Journal of
Environmental Science
and Technology

CrossMark
← click for updates

Removal of Mn(II) from Ground Water by Solid Wastes of Sugar Industry

Salwa A. Ahmed, Ahmed M. El-Roudi and Alaa A.A. Salem
Department of Chemistry, Faculty of Science, Minia University, Minia, Egypt

Corresponding Author: Salwa A. Ahmed, Department of Chemistry, Faculty of Science, Minia University, Minia, Egypt

ABSTRACT

The potential to remove or reduce the risk of Mn(II) from ground water through adsorption using Sugar Cane Bagasse (SCB) and Beet Pulp (BP) as a low cost natural wastes was investigated. The SCB and BP were characterized using Fourier transform infrared spectra (FT-IR) and Scanning Electron Microscope (SEM). The adsorption was taken in batch experiments under different parameters such as pH (2.0-10.0), weight of phase (0.25-2.5 g), contact times (10-180 min), initial concentration (2.0-10.0 ppm). Under the optimum conditions, the percentage removals of Mn(II) using SCB and BP were 62.5 and 86.36%, respectively. The rate limiting step of the adsorption was studied using different kinetic models such as pseudo-first-order, pseudo-second-order adsorption equation, elovich equation and the intraparticle diffusion model. Kinetics data was best fitted with the pseudo-second-order type. This method has been successfully applied for reduce the risk of Mn(II) from ground water samples.

Key words: Adsorption, Mn(II), sugarcane bagasse, beet pulp, kinetic models, ground water samples

INTRODUCTION

Manganese is one of the chemical risks in ground water in Egypt. Ground water is a major source of human activities especially in village or small cities as well as that it's far from surface water. Contamination of ground water can occur due to dissolving of minerals or rocks in earth crust, agricultural leaching or leaching from industrial pollutants such as electroplating, metal finishing, metallurgy, chemical manufacturing, mining and battery manufacturing. When dissolved in water, manganese reaches the surface of ground water and exposes to air, it becomes insoluble and makes water brown or red (Esfandiar *et al.*, 2014). Manganese with low level concentration cause some problems such formation of oxide deposits in pipelines, discoloration of water and laundry as well as impart an unpleasant metallic taste (Emmanuel and Rao, 2009; Heal *et al.*, 1995). In addition, the problems of manganese with high level concentration include health concerns, aesthetic and economic problems (Jusoh *et al.*, 2005; Tekerlekopoulou and Vayenas, 2007). It is dangerous` for brain tissue and affects the central nervous system. Also, the presence of high levels of manganese creates neurological disorders such as Parkinson's disease (Esfandiar *et al.*, 2014). In Egypt, the maximum recommended level of Mn(II) in drinking water is 0.4 mg L^{-1} and according to U.S. Environmental Protection Agency, the maximum limit for manganese in drinking water is 0.05 mg L^{-1}.

Because of that problems occur due to presence of manganese in water, as well as of their toxicity, non-biodegradability and persistent nature, their removal becomes an absolute necessary.

Conventional methods were used for removing manganese ions include chemical precipitation, chemical oxidation and reduction, ion exchange, electrochemical treatment. These methods are expensive and generation of toxic sludge.

Chemical oxidation followed by physical filtration has been used extensively and remains one of the most common approaches to manganese removal (Kohl and Medlar, 2006). Several oxidizing agents can be used for the chemical oxidation of manganese including oxygen, ozone, potassium permanganate, chlorine dioxide and hypochlorous acid . However, the risk of this technique is in the formation of harmful secondary byproducts. So, environmentally friendly processes, therefore, need to be developed to clean-up the environment without creating harmful waste by products as Solid Phase Extraction (SPE) techniques (Soliman and Ahmed, 2009). In fact, SPE has become known as an effective tool for separation and advancement of different inorganic and organic analytes. It has a few focal points over different systems including reusability and stability of the solid phase, easiness of separation and enrichment under dynamic conditions, no requirement for organic solvents and insignificant expenses because of low utilization of reagents. Recently, numerous higher plants biomass materials utilized as solid phase extractors and they have good adsorption properties such as sugarcane bagasse (Esfandiar *et al.*, 2014), maize husk (Adeogun *et al.*, 2013) and rice husk ash (Zhang *et al.,* 2014).

Sugarcane bagasse and beet pulp are the kind of byproducts obtained from Abou-Korkas Sugar Factory, El-Minia, Egypt. They contain cellulose, hemi-cellulose and lignin. This variety of chemical compositions and consequently functional groups make SCB and BP showed different efficiencies for removal of heavy metal ions such as for SCB Fe(III) (Soliman *et al.*, 2011a), Cd(II) (Garg *et al.*, 2008), Cr(IV) and Ni(II) (Rao *et al.*, 2002) and for BP Ni(II) and Cu(II) (Reddad *et al.*, 2002). According to best of our knowledge no paper has been done for removal of Mn(II) from ground water using BP as low cost adsorbent. So the aim of the present study is to investigate the ability of using both SCB and BP for removal of Mn(II) from aqueous solutions under different parameters using batch technique as well as applying it to remove Mn(II) from real water samples.

MATERIALS AND METHODS

Chemical and reagents: All chemicals and reagents used were of analytical grade and were purchased from E. Merck, India/Germany: hydrochloric acid, nitric acid, phosphoric acid, sodium hydroxide, standard solution of Mn(II) (1000 mg L^{-1}), hydrogen peroxide 30%, ammonium persulphate, mercury sulfate and silver nitrate.

Special reagent used for determination of Mn(II) ions prepared as: dissolve 75.0 g mercuric sulphate ($HgSO_4$) in 400 mL concentrated nitric acid (HNO_3) and 200 mL distilled water. Add 200 mL 85% phosphoric acid (H_3PO_4) and 35 mg silver nitrate ($AgNO_3$) to the above solution. Dilute the solution to 1 L.

The test solutions were prepared by diluting a known volume of the standard Mn(II) with double distilled water to the required initial concentration (0.5-10 mg L^{-1}).

About 0.1 N HCl and 0.1 N NaOH solutions are used for pH adjustment. Sugar Cane Bagasse (SCB) as well as sugar Beet Pulp (BP) were obtained from Abou-Korkas Sugar Factory, El-Minia, Egypt. Water samples including: Drinking Surface Water (DSW) and Drinking Ground Water (DGW) were collected from El-Minia governorate, Egypt. Doubly Distilled Water (DDW) was obtained from our lab.

