and consequently functional groups make these two adsorbents show different efficiencies for removal and extraction of metal ions over a wide range of pH [25]. According to the chemical structure shown in Fig. 1, the interaction of Pb(II) ions onto SCB and BP adsorbents is mainly based on coordination due to the presence of oxygen donor atoms of methoxy, carboxyl, and hydroxyl groups. However, the binding of Na(I) ions onto the two adsorbents is basically due to ion exchange mechanism.

3.5. Effect of weight of SCB and BP adsorbents

The weights of SCB and BP adsorbents were varied from 0.1 to 5.0 g. Fig. 6(a) represents the relation between the weight of SCB adsorbent and percentage of extraction of Pb(II) at pH 5.0 and of Na(I) at pH 6.0. It may be observed that on increasing the weight of SCB from 0.1−4.0 g, the percentage of extraction of Pb(II) and Na(I) increased from 27.0% to 100.0 ± 1.0% and from 18.0% to 97.5 ± 0.1%, respectively and remained constant up to 4.0 g. On the other hand (Fig. 6(b)) records the BP weight profile vs. Pb(II) at pH 5.0 and Na(I) at pH 10.0 adsorbed per unit mass. It was found that, the percentage of extraction increased for Pb(II) from 50.0% to 100.0 ± 0.5% and for Na(I) from 35.0% to 98.9 ± 0.1% at 0.1−2.0 g and remained constant up to 2.0 g.

3.6. Effect of shaking time (kinetic studies)

Shaking time is an important factor in the process of evaluation of the SCB and BP. The batch experiments were carried out at different contact times 10, 30, 45, 60, 90, and 120 min for SCB with Pb(II) concentration (0.1 mmol) at pH 5.0 and for Na(I) concentration (0.01 mmol) at pH 6.0. The experiment repeated for BP adsorbent with the same Pb(II) concentration at pH 5.0 and for Na(I) concentration at pH 10.0 and 50.0 mL

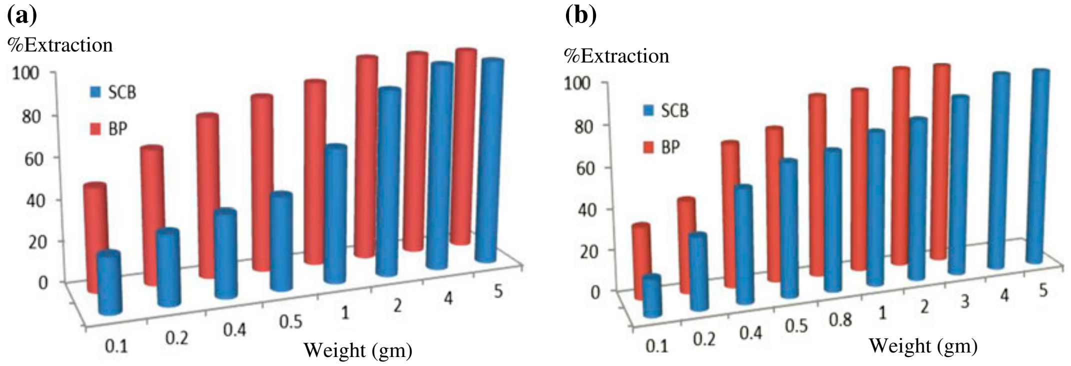


Fig. 6. Effect of SCB and BP weight on % extraction of (a) Pb(II) and (b) Na(I).

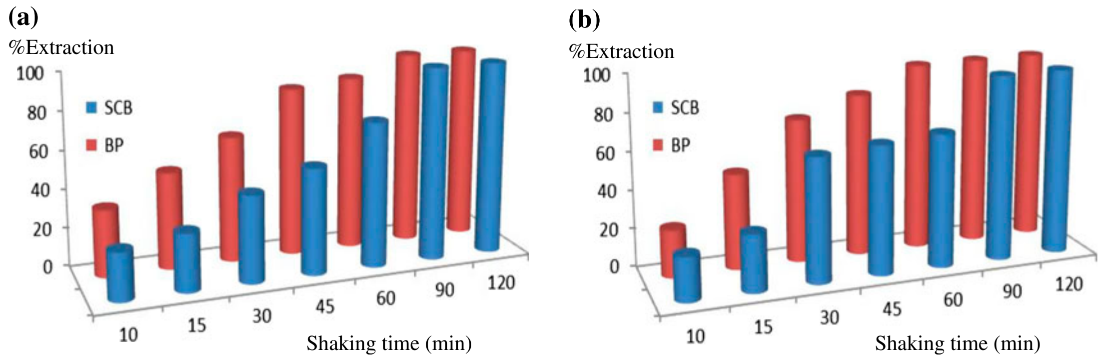


Fig. 7. % Extraction of (a) Pb(II) and (b) Na(I) as a function of shaking time using SCB and BP.

contact solution. Results of percentage of extraction of Pb(II) and Na(I) using SCB and BP as a function of shaking time intervals are represented in Fig. 7(a) and (b). The equilibrium is reached within 120 and 90 min of contact for SCB and BP, respectively, and reached a saturation level. In the beginning, the ions adsorbed occupied selectively the active sites on SCB and BP. As the contact time increased, the active sites on the adsorbent were filled. The results which are plotted in Fig. 7(a) and (b) clearly indicated that the equilibrium for Pb(II) and Na(I) is attained in 120 min of contact using SCB and in 90 min using BP.

The adsorption kinetic data of Pb(II) and Na(I) measured on SCB and BP adsorbents, were analyzed in terms of pseudo-second-order adsorption equation [32]. This equation can be written as follows:

$$t/Q_t = 1/k_2Q_e^2 + (1/Q_e)t \qquad (2)$$

Here, $k_2Q_e^2$ is the initial adsorption rate (mmol g^{-1} min^{-1}), k_2 (g mmol^{-1} min^{-1}) is the rate constant of adsorption, Q_e (mmol g^{-1}) the amount of metal ion sorbed at equilibrium, and Q_t (mmol g^{-1}) the amount of metal ion on the surface of the adsorbent at time t (min). υ_o and Q_e can be obtained from the intercept and slope of a plot of t/Q_t vs. t (Fig. 8), respectively. Therefore, $k_2Q_e^2$ calculated to be 5.945×10^{-4} and 0.699×10^{-4}, $Q_e = 4.0 \times 10^{-2}$ and 3.7×10^{-3} mmol g^{-1}, and $k_2 = 0.371$ and 5.1 g mmol^{-1} min^{-1} and $r^2 = 0.962$ and 0.973 using SCB for Pb(II) and Na(I), respectively. $k_2Q_e^2$ equal 2.906×10^{-3} and 3.514×10^{-4}, $Q_e = 5.99 \times 10^{-2}$ and 5.85×10^{-3} mmol g^{-1}, and $k_2 = 0.835$ and 10.27 g mmol^{-1} min^{-1} and $r^2 = 0.996$ and 0.996 using BP for Pb(II) and Na(I) ions, respectively. Since the kinetic of the uptake has to be determined in order to establish the time course of the uptake process, the previous results of correlation factors showed that the adsorption kinetic data were best fitted with the pseudo-second-order model.

3.7. Effect of initial metal ion concentrations (adsorption isotherm studies)

Interaction of adsorbent with adsorbate such as metal ion is heavily dependent on the initial concentration of adsorbate. The adsorption of metal ion is considered as a combination of various physicochemical and stereochemical factors which are basically depend on the interacting species. The potential affinity between adsorbate and adsorbent, bond energy and adsorption capacity can be determined by construction of various isotherm models. In addition, the adsorption isotherm can be used to describe the distribution of the adsorbed molecules between the liquid and solid phases at equilibrium state. Such evaluations are generally applied to provide important and valuable information for optimizing the experimental conditions for adsorbent applications. The two most commonly employed isotherm models for describing adsorption of metal ions by different adsorbents and bio-adsorbents are the Langmuir and Freundlich [3,15]. To find out the mechanistic parameters associated with Pb(II) and Na(I) adsorption, the results obtained by the adsorption experiments were analyzed as follows. The adsorption isotherms for binding of Pb(II) and Na(I) with SCB and BP were determined by the batch technique at pHs 5.0, 6.0, and 10.0, respectively. Thus, solutions of Pb(II) and Na(I) in the concentration range 2.0×10^{-4}–2.0×10^{-3} M were shaken for 120 and 90 min with a constant weight 4.0 and 2.0 g of SCB and BP, respectively.

The Freundlich model assumes a heterogeneous adsorption surface with sites having different adsorption energies [33]. Linearized form of the Freundlich equation was given by the following equation [34]:

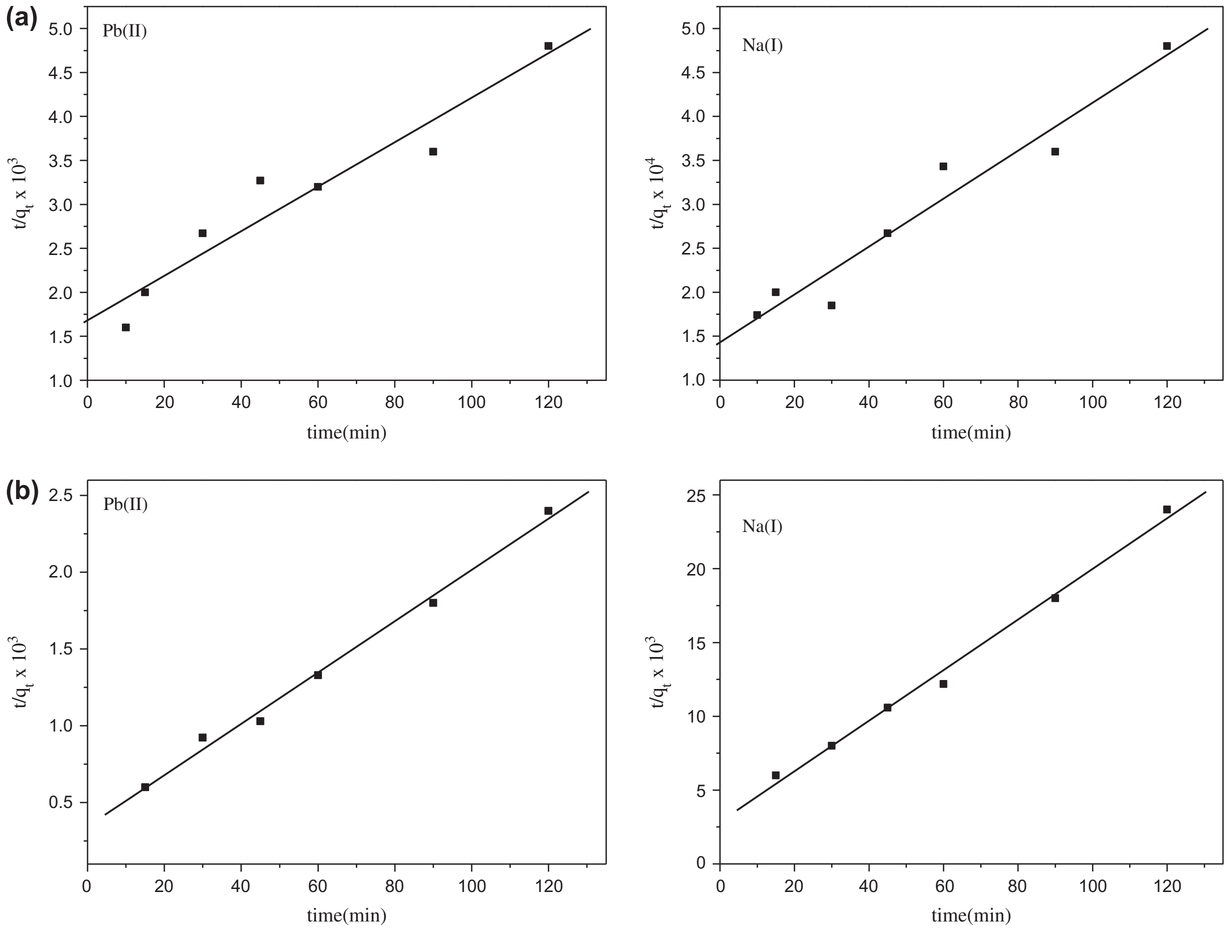


Fig. 8. Pseudo-second-order kinetic plots for the sorption of Pb(II) and Na(I) on: (a) SCB and (b) BP.

$$\log Q_e = \log K_\mathrm{F} + n \log C_e, \text{(linear form)} \tag{3}$$

where Q_e is the equilibrium metal ion concentration on adsorbent (mmol g^{-1}), C_e is the equilibrium concentration of the metal ion (mmol L^{-1}), K_F is the Freundlich constant (mmol g^{-1}) which indicates the adsorption capacity and represents the strength of the adsorptive bond, and n is the heterogeneity factor which represents the bond distribution, Fig. 9(a) and (b). The values of K_F and n were presented in Table 2. From this table, it is clearly showed that the data of adsorption isotherm using SCB and BP adsorbents with Pb(II) are well fitting to the Freundlich model [35]. A value of $1/n < 1$ represents an isotherm, where the marginal sorption energy increases with increasing surface concentration. This value can be also interpreted by assuming strong adsorption, strong intermolecular attraction within the adsorbent layers, and high penetration of the solute in the adsorbent and mono-functional nature of the adsorbate [36]. Thus, the initial concentration of metal ion in solution remarkably influenced on the equilibrium uptake of Pb(II) by SCB and BP adsorbents due to higher availability of metal ion for adsorption. Moreover, a high driving force to overcome all mass transfer resistance of metal ion between the aqueous solution and adsorbent is suggested in the presence of high initial metal ion concentration. This also results in higher probability of collision between metal ion and adsorbent as well as higher metal uptake.

Distribution of metal ions between liquid and solid adsorbent could be also described by Langmuir adsorption isotherm. It is based on the assumption that metal ions are chemically adsorbed on a fixed number of well-defined sites. Each site could hold only one ion (monolayer adsorption); all site are energetically equivalent (homogeneous surface); and there is no interaction between the ions [2]. The linearized Langmuir isotherm allows the calculation of adsorption capacities and the Langmuir constant. The model is described by the following equation [37]:

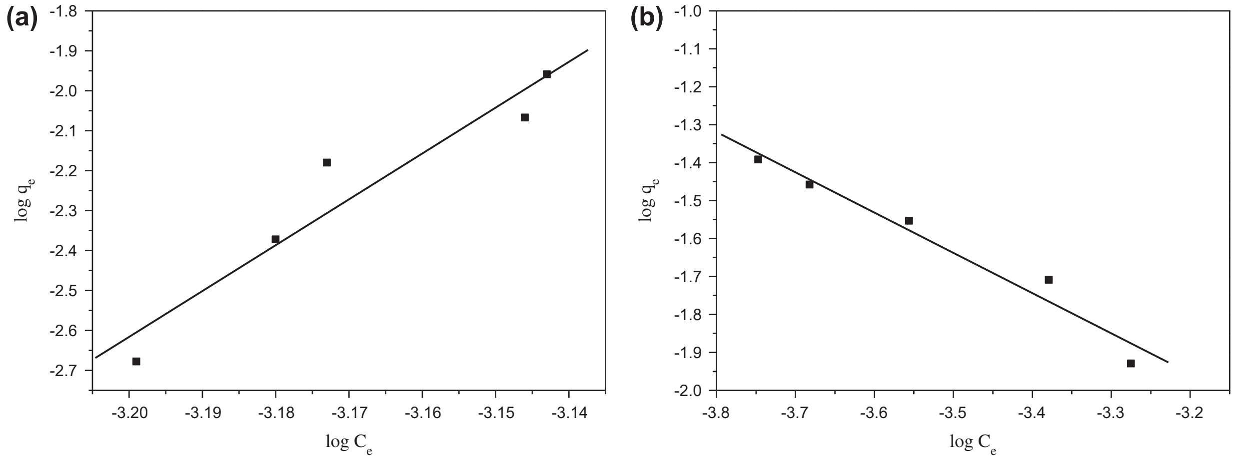


Fig. 9. Freundlich plot for the sorption of Pb(II) on (a) SCB and (b) BP at constant temperature.

Table 2
Parameters of Freundlich and Langmuir isotherm constants for binding of Pb(II) and Na(I) using SCB and BP at room temperature

		Freundlich constants			Langmuir constants			
Sorbent	Metal ion	K_F	$1/n$	r^2	Q_o[a]	b[b] × 10^4	r^2	R_L
SCB	Pb(II)	2.39×10^{-3}	0.087	0.958	5.38×10^{-3}	6.41	0.189	0.008
	Na(I)	3.71×10^{-3}	4.016	0.897	8.77×10^{-3}	1.39	0.985	0.066
BP	Pb(II)	3.80×10^{-2}	0.943	0.981	8.98×10^{-3}	0.58	0.962	0.079
	Na(I)	7.94×10^{-3}	3.012	0.757	18.18×10^{-3}	1.10	0.976	0.016

[a] mmol g^{-1}.
[b] ml/mmol.

$$C_e/Q_e = (1/Q_o)C_e + (1/Q_o b), \text{(linear form)} \qquad (4)$$

where C_e and Q_e are the equilibrium concentrations of adsorbate in the liquid and adsorbed phases in mmol ml^{-1} and mmol g^{-1}, respectively [38]. Q_o (mmol g^{-1}) and b (ml $mmol^{-1}$) are Langmuir constants, which are related to maximum adsorption capacity of Pb(II) and Na(I) and affinity parameter, respectively, using SCB and BP adsorbents. These constants can be calculated from the intercept ($1/Q_o b$) and slope ($1/Q_o$) of the linear plot, C_e/Q_e vs. C_e given in Fig. 10(a–c). The correlation coefficient (r^2) showed that the Langmuir model fitted the results better than Freundlich model for BP with Pb(II) and Na(I) and for SCB with Na(I) as shown in Table 2. Moreover, the essential characteristics of the Langmuir isotherm can also be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, R_L, which is defined as: $R_L = 1/(1 + bC_o)$ where, b is the Langmuir constant (indicates the nature of adsorption and the shape of the isotherm accordingly) and C_o is the initial concentration of analyte. The R_L value indicates the type of the isotherm [38]. The R_L for Pb(II) and Na(I) adsorption were also calculated in Table 2 and supported a highly favorable adsorption process based on Langmuir model.

4. Applications

4.1. Removal of Pb(II) from environmental water samples

In order to demonstrate the validity of the studied method in the batch system, the accuracy and precision were investigated using different water samples: WW, DTW, MW, and GW spiked with a known amount of Pb(II). The spiked concentrations of lead ions were set at the regulatory levels of heavy metals in an aqueous solution. Individual water solutions (50 mL) containing 10.0 ppm of Pb(II) were stirred with each SCB and BP