Instrumentation: Infrared spectra of adsorbent before and after Mn(II) adsorption were obtained using FT-IR Model 410 JASCO (Japan) in the range 4000-400 cm^{-1}. Scanning Electron Microscope

(SEM) analysis obtained using JSM-5400 LV JEOL (Japan). GENWAY pH-meter Model 3510 calibrated against three standard buffer solutions at pH 4.0, 7.00 and 10.00 was used for all pH measurements. Flocculator lovibond (Germany) instrument which used for mix the material with a solution at 150 rpm for varied times. Biochrom Libra S12 spectrophotometer (England) which used for determined Mn(II) as the pink colored was formed when ammonium persulphate was added into Mn(II) after boiling and concentration was determined spectrophotometrically at 525 nm (Rand *et al.*, 1976).

Treatment of the adsorbent: Sugar cane bagasse as well as beet pulp were first washed thoroughly with distilled water to remove the dust particles, then soaked overnight in 0.1 N NaOH solutions and again washed well with DDW. Then these were soaked in 0.1 N CH_3COOH for a period of 2-3 h to remove the traces of NaOH. These were thoroughly washed again with DDW until the wash water became colorless and pH became neutral, well dried (Rao *et al.*, 2002), powdered and sieved before use. The average particle size was below 0.75 mm.

Equilibrium studies: The percentage removal of Mn(II) ions toward SCB and BP were determined in triplicate under static conditions by the batch equilibrium technique. The 0.5 g of the adsorbent was added to a mixture of 500 mL of 2 mg L^{-1} of Mn(II) ion and a buffer solution of pH 1.0-10.0. This mixture was mechanically stirring for 10 min at room temperature to attain equilibrium. The adsorbent was separated by filtration, washed with DDW and the unretained Mn(II) in the filtrate was determined by Biochrom Libra S12 spectrophotometer. For pH adjustment, solutions of 0.1 M HCl and 0.1 M NaOH were used. The equation of percentage of removal could be obtained as follows:

$$Removal\ (\%) = \frac{C_\circ - C_e}{C_\circ} \times 100$$

and the amount of metal adsorbed (Q, mg g^{-1}) was calculated as the following equation:

$$Q = (C_\circ - C_e)\ \frac{V}{W}$$

where, $C_\circ$ and C_e are equal to the initial concentration and final concentration of Mn(II) in milligram per liter, respectively, V is the volume of the solution in liter and W is the mass of the adsorbent in gram. Moreover, the effect of contact time on Mn(II) uptake was determined under the same batch conditions but at different contact times (10, 30, 45, 60, 90,120,150 and 180 min) and at the pH 6.0. The effects of Mn(II) concentration (2.0-10.0 mg L^{-1}) and weight of adsorbent (0.25-2.5 g) on its percentage removal by the adsorbent were also systematically investigated (Ahmed, 2011).

RESULTS AND DISCUSSION
Characterization of adsorbents
FT-IR spectroscopy: Functional groups in SCB as well as BP powder were determined using FT-IR spectroscopy (Fig.1a-b and 2a-b). The SCB and BP are cellulosic materials mainly contains cellulose, hemi-cellulose and lignin. The FT-IR spectra of SCB and BP before and after adsorption of Mn(II) were performed to determine the vibration frequency changes in their functional groups within the range of 4000-400 cm^{-1}. The SCB powder spectrum (Fig. 1a, b) showed numbers of
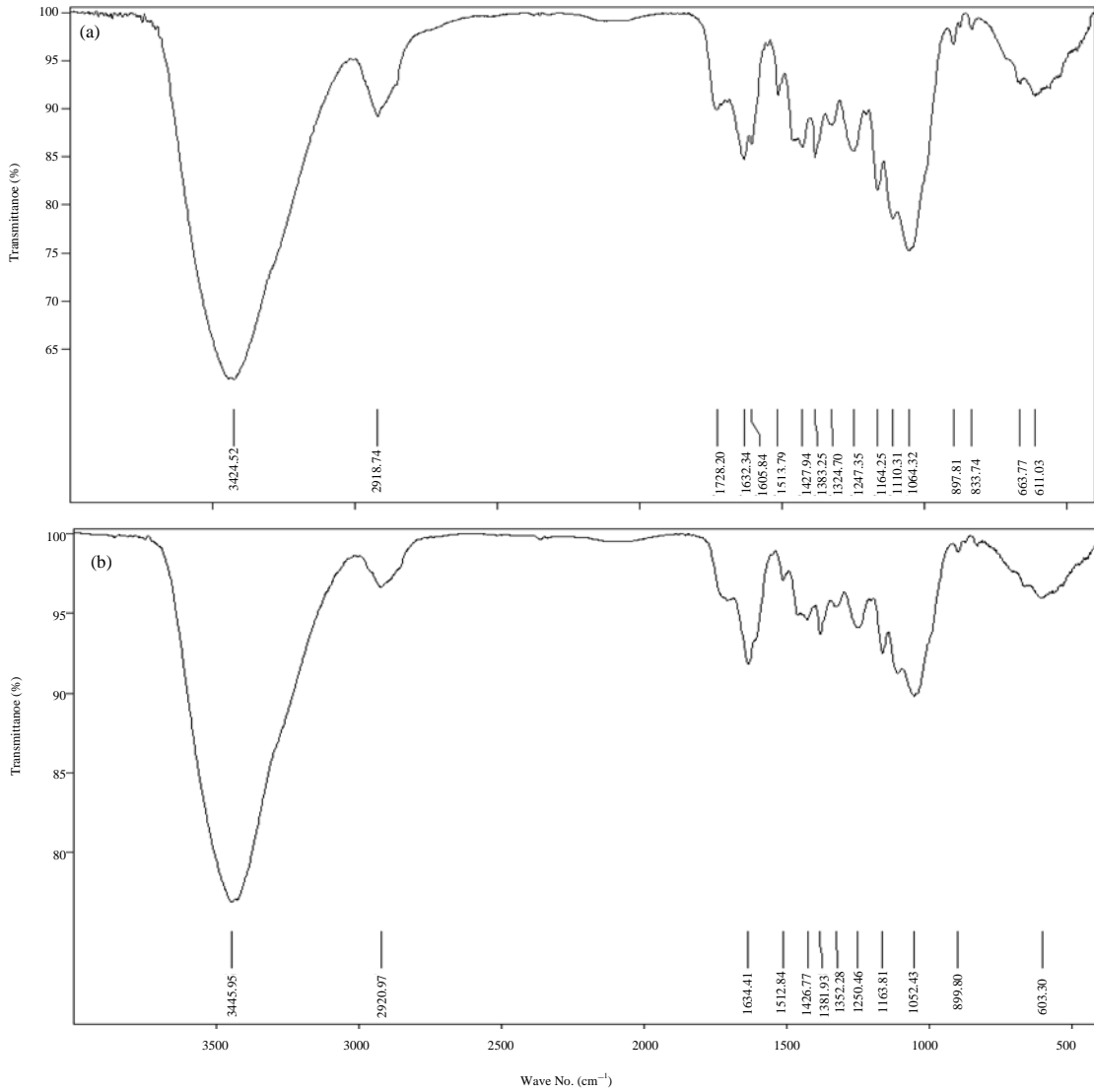
Fig. 1(a-b): FT-IR spectra of (a) Sugar cane bagasse and (b) Sugar cane bagasse-Mn(II) phases

major intense bands, around 3424.52, 2918.74, 1728.20, 1632.34, 1513.79, 1427.94, 1383.25, 1324.70, 1247.35, 1054.32 and 897.81 cm^{-1} are associated with the native bagasse (Karnitz *et al.*, 2007). The broad band around 3424.52 cm^{-1} is attributed to the existence of free and intermolecular bonded hydroxyl groups. The peaks assigned at 2952.72 cm^{-1} represented aliphatic C–H stretching vibrations. The presence of the small peak at 1728.20 cm^{-1} is attributed to carbonyl stretching functional group in ester and carboxyl group in hemicelluloses (Pehlivan *et al.*, 2008). Two overlapped bands at around 1641.25 and 1427.94 cm^{-1} in FT-IR spectra were assigned to the asymmetric and symmetric stretch modes of the –COO group. The small bands at 1605.84, 1513.79, 1427.94 and 1324.70 cm^{-1} correspond to the aromatic skeletal vibrations, ring connecting with C–O stretching in lignin (Sun *et al.*, 2003). The bands at 1383.25 and 1247.35 cm^{-1} are
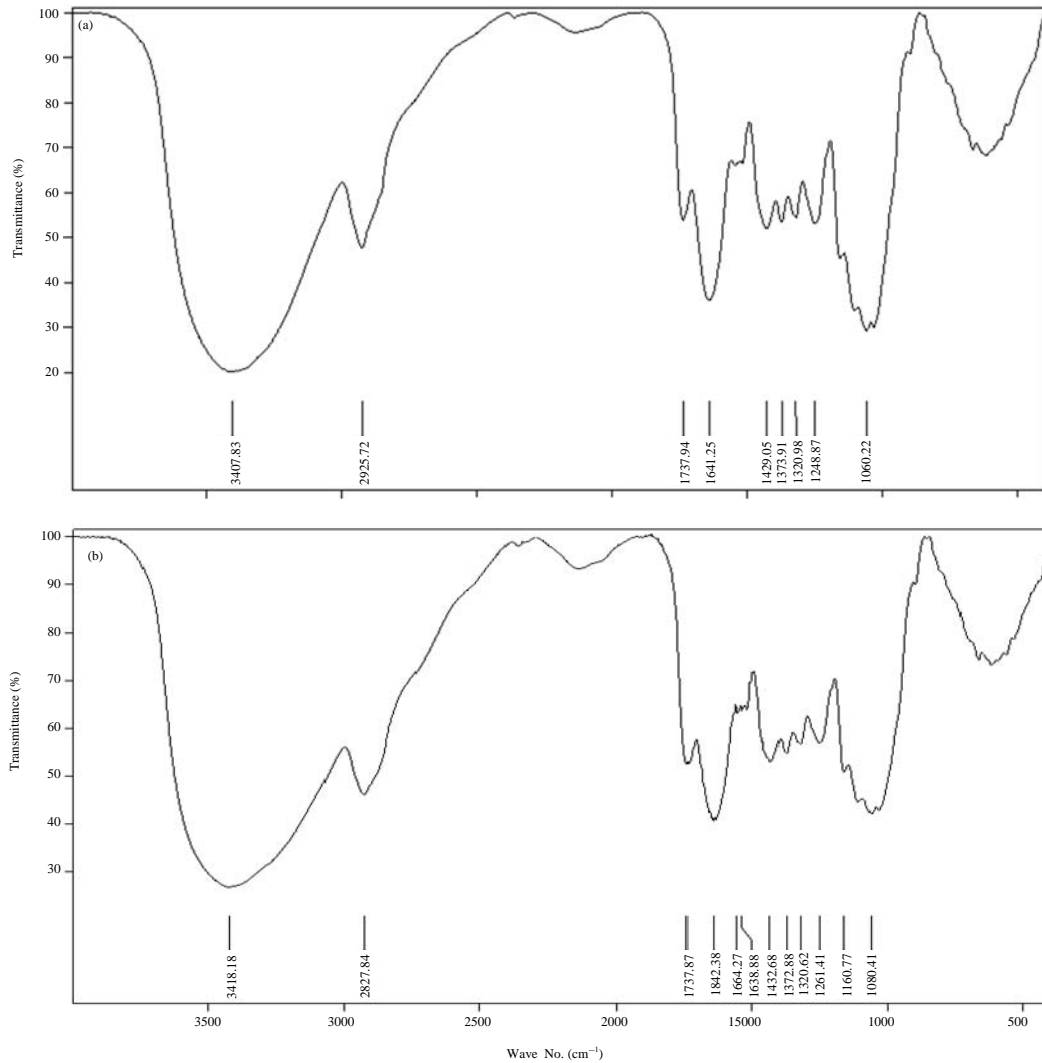
Fig. 2(a-b): FT-IR spectra of (a) Beet pulp and (b) Beet pulp-Mn(II) phases

attributed to absorption by C–H and C–O stretching in acetyl group in hemicelluloses, respectively. The strong band at 1054.32 cm^{-1} due to C–O stretching group in cellulose. The small sharp band at 897.81 cm^{-1} is originated from the glucosidic linkages between the sugar units in hemicelluloses and cellulose (Soliman *et al.*, 2011b).