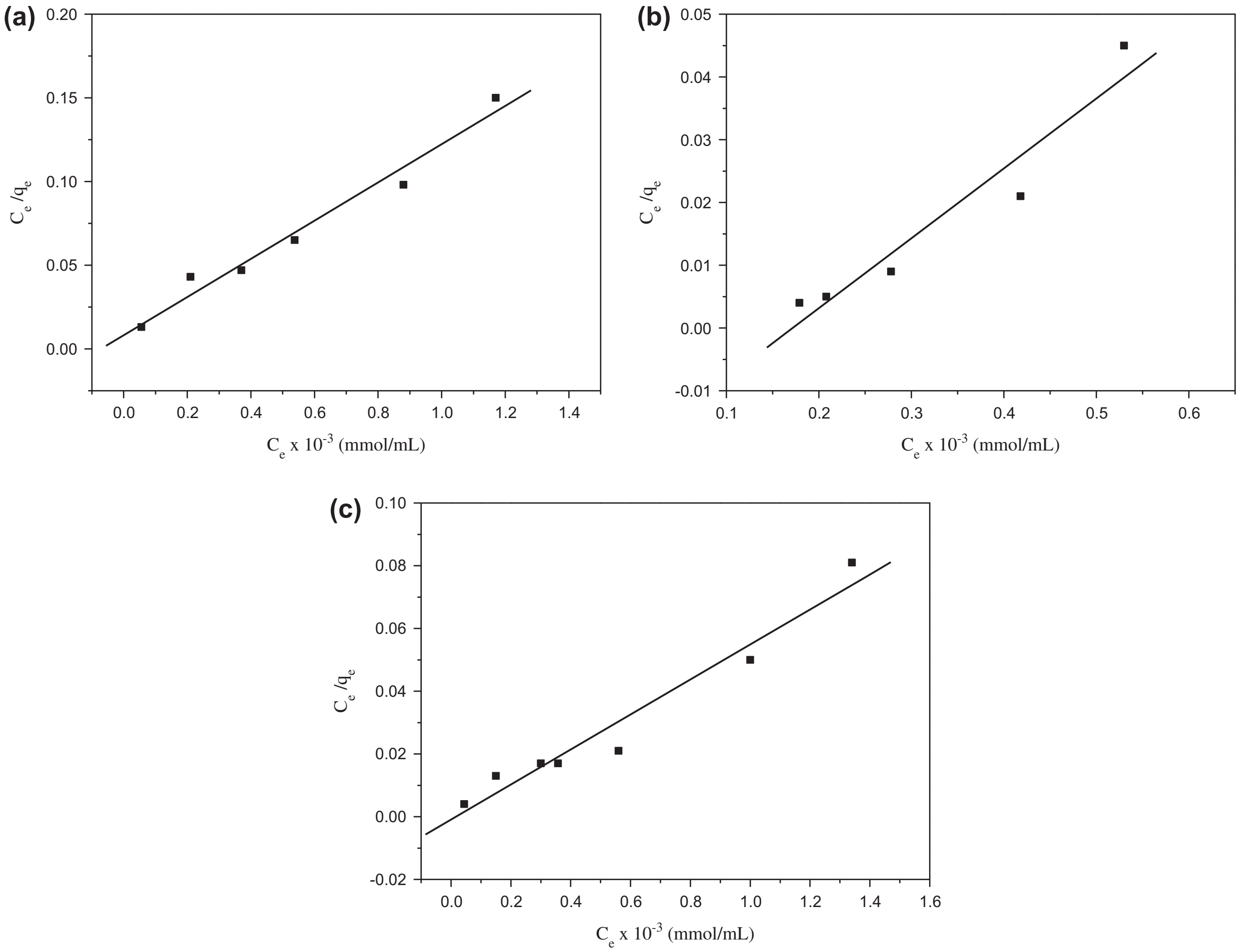


Fig. 10. Langmuir plot for the sorption of (a) Na on SCB, (b) Pb(II) and (c) Na(I) on BP at constant temperature.

(4.0 g) at pH 5.0 for 120 min at 25°C. Ten milliliter of the effluent solution taken at the end of the experiment (the residual concentrations of lead ions) were determined using atomic absorption spectrophotometry. Under the previous optimum conditions, the method validation was performed by repeating the same experiment five times. The accuracy and precision were calculated as the recovery percentage and relative standard deviation percentage (RSD%).

The method validation should be investigated in order to check the accuracy and precision of the new proposed removal method. The following equation was used for calculation of percentage of removal of Pb(II) ions:

$$\text{Percentage of removal} = (C_i - C_f/C_i) \times 100 \qquad (5)$$

where C_i is the initial concentration of Pb(II) and C_f is its concentration in filtrate. Good agreement was obtained between the added and recovered analyte contents using the experimental procedure. The percentage of recovery calculated for the standard additions was always higher than 95.0%, thus, confirming the accuracy of the procedure. RSD% values for the determination of the analytes in the spiked samples were in range of 0.544–1.532%, Table 3. Therefore, SCB and BP were suitable for extraction and removal of the lead ions. The precision of the method (RSD and RSD %) are acceptable according to the established references [2,39]. Moreover, the results were also compared statistically with the reference method. The *F*- and *t*-values did not exceed the theoretical ones (Table 3), indicating no significant difference [2,40].

Table 3
Recovery and precision of Pb(II) spiked natural water samples with SCB and BP using batch technique

Sample	% Recovery SCB	[a]RSD %	*F*-value	*t*-value	% Recovery BP	RSD %	*F*-value	*t*-value	[b]% Recovery in reference method [2,40]
Wastewater	103.2 ± 0.35	0.339	0.122	2.259	102.7 ± 0.45	0.438	0.202	1.163	102.0 ± 0.4
Drinking tap-water	97.89 ± 0.50	0.511	2.250	0.712	96.48 ± 0.53	0.549	2.341	0.302	97.2 ± 1.4
Mineral water	95.20 ± 1.15	1.208	1.322	–	97.50 ± 1.30	1.333	1.690	–	–
Groundwater	95.77 ± 1.00	1.044	1.000	0.583	96.2 ± 1.20	1.247	1.440	1.046	95.3 ± 1.5

$N = 5$.

Experimental conditions: 10.0 ppm of Pb(II) ions are spiked in: WW, DTW, MW, and GW samples, weight of phase 4.0 g and the sample volume 50 ml at pH 5.0.

[a]RSD% relative standard deviation percentage of the recovery, $F_{\text{critical}} = 6.39$, $t_{\text{critical}} = 2.306$, at the 95% confidence level.

[b]% Recovery by the reference method with ($N = 5$).