Generally, the binding of metal ions to adsorbents may be proceed via complexation with functional groups, ionic exchange, surface precipitations and chemical reaction with surface sites. Regarding FT-IR for SCB after Mn(II) 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 is judging from shifts in their position, shape or band intensity from 1054.32, 1728.20, 1427.94 and 3424.52 cm^{-1} to 1053.97, 1703.58, 1461.54 and 3442.54 cm^{-1} of ν(–O–C), ν(–COOH) and ν(–OH) for SCB before and after Mn(II) adsorption, respectively. The results indicate the participation of these groups via oxygen for Mn(II) binding to SCB in agreement with Person principal for hard-soft acids and bases (Pearson, 1963).

Due to the similarity of SCB with BP in the composition, BP powder spectrum (Fig. 2a, b) showed number of major intense bands similar to that in SCB around 3407.83, 2952.72, 1737.94, 1641.25, 1429.05, 1320.98, 1248.87 and 1060.22 cm^{-1}. The broad band around 3407.83 cm^{-1} is attributed to the existence of free and intermolecular bonded hydroxyl groups and the band around 2952.72 cm^{-1} represented aliphatic C–H stretching vibrations (Kamnev *et al.*, 1998). The presence of the peak at 1737.94 cm^{-1} which is attributed to carbonyl functional group in ketones, aldehydes and carboxylic acids. Two overlapped bands at around 1641.25 and 1429.05 cm^{-1} in FT-IR spectra were assigned to the asymmetric and symmetric stretch modes of the COO– group. The strong band at 1060.22 cm^{-1} due to C-O group (Sun and Hughes, 1998). Regarding FT-IR for BP after Mn(II) 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 is judging from shifts in their position, shape or band intensity from 1060.22, 1429.05, 1641.25, 1737.94 and 3407.83 cm^{-1} to 1060.41, 1432.56, 1642.38, 1737.97 and 3419.19 cm^{-1} of v(–O–C), v(–COOH) and v(–OH) for BP before and after Mn(II) adsorption, respectively.

Scanning electron microscopy: The surface morphology of SCB and BP before and after of Mn(II) adsorption was analyzed using scanning electron microscopy (Fig. 3a-d). The microphotograph before Mn(II) adsorption revealed the presence of pores and rough surface with
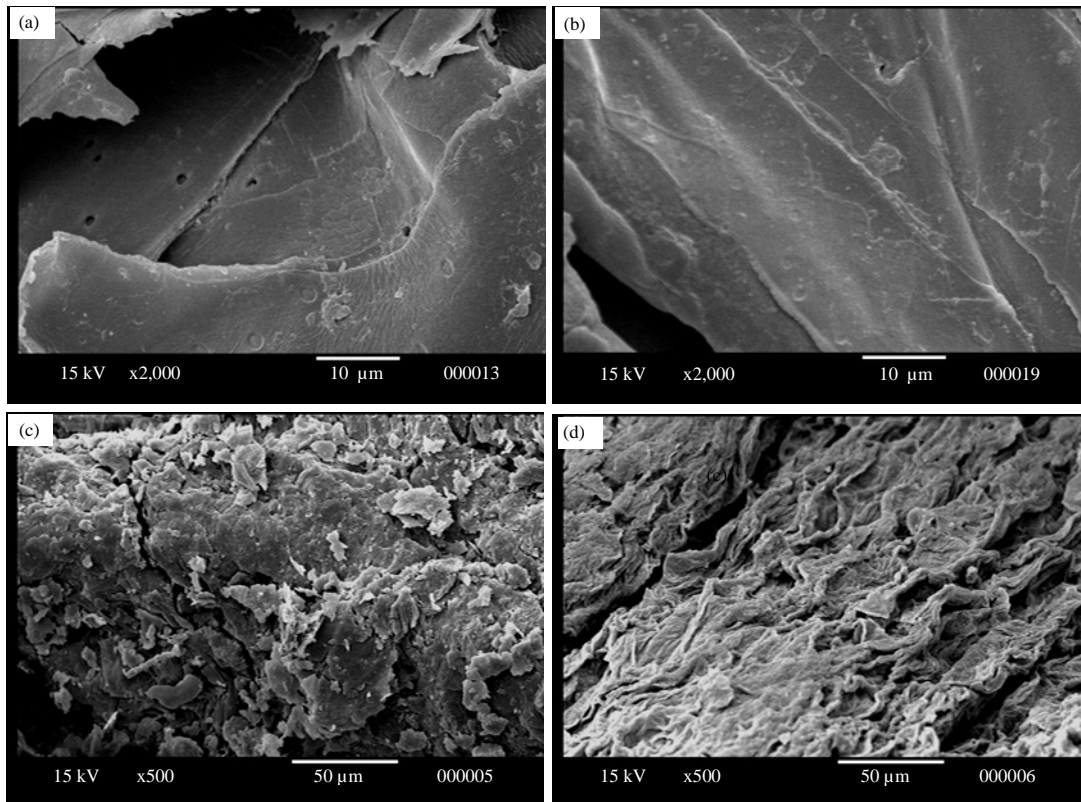

Fig. 3(a-d): Scanning electron microscopic images of (a) SCB, (b) SCB-Mn(II) phase, (c) BP and (d) BP-Mn(II) phase

narrow thickness between fibers which is an important factor for facilitating the mass transfer rate of metal ions toward the surface and consequently improving its adsorption capacity (Yilmaz *et al.*, 2014). After Mn(II) adsorption the micrograph revealed the presence of smooth surface with narrow thickness. These changes of the structure of adsorbent confirm the presence of Mn(II) on their surface.

Effect of initial pH: The pH value of the heavy metals plays an important role in the adsorption process on not only the site dissociation of the adsorbent surface but also on the solution chemistry of the metals, which include; hydrolysis, complexation by organic and inorganic ligands, redox reactions, precipitation, the speciation and the adsorption availability of the heavy metals (Rengaraj *et al.*, 2001). This is clearly indicated as shown in Fig. 4 for the uptake of Mn(II) ions as a function of pH (1.0-10.0). Therefore, at low pH values (pH<3.0) SCB and BP showed very low tendency for uptake of Mn(II) due to protonation of its functional groups or competition of H^+ with metal ion for binding sites (Adeogun *et al.*, 2013). These uptake values increased with increasing pH from 3.0-6.0. The binding capacities reached their maximum percentage removal around pH 6.0. At pH<6.0 Mn(II) was precipitated due to presence of OH^- forming manganese hydroxide precipitate. Thus, the maximum adsorption was obtained at pH 6.0 for SCB and BP (Mohan and Singh, 2002; Khalilnezhad *et al.*, 2014).