Table 4
Effect of reducing sodium ion concentrations using SCB and BP sorbents on weight and leaf area (growth parameters) of (a) zea maize and (b) wheat plants

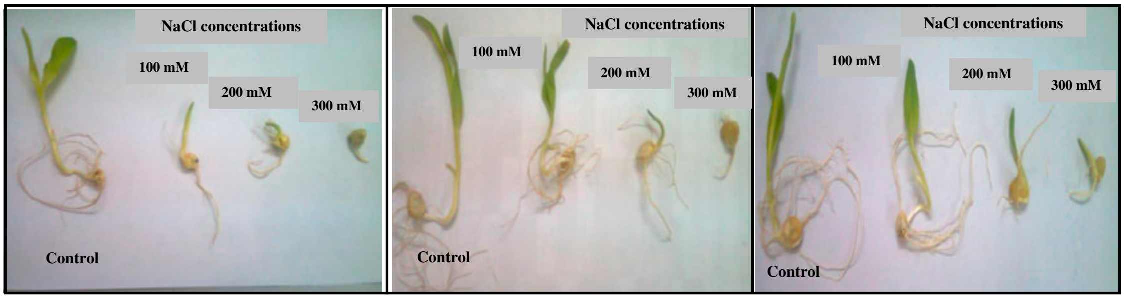
Na(I) concentrations (mM)	Percentage of weight of zea maize and wheat attributed to control sample [0.00 mM Na(I)]			Percentage of leaf area of zea maize and wheat attributed to control sample [0.00 mM Na(I)]		
	Reference[a]	BP	SCB	Reference[a]	BP	SCB
(a) Zea maize						
0.00	100.0	122.91	108.85	100.0	107.51	109.42
100.0	54.16	88.54	80.72	16.46	75.55	60.89
200.0	40.10	68.22	64.58	2.85	13.32	6.66
300.0	17.71	30.21	23.69	0.40	1.43	0.00
LSD (5%)	0.02			1.647		
(b)wheat plants						
0.00	100.0	71.25	126.25	100.00	135.09	125.15
100.0	93.35	83.75	132.50	125.15	104.68	69.00
200.0	28.75	54.15	48.35	0.40	6.43	28.65
300.0	4.40	0.00	6.02	0.06	0.00	3.60
LSD (5%)	0.002			0.347		

[a]Reference: percentage of weight of zea maize and wheat after irrigation with saline water (water contained different Na(I) concentrations) without treatment with sorbent.

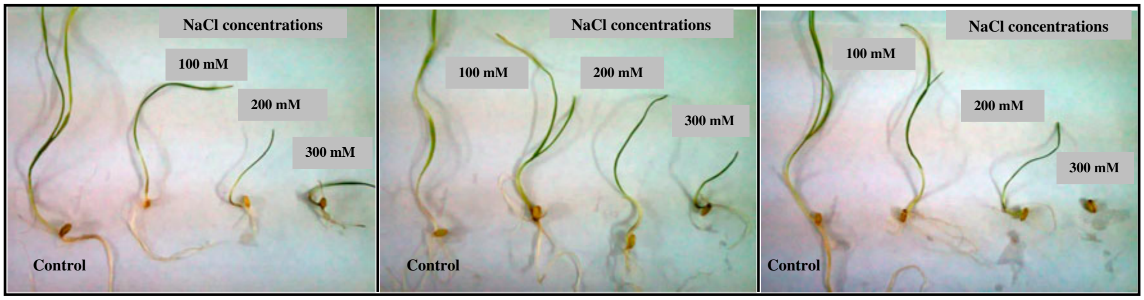
4.2. Reduce the sodium ion concentrations (salinity) from irrigation water for improvement the growth of plants

Prepare different concentrations of NaCl (0.00, 100, 200, and 300 mM) using DDW and justify the pH to the suitable value for growing zea maize and wheat cultivars (pH 7.0). 4.0 g each of SCB and BP are soaked in the previous concentrations of NaCl overnight at room temperature and then filtered. The filtrate is used for irrigation of zea maize and wheat plants. The improvement of the growth of the two plants can be traced by calculation of their weight and leaf area (growth parameters). The results were compared statistically using SPSS program with reference samples.

From the previous results of batch studies it was concluded that, SCB and BP adsorbents could be suitable for adsorption of sodium ions (percentage of extraction >95.0%) at the optimum pH 6.0 and 10.0, respectively. However, at these pH values, the plants are not well grown. So, it is necessary to compromise between the pH values suitable for reducing sodium ion concentrations in water and at the same time permit to well growth of the plants. As shown in Fig. 5, at pH 7.0 (which is suitable for growing plants), the



Reference (zea maize) with SCB with BP



Reference (wheat) with SCB with BP

Fig. 11. Effect of reducing the sodium ions concentrations in water on growth of zea maize and wheat plants using SCB and BP sorbents. Experiment conditions: 4.0 g of each SCB and BP are soaked in 100, 200, and 300 mM of NaCl overnight at room temperature and then filtered. The filtration was used for irrigation of zea maize and wheat cultivars. After 10 d, weight and leaf area of the two plants were calculated corresponding to control samples (0.00 mM of Na(I)).

percentage of extraction of Na(I) using SCB and BP is calculated to be 60.0 and 88.0%, respectively. These values are acceptable for reducing sodium ions concentrations in water for improvement of the growth of plants [41]. Therefore, the effects of increasing concentrations of Na(I) using SCB and BP adsorbents on the weight and leaf area (growth parameters) of zea maize and wheat plants were investigated at pH 7.0 as shown in Table 4(a) and (b) and Fig. 11. The data in Table 4(a) and (b) showed that the growth parameters of the two plants was decreased with increasing Na(I) concentrations in reference samples (without treatment of the two adsorbents). On the other hand, these parameters was improved after adsorption of Na(I) using SCB and BP as compared with reference samples.