Effect of adsorbent dose: The dose of the adsorbent was varied from 0.25-2.0 g keeping all the other experimental variables constant (Fig. 5). For SCB it was found that on increasing the adsorbent weight until 1.5 g, percentage removal of Mn(II) gradually increases from 37-52.5% and for BP, on increasing the from 0.5-1.0 g the percentage removal of Mn(II) gradually increases from 65.25-83.05%.

This due to an increase in adsorbent dose generally increases the adsorbent surface area as well as increase binding sites. The Mn(II) percentage removal decrease with increase in adsorbent dose after 1.5 and 1.0 g for SCB and BP, respectively. This phenomenon was attributed to at high adsorbent dosages Mn(II) is insufficient to cover all the exchangeable sites on the adsorbent, usually resulting in low metal uptake. In addition, the interference between binding sites due to increased adsorbent dosages cannot be over ruled, as this may result in a low specific uptake (Vijayaraghavan *et al.*, 2009).
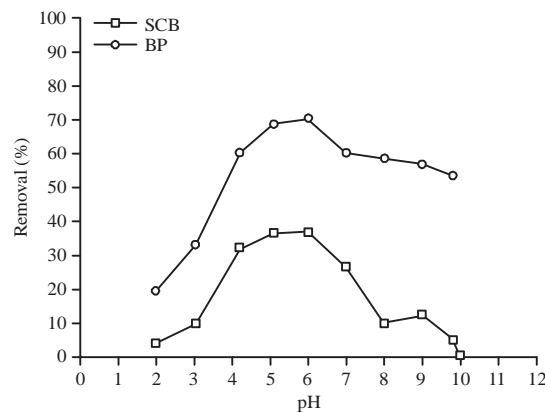

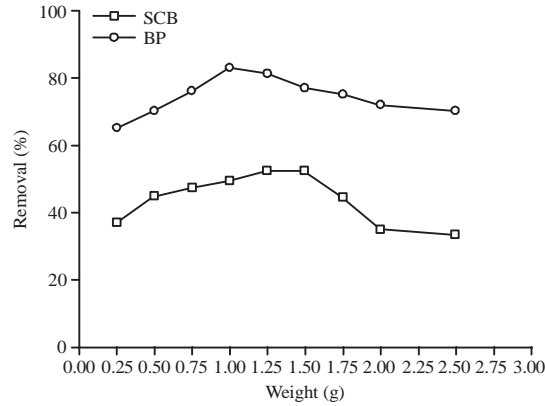Fig. 4: Percentage removal of Mn(II) as a function of pH using SCB and BP

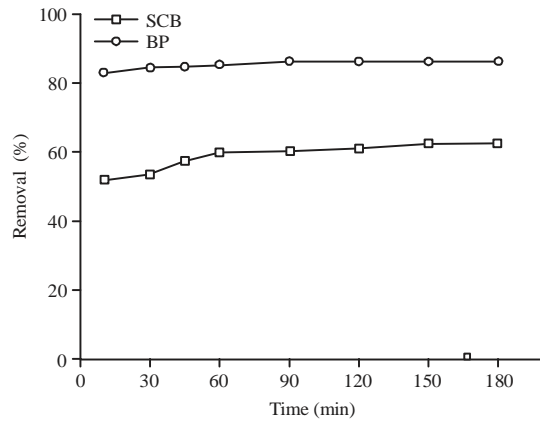Fig. 5: Effect of SCB and BP weight on percentage removal of Mn(II)

Fig. 6: Percentage removal of Mn(II) as a function of time using SCB and BP

Influence of equilibrium time: Equilibrium time is an important factor in the process of evaluation of the adsorbent. The batch experiments were carried out at different contact times (10, 30, 45, 60, 90, 120, 150 and 180 min) using Flocculator instrument with 1.5 g for SCB and 1.0 g for BP of adsorbent dose, Mn(II) concentration equal 2.0 mg L^{-1} at a pH of 6.0 and 500 mL contact solution. The obtained results in Fig. 6 showed that the equilibrium is reached after 150 min and the percentage removal increased from 52.5-62.5% for SCB. As well as for BP the equilibrium was reached after 90 min and the percentage removal increased from 83.05-86.36%. In the beginning, the ions adsorbed, occupied the active sites on the phases. As the contact time increased, the active sites on the adsorbent were filled.

Influence of Mn(II) concentration: The adsorption of metal ion on the adsorbent is heavily dependent on the initial concentration of the metal ion. The effect of Mn(II) concentration on its percentage removal was studied at concentrations of 0.5-10 mg L^{-1} at fixed adsorbent dose of 1.5 and 1.0 g for SCB and BP, respectively, pH 6.0 and contact time 150, 90 min for SCB and BP, respectively as shown in Fig. 7. The results indicated that the percentage removal of Mn(II) decreased with increased the initial concentration of Mn(II) 76-37% and 90.91-66.627% for SCB and BP, respectively. This indicates that the percentage removal is highly dependent on the initial
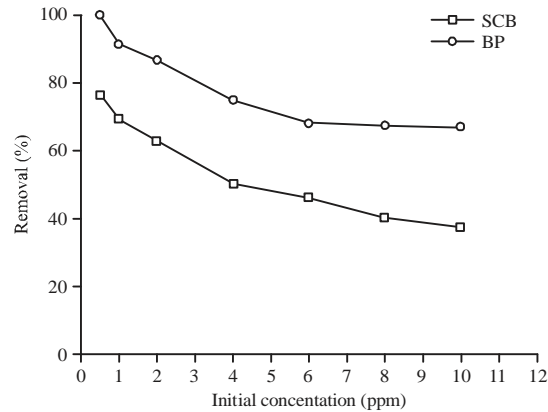
Fig. 7: Percentage removal of Mn(II) as a function of initial concentration Mn(II) using SCB and BP

concentration of Mn(II) in solution. A higher initial concentration provides an important driving force to overcome all mass transfer resistances of the pollutant between the aqueous and solid phases, thus increases the uptake. Uptake of the Mn(II) also increased with increasing the initial metal concentration tending to saturation at higher metal concentrations.

Adsorption kinetic models: The equilibrium time experimental results can be used to study the rate limiting step in the adsorption process. The adsorption process may be controlled either by one or more steps like film or external diffusion, pore diffusion, surface diffusion and adsorption on the pore surface or a combination of more than one step. In batch adsorption, the diffusive mass transfer can be related by an apparent diffusion coefficient, which will fit the experimental adsorption data.