5. Conclusion

SCB and BP as natural solid phase extractors have the following advantages: (a) benign lignocellulosic materials, inexpensive (sugar cane industry wastes) and rich in oxygen-containing functional groups; (b) pronounced capability for high extraction of Pb(II) and Na(I) ions with no need for chemical modification; (c) applicable for selective removal of Pb(II) from different natural water samples using batch technique; (d) successful reducing of the concentration of sodium ions from irrigation water based on positive parameters used for measuring zea maize and wheat production.

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References

[1] H. Arslanoglu, H.S. Altundogan, F. Tumen, Heavy metals binding properties of esterified lemon, J. Hazard. Mater. 164 (2009) 1406–1413.
[2] S. Khazaeli, N. Nezamabadi, M. Rabani, H.A. Panahi, A new functionalized resin and its application in flame atomic absorption spectrophotometric determination of trace amounts of heavy metal ions after solid phase extraction in water samples, Microchem. J. 106 (2013) 147–153.
[3] H.M. Al-bishri, T.M. Abdel-Fattah, M.E. Mahmoud, Immobilization of [Bmim$^+$ Tf$_2$N$^-$] hydrophobic ionic liquid on nano-silica-amine sorbent for implementation

in solid phase extraction and removal of lead, J. Ind. Eng. Chem. 18 (2012) 1252–1257.

[4] M. Danish, R. Hashim, M. Rafatullah, O. Sulaiman, A. Ahmad, A. Govind, Adsorption of Pb(II) ions from aqueous solutions by date bead carbon activated with $ZnCl_2$, Clean–Soil, Air, Water 39 (2011) 392–399.

[5] World Health Organization, Guidelines for Drinking Water, WHO, Geneva, 1993.

[6] K. Zhang, W.H. Cheung, M. Valix, Roles of physical and chemical properties of activated carbon in the adsorption of lead ions, Chemosphere 60 (2005) 1129–1140.

[7] C. Bélavári, E. Andrási, Z. Molnár, É. Bertalan, Determination of alkali metals in control and AD brain samples by different techniques, Microchem. J. 79 (2005) 367–373.

[8] M.C. Shannon, C.O. Qualset, Benefits and limitations in breeding salt-tolerant crops, California Agric. 38 (1984) 33–34.

[9] E.V. Maas, J.A. Poss, Salt sensitivity of wheat at different growth stages, Irrig. Sci. 10 (1989) 29–40.

[10] S. Khatun, T.J. Flowers, Effects of salinity on seed set in rice, Plant, Cell Environ. 18 (1995) 61–67.

[11] W.J. Katembe, I.A. Ungar, J.P. Mitchell, Effect of salinity on germination and seedling growth of two atriplex species (Chenopodiaceae), Ann. Bot. 82 (1998) 167–175.

[12] D.H. Kim, K.T. Aldridge, J.D. Brookes, G.G. Ganf, The effect of salinity on the germination of *Ruppia tuberosa* and *Ruppia megacarpa* and implications for the Coorong: A coastal lagoon of southern Australia, Aquat. Bot. 111 (2013) 81–88.

[13] A. Läuchli, E. Epstein, Plant responses to saline and sodic conditions, in: K.K. Tanji (Ed.). Agricultural Salinity Assessment and Management, ASCE Manuals and Reports on Engineering Practice, vol. 71, American Society of Civil Engineers (ASCE), New York, NY, 1990, pp. 113–137.

[14] M.E. Mahmoud, M.M. Osman, O.F. Hafez, A.H. Hegazi, E. Elmelegy, Removal and preconcentration of lead (II) and other heavy metals from water by alumina adsorbents developed by surface-adsorbed-dithizone, Desalination 251 (2010) 123–130.

[15] E.M. Soliman, S.A. Ahmed, Solid-phase extractors based on 8-aminoquinoline and 2-aminopyridine covalently bonded to silica gel for the selective separation and determination of calcium in natural water and pharmaceutical samples, Anal. Sci. 26 (2010) 473–478.

[16] E.M. Soliman, S.A. Ahmed, A.A. Fadl, Removal of calcium ions from aqueous solutions by sugar cane bagasse modified with carboxylic acids using microwave-assisted solvent-free synthesis, Desalination 278 (2011) 18–25.

[17] E.M. Soliman, S.A. Ahmed, A.A. Fadl, Reactivity of sugar cane bagasse as a natural solid phase extractor for selective removal of Fe(III) and heavy-metal ions from natural water samples, Arab. J. Chem. 4 (2011) 63–70.

[18] A.M.A. Nada, A.A. El-Gendy, S.H. Mohamed, Banana leaves as adsorbents for removal of metal ions from waste water, Carbohydr. Polym. 82 (2010) 1025–1030.

[19] S.A. Ahmed, Batch and fixed-bed column techniques for removal of Cu(II) and Fe(III) using carbohydrate natural polymer modified complexing agents, Carbohydr. Polym. 83 (2011) 1470–1478.

[20] R. Kumar, M.A. Barakat, E.M. Soliman, Removal of tannic acid from aqueous solution by magnetic carbohydrate natural polymer, J. Ind. Eng. Chem. 20 (2014) 2992–2997.

[21] H.S. Altundogan, N.E. Arslan, F. Tumen, Copper removal from aqueous solutions by sugar beet pulp treated by NaOH and citric acid, J. Hazard. Mater. 149 (2007) 432–439.

[22] X. Luo, Z. Deng, X. Lin, C. Zhang, Fixed-bed column study for Cu^{2+} removal from solution using expanding rice husk, J. Hazard. Mater. 187 (2011) 182–189.

[23] M. Rao, A.V. Parwate, A.G. Bhole, Removal of Cr^{6+} and Ni^{2+} from aqueous solution using bagasse and fly ash, Waste Manage. 22 (2002) 821–830.

[24] W.S. Wan Ngah, M.A.K.M. Hanafiah, Removal of heavy metal ions from wastewater by chemically modified plant wastes as adsorbents: A review, Bioresour. Technol. 99 (2008) 3935–3948.

[25] U. Garg, M.P. Kaur, G.K. Jawa, D. Sud, V.K. Garg, Removal of cadmium (II) from aqueous solutions by adsorption on agricultural waste biomass, J. Hazard. Mater. 154 (2008) 1149–1157.

[26] E. Pehlivan, S. Cetin, B.H. Yanik, Equilibrium studies for the sorption of zinc and copper from aqueous solutions using sugar beet pulp and fly ash, J. Hazard. Mater. 135 (2006) 193–199.

[27] J.L.G. Torresdey, G. de la Rose, J.R.P. Videa, Use of phytofiltration technologies in the removal of heavy metals: A review, Pure Appl. Chem. 76 (2004) 801–813.

[28] R. Pearson, Hard and soft acids and bases, J. Am. Chem. Soc. 85 (1963) 3533–3539.

[29] F. Li, H. Jiang, S. Zhang, An ion-imprinted silica-supported organic–inorganic hybrid sorbent prepared by a surface imprinting technique combined with a polysaccharide incorporated sol–gel process for selective separation of cadmium(II) from aqueous solution, Talanta 71 (2007) 1487–1493.

[30] V. Yilmaz, Z. Arslan, O. Hazer, H. Yilmaz, Selective solid phase extraction of copper using a new Cu(II)-imprinted polymer and determination by inductively coupled plasma optical emission spectroscopy (ICP-OES), Microchem. J. 114 (2014) 65–72.

[31] S. Rengaraj, K.H. Yeon, S.H. Moon, Removal of chromium from water and wastewater by ion exchange resins, J. Hazard. Mater. 87 (2001) 273–287.

[32] Y.S. Ho, G. McKay, Pseudo-second order model for sorption processes, Process Biochem. 34 (1999) 451–465.

[33] L. Bai, H. Hu, W. Fu, J. Wan, X. Cheng, L. Zhuge, L. Xiong, Q. Chen, Synthesis of a novel silica-supported dithiocarbamate adsorbent and its properties for the removal of heavy metal ions, J. Hazard. Mater. 195 (2011) 261–275.

[34] H. Freundlich, Ueber die adsorption in loesungen (About the adsorption in solutions), Z. Phys. Chem. 57 (1907) 385–470.

[35] A. Delle Site, Factors Affecting Sorption of Organic Compounds in Natural Sorbent/Water Systems and Sorption Coefficients for Selected Pollutants. A Review, J. Phys. Chem. Ref. Data 30 (2001) 187–439.

[36] G. Limousin, J.P. Gaudet, L. Charlet, S. Szenknect, Sorption isotherms: A review on physical bases, modeling and measurement, Appl. Geochem. 22 (2007) 249–255.

[37] I. Langmuir, The adsorption of gases on plane surfaces of glass, MICA and platinum, J. Am. Chem. Soc. 40 (1918) 1361–1403.

[38] M.M. Rao, D.H.K.K. Reddy, P. Venkateswarlu, Removal of mercury from aqueous solutions using activated carbon prepared from agricultural by-product/waste, J. Environ. Manage. 90 (2009) 634–643.

[39] R.L. Mark, Validation and Qualification in Analytical Laboratories, Interpharm Press, IL, 1999.

[40] M. Ghaedi, M. Montazerozohori, M. Soylak, Solid phase extraction method for selective determination of Pb(II) in water samples using 4-(4-methoxybenzylidenimine) thiophenole, J. Hazard. Mater. 142 (2007) 368–373.

[41] M.A.K. Shaddad, H.M. Abd El-Samad, D. Moustafa, Role of gibberellic acid (GA3) in improving salt stress tolerance of two wheat cultivars, Int. J Plant Physiol. Biochem. 5 (2013) 50–57.