The adsorption kinetic for binding of Mn(II) on to SCB and BP were determined by the batch technique at pH 6.0, solutions of Mn(II) in the concentration is 2 mg L^{-1}, time stirred in the range 10-180 min for SCB and 10-120 min for BP with a constant dose 1.5 and 1.0 g of SCB and BP, respectively. Several adsorption kinetic models have been established to understand the adsorption kinetics and rate-limiting step. These include pseudo-first-order, pseudo-second-order adsorption equation, elovich equation and the intraparticle diffusion model.

Pseudo-first-order model: Pseudo-first-order assumes that the adsorption of the adsorbate is directly proportional to the amount of available active sites on the adsorbent surface (Lagergren, 1898; Ho and McKay, 2002). It is usually described as:

$$\text{Log } (q_e - q_t) = \log q_e - (k_1/2.303) \, t \tag{1}$$

where, k_1 ($\min^{-1}$) is the rate constant of the pseudo-first-order adsorption, q_t (mg g^{-1}) denotes the amount of adsorption at time t (min) and q_e (mg g^{-1}) is the amount of adsorption at equilibrium. The plot values of log ($q_e - q_t$) vs. t should give a linear relationship which k_1 can be determined from the slope as show in Table 1.

Pseudo-second-order model: Pseudo-second-order adsorption (Eq. 2) assumes that the rate limiting step may be chemical adsorption involving valence forces through sharing or exchange of electrons between the adsorbent and adsorbate (Malik, 2004). This equation can be written as:

Table 1: kinetic parameters for Mn(II) adsorption

Kinetic model	Sugarcane bagasse	Beet pulp
Pseudo-first-order		
q_e (mg g^{-1})	0.122	0.96
K_1(min^{-1})	0.0299	0.119
r^2	0.863	0.703
Pseudo-second-order		
q_e (mg g^{-1})	0.423	0.869
K_1(min^{-1})	0.709	0.704
r^2	0.999	0.999
Elovich model		
α (mg g^{-1} min^{-1})	2582.724	7.4×10^{22}
β (g mg^{-1})	39.841	71.531
r^2	0.9495	0.963
Intraparticle diffusion model		
k_{id}(mg g^{-1} min$^{-0.5}$)	0.344	0.663
r^2	0.957	0.990

$$t/q_t =1/k_2 \, q_e{}^2 +t/q_e \tag{2}$$

where, k_2 (g mg^{-1} min^{-1}) is the rate constant of adsorption, q_e (mg g^{-1}) is the amount of Mn(II) adsorbed at equilibrium and q_t(mg g^{-1}) the amount of Mn(II) on the surface of the adsorbent at any time t (min). k_2 and q_e can be obtained from the intercept and slope of plot of t/qt vs. t (Fig. 8a-b and Table 1).

Elovich model: Elovich model (Chien and Clayton, 1980) equation is generally expressed as Eq. 3:

$$dq_t /dt = \alpha \exp (-\beta \, q_t) \tag{3}$$

Equation can be simplified by considering $\alpha\beta \gg t$ and by applying the boundary conditions: t = 0 at t = 0 and $q_t = q_t$ at t = t, Eq. 4 become:

$$q_t =1/\beta \ln(\alpha\beta) +1/\beta \ln(t) \tag{4}$$

which, α is the initial adsorption rate (mg g^{-1} min^{-1}) and β is the adsorption constant (g mg^{-1}) during any one experiment which related to the extent of surface coverage and activation energy for chemisorption. We drown the values of q_t vs. ln(t). The plot of this should give a linear relationship with a slope of (1/β) and an intercept of (1/β) ln (α β) as shown in Table 1.

Intraparticle diffusion model: The intraparticle diffusion model often the rate controlling step, is the possible method of movement of the ions from solution into the adsorbent and is expressed (Sparks, 2013; Khezami and Capart, 2005) as Eq. 5:

$$q_t =k_{id} \, t^{0.5} \tag{5}$$

A linearised form is Eq. 6:

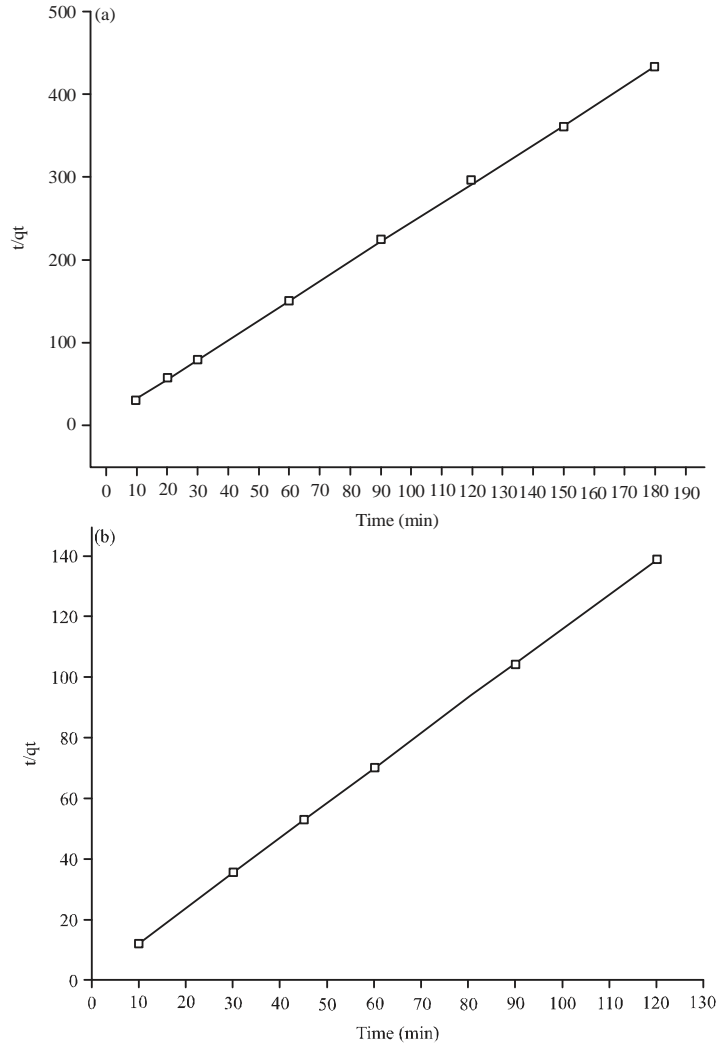$$\log q_t = \log k_{id} +0.5 \log t \tag{6}$$

Fig. 8(a-b): (a) Pseudo-second-order kinetic plots for the adsorption of Mn(II) on (a) SCB and
(b) BP

where, q_t is the amount Mn(II) adsorbed, t is the contact time and k_{id} is the intraparticle diffusion coefficient. By drown the values of log q_t vs. 0.5 log t, it should give a straight line with a positive intercept for intra-particle diffusion controlled adsorption process.

From kinetic studies correlation coefficient value for the second order kinetic model is the highest value ($r^2 = 0.999$) for SCB and BP. As well as the better agreement between calculated $q_e = 0.423$ mg g^{-1} and the experimental $q_e = 0.417$ mg g^{-1} value for SCB and for BP calculated $q_e = 0.869$ mg g^{-1} and the experimental $q_e = 0.864$ mg g^{-1}. This values indicate that the second order kinetic model is more suitable and can be applied for the adsorption process of Mn(II) using SCB and BP as an adsorbent. From the data of intraparticle diffusion model($r^2 = 0.957$ for SCB and $r^2 = 0.990$ for BP) this means that the intraparticle diffusion is indeed present in the adsorption of Mn(II) but that it is not the rate controlling step.

Comparison of adsorption of Mn(II) using SCB and BP with alternative natural adsorbents: The capacities of SCB and BP to remove manganese ions with compared to other

Table 2: Comparison of adsorption capacities of different adsorbents for the Mn(II) removal

Adsorbents	Qe (mg g^{-1})	C$_o$ (mg L^{-1})	pH	Time (min)	References
Chitin	0.643	10	8.62	120	Robinson Lora and Brennan (2010)
Kaolinite	0.446	1029		120	Yavuz (2003)
Cyan bacterium gloeothece magna	0.473-0.906	1-5	7.4	60	Mohamed (2001)
Untreated activated carbon	0.84	10	5.4	60	Ucer *et al.* (2006)
Tannic acid immobilized activated carbon	1.13	10	-	60	Ucer *et al.* (2006)
Maize husk	1.060	50	2	30	Adeogun (2013)
Oxalic acid modified maize husk	1.09	50	2	30	Adeogun (2013)
Sugarcane bagasse	0.417	2	6	150	This work
Beet pulp	0.864	2	6	90	This work

Table 3: Recovery of Mn(II) samples with sugar cane bagasse and beet pulp using batch technique

Samples	Concentration of metal ion in (mg L^{-1})						Recovery SCB (%)	Recovery BP (%)
	Mn(II)	Mg(II)	Fe(III)	Ca(II)	Cl$^-$	SO$^{-2}_4$		
DDW	2.0	-	-		-	-	62.5	86.34
DSW	2.0	30	0.0	88	22	24	61.5	82.2
DGW (1)	0.7	53	0.1	140	30	28	61.3	83.33
DGW (2)	0.9	110	0.3	260	78	70	60.0	75.7
DGW (3)	0.8	114	0.5	232	70	84	60.5	75.9

DDW: Doubly distilled water, DSW: drinking surface water, DGW: Drinking ground water, SCB: Suger cane bagasse, Bp: Beet pulp

natural material were showed in Table 2. The comparison is based on their adsorption capacity q$_e$ (mg g^{-1}), pH, equilibrium time as well as the initial concentration of metal ion. The results for this study showed that BP is a good adsorbent for manganese ions. Although, some materials exhibit capacity close to or better than that of BP, it was applied for removal of Mn(II) from real water samples.

Removal of Mn(II) from different water samples: Uptake experiments were carried out using different natural water samples: DSWand DGW. About 1.5 and 1.0 g powder of SCB and BP, respectively were conditioned with 500.0 mL of water sample spiked Mn(II) at concentration of 2 mg L^{-1} or naturally contain Mn(II) with different concentrations (adjusted at pH 6.0 by fine addition of concentrated HCl) with stirring for 150 and 90 min for SCB and BP, respectively. The solution (free from the suspended solid phase) was taken at the end of the experiment where the residual concentration of Mn(II) was determined via Biochrom Libra S12 Table 3.

Although, the presence of anions such as (Cl$^-$, SO$^{-2}_4$) and cations such as Ca(II), Mg(II), Fe(III) with different concentrations in water samples, BP showed good results of recovery and Mn(II) remain in filtrate less than the allowable limit in Egypt.

CONCLUSION

Sugar cane bagasse and BP as natural solid phase extractors have the following advantages: benign lignocellulosic materials, inexpensive (sugar industry wastes) and rich in oxygen-containing functional groups. The optimal conditions for Mn(II) removal was studied. It was observed for SCB that the maximum removal occurs at pH 6.0 with an adsorbent dosage of 1.5 g and maximum stirring time of 150 min, with an initial concentration 2 mg L^{-1}. The amount of adsorption at equilibrium (q$_e$) is 0.417 mg g^{-1}. As well as for BP the optimal conditions for Mn(II) removal was studied. It was observed that the maximum removal occurs at pH 6.0 with an adsorbent dosage of 1.0 g and maximum stirring time of 90 min, with an initial concentration 2 mg L^{-1}. The amount of adsorption at equilibrium (q$_e$) is 0.864 mg g^{-1}. The pseudo-second-order model better describes the adsorption kinetics for SCB and BP. The adsorption of Mn(II) involves the intraparticle diffusion but that it is not the rate-controlling step. The SCB and BP were applicable for reduce the risk of Mn(II) from ground water using batch technique.

REFERENCES

Adeogun, A.I., M.A. Idowu, A.E. Ofudje, S.O. Kareem and S.A. Ahmed, 2013. Comparative biosorption of Mn(II) and Pb(II) ions on raw and oxalic acid modified maize husk: Kinetic, thermodynamic and isothermal studies. Applied Water Sci., 3: 167-179.

Ahmed, S.A., 2011. Batch and fixed-bed column techniques for removal of Cu(II) and Fe(III) using carbohydrate natural polymer modified complexing agents. Carbohydrate Polymers, 83: 1470-1478.

Chien, S.H. and W.R. Clayton, 1980. Application of elovich equation to the kinetics of phosphate release and sorption in soils. Soil Sci. Soc. Am. J., 44: 265-268.

Emmanuel, K.A. and A.V. Rao, 2009. Comparative study on adsorption of Mn(II) from aqueous solutions on various activated carbons. E-J. Chem., 6: 693-704.

Esfandiar, N., B. Nasernejad and T. Ebadi, 2014. Removal of Mn(II) from groundwater by sugarcane bagasse and activated carbon (a comparative study): Application of Response Surface Methodology (RSM). J. Ind. Eng. Chem., 20: 3726-3736.

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

Heal, K.V., P.E. Kneale and A.T. Donald, 1995. Manganese mobilization and runoff process in upland catchments. Proceedings of the 5th National Hydrology Symposium, September 4-7, 1995, Heriot-Watt University Edinburgh, pp: 911-918.

Ho, Y. and G. McKay, 2002. Application of kinetic models to the sorption of copper (II) on to peat. Adsorption Sci. Technol., 20: 797-815.

Jusoh, A.B., W.H. Cheng, W.M. Low, A. Nora'aini and M.J.M.M. Noor, 2005. Study on the removal of iron and manganese in groundwater by granular activated carbon. Desalination, 182: 347-353.

Kamnev, A.A., M. Colina, J. Rodriguez, N.M. Ptitchkina and V.V. Ignatov, 1998. Comparative spectroscopic characterization of different pectins and their sources. Food Hydrocolloids, 12: 263-271.

Karnitz, Jr. O., L.V.A. Gurgel, J.C.P. de Melo, V.R. Botaro, T.M.S. Melo, R.P. de Freitas Gil and L.F. Gil, 2007. Adsorption of heavy metal ion from aqueous single metal solution by chemically modified sugarcane bagasse. Bioresour. Technol., 98: 1291-1297.

Khalilnezhad, R., M.E. Olya, M. Khosravi and R. Marandi, 2014. Manganese biosorption from aqueous solution by *Penicillium camemberti* biomass in the batch and fix bed reactors: A kinetic study. Applied Biochem. Biotechnol., 174: 1919-1934.

Khezami, L. and R. Capart, 2005. Removal of Chromium(VI) from aqueous solution by activated carbons: Kinetic and equilibrium studies. J. Hazard. Mater., 123: 223-231.

Kohl, P.M. and S.J. Medlar, 2006. Occurrence of Manganese in Drinking Water and Manganese Control. American Water Works Association, New York, USA., ISBN-13: 9781583215043, Pages: 184.

Lagergren, S., 1898. Zur theorie der sogenannten adsorption geloster stoffe, K. Sven. Vetenskapsakad. Handl., 24: 1-39.

Malik, P.K., 2004. Dye removal from wastewater using activated carbon developed from sawdust: Adsorption equilibrium and kinetics. J. Hazard. Mater., 113: 81-88.

Mohamed, Z.A., 2001. Removal of cadmium and manganese by a Non-toxic strain of the freshwater cyanobacterium *Gloeothece magna*. Water Res., 35: 4405-4409.

Mohan, D. and K.P. Singh, 2002. Single- and multi-component adsorption of cadmium and zinc using activated carbon derived from bagasse-an agricultural waste. Water Res., 36: 2304-2318.

Pearson, R.G., 1963. Hard and soft acids and bases. J. Am. Chem. Soc., 85: 3533-3539.

Pehlivan, E., B.H. Yanik, G. Ahmetli and M. Pehlivan, 2008. Equilibrium isotherm studies for the uptake of cadmium and lead ions onto sugar beet pulp. Bioresour. Technol., 99: 3520-3527.

Rand, M.C., E.G. Arnold and J.T. Michael, 1976. Standard methods for the examination of water and wastewater. American Public Health Association, American Water Works Association and Water Pollution Control Federation.

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

Reddad, Z., C. Gerente, Y. Andres, M.C. Ralet, J.F. Thibault and P. Le Cloirec, 2002. Ni(II) and Cu(II) binding properties of native and modified sugar beet pulp. Carbohydr. Polym., 49: 23-31.

Rengaraj, S., K.H. Yeon and S.H. Moon, 2001. Removal of chromium from water and wastewater by ion exchange resins. J. Hazard. Mater., 87: 273-287.

Robinson-Lora, M.A. and R.A. Brennan, 2010. Biosorption of manganese onto chitin and associated proteins during the treatment of mine impacted water. Chem. Eng. J., 162: 565-572.

Soliman, E.M. and S.A. Ahmed, 2009. Selective separation of silver(I) and mercury(II) ions in natural water samples using alumina modified thiouracil derivatives as new solid phase extractors. Int. J. Environ. Anal. Chem., 89: 389-406.

Soliman, E.M., S.A. Ahmed and A.A. Fadl, 2011a. 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. Arabian J. Chem., 4: 63-70.

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

Sparks, D.L., 2013. Kinetics of Soil Chemical Processes. Academic Press, San Diego, CA.

Sun, J.X., X.F. Sun, R.C. Sun, P. Fowler and M.S. Baird, 2003. Inhomogeneities in the chemical structure of sugarcane bagasse lignin. J. Agric. Food Chem., 51: 6719-6725.

Sun, R. and S. Hughes, 1998. Extraction and physico-chemical characterization of pectins from sugar beet pulp. Polym. J., 30: 671-677.

Tekerlekopoulou, A.G. and D.V. Vayenas, 2007. Ammonia, iron and manganese removal from potable water using trickling filters. Desalination, 210: 225-235.

Ucer, A., A. Uyanik and S.F. Aygun, 2006. Adsorption of Cu(II), Cd(II), Zn(II), Mn(II) and Fe(III) ions by tannic acid immobilised activated carbon. Sep. Purif. Technol., 47: 113-118.

Vijayaraghavan, K., T.T. Teo, R. Balasubramanian and U.M. Joshi, 2009. Application of *Sargassum* biomass to remove heavy metal ions from synthetic multi-metal solutions and urban storm water runoff. J. Hazard. Mater., 164: 1019-1023.

Yavuz, O., Y. Altunkaynak and F. Guzel, 2003. Removal of copper, nickel, cobalt and manganese from aqueous solution by kaolinite. Water Res., 37: 948-952.

Yilmaz, V., Z. Arslan, O. Hazer and H. Yilmaz, 2014. 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: 65-72.

Zhang, Y., J. Zhao, Z. Jiang, D. Shan and Y. Lu, 2014. Biosorption of Fe(II) and Mn(II) ions from aqueous solution by rice husk ash. BioMed Res. Int. 10.1155/2014/973095