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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

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Abstract This work introduces the feasibility of using sugar cane bagasse (SCB) – a sugar cane industry waste – as a selective solid phase extractor for Fe(III). The order of metal uptake capacities in $\mu\text{mol g}^{-1}$ for the extraction of six tested metal ions from aqueous solution using static technique is Fe(III) > Cu(II) > Pb(II) > Zn(II) > Cd(II) > Co(II). Since SCB exhibits remarkable binding characteristics for Fe(III), special interest was devoted for optimizing its uptake and studying its selectivity properties under static and dynamic conditions. In this respect, batch experiments were carried out at the pH range 1.0–4.0, initial concentration of metal ion (10–100 μmol), weight of phase (25, 50, 75, 100, 125 and 150 mg) and shaking time (10, 30, 45, 60, 90, 120 and 150 min). FT-IR spectra of SCB before and after uptake of Fe(III) were recorded to explore the nature of the functional groups responsible for binding of Fe(III) onto the studied natural biosorbent. The equilibrium data were better fitted with Langmuir model ($r^2 = 0.985$) than Freundlich model ($r^2 = 0.934$). Moreover, Fe(III) sorption was fast and completed within 60 min. The adsorption kinetics data were best fitted with the pseudo-second-order type. As a view to find a suitable application of SCB based on its unique property as a benign sorbent, it was found that, Fe(III) spiked natural water samples such as doubly distilled water (DDW), drinking tap water (DTW), natural drinking water (NDW), ground water (GW) and Nile River water (NRW) was quantitatively recovered (>95.0%) using batch and column experiments, with no matrix interferences.

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1. Introduction

In recent years, research interest has increased in terms of the use of natural and/or agricultural adsorbents to overcome the environmental pollution (Nagh and Hanafiah, 2008; Mohan and Pittman, 2006). Increasing attention has also been focused on the separation, preconcentration and/or determination of trace heavy-metal ions in the environment using these sorbents

(Tarley et al., 2004). The sugar industry is one of the most important agriculturally based industries. Sugar cane bagasse (SCB) or bagasse as it is generally called is a representative example of these adsorbents. It is used either as a fuel for the boilers by the sugar factory or as a raw material for the manufacture of pulp and paper products (Rowell and Keany, 1991; Sun et al., 2004). The application of agro-industrial residues in industries provides alternative substrates to synthetic adsorbents or exchangers participating in solving pollution problems. Pollution of natural water resources by heavy-metal ions is one of the most important problems faces and threats the world. These contaminants are produced from liquid wastes discharged from a number of industries such as electroplating, dyes and dye intermediates, textiles, tanneries, oil refineries, electroplating, mining, smelters, etc. (Ali and Gupta, 2007; Gupta et al., 2009; Ayyappan et al., 2005). The industrial wastes reach water effluent without any treating making series problem of heavy metal accumulation in the infected water. Some of those metals are accumulated in living organisms and produce diseases and disorders (Gupta et al., 2003; Mohan and Singh, 2002). Moreover, heavy-metal ions are supposed to be very toxic and carcinogenic in nature (Nagh and Hanafiah, 2008; Mohan and Pittman, 2006) and it is also well known that heavy metals can damage nerves, liver and bones and also interfere with the normal functioning of various metallo-enzymes (Garg et al., 2008). The determination of trace of these ions in aquatic samples is particularly difficult because of the complex matrix and the usually low concentration of these elements in such samples, which these requires sensitive instrumental techniques and frequently a preconcentration step. For solving this problem and preventing its danger, a number of methods are available for the separation and/or determination of these toxic metal ions present in aqueous solutions. These include ion exchange, solvent extraction, reverse osmosis, precipitation co-precipitation and adsorption (Rao et al., 2002). Solid phase extraction technique (SPE) has become known as a powerful tool for separation and enrichment of various inorganic and organic analytes (Mahmoud and Gohar, 2000; He et al., 2008; Ahmed, 2008). The basic principle of SPE is the transfer of the analyte from the aqueous phase to bind to active sites of the adjacent solid phase. SPE is an attractive separation preconcentration technique for heavy-metal ions with some important advantages (simplicity, flexibility, economic, rapid, higher enrichment factors, absence of emulsion, low cost because of lower consumption of reagents, more importantly environment friendly) (Soliman and Ahmed, 2009; Soliman et al., 2006). Various solid substrates have been successfully used as solid phase extractors for the determination and separation of heavy-metal ions at trace levels (Mahmoud et al., 2000; Soliman et al., 2002, 2004). In this context, SCB used as natural SP-extractor in three main forms: fly ash, activated carbon and native or raw bagasse for the purposes of separation, determination or removal of different types of pollutants. These include, heavy-metal ions (Gupta et al., 1998a, 1999; Gupta and Sharma, 2003; Gupta and Ali, 2004; Ayyappan et al., 2005; Gupta et al., 2003; Mohan and Singh, 2002; Garg et al., 2008; Rao et al., 2002; Gupta and Ali, 2000; Rao et al., 2009), dyes (Srivastava et al., 1995a,b; Gupta et al., 1998b, 2000, 2005; Gupta and Suhas, 2009; Mane et al., 2007, 2005) and pesticides (Gupta and Ali, 2001; Gupta et al., 2006; Akhtar et al., 2007; Gupta et al., 2002). Regarding to heavy-metal ions, several papers were directed to study the

separation and removal of one, two or three at the most of metal ions. Bagasse fly ash was used for the removal or uptake of copper and zinc (Gupta and Ali, 2000), chromium and nickel (Rao et al., 2002), lead and chromium (Gupta and Ali, 2004) cadmium and nickel (Gupta et al., 2003). Bagasse activated carbon was also used for removal of Cd(II) and Zn(II) (Mohan and Singh, 2002), Hg(II) (Rao et al., 2009) and Pb(II) (Ayyappan et al., 2005). However, too limited publications were directed to the use of its raw or native form for purposes of removal of metal ions (Garg et al., 2008; Rao et al., 2002).

In our study, considering the growing interest for using the agricultural wastes, the research summarized herein was part of the investigations conducted to evaluate and compare the efficiency of raw sugar cane bagasse (SCB) for binding to a number of different heavy-metal ions including: Fe(III), Co(II), Cu(II), Zn(II), Cd(II) and Pb(II). SCB was found to have the highest capacity in selective extraction of Fe(III) from aqueous solutions compared to the other tested metal ions. Taking into consideration the important role played by Fe(III) in biological systems, it was found that, cells use iron catalytically in many important and diverse reactions, e.g., electron transport, nitrogen fixation, detoxification, etc. Its bioavailability depends on its redox state and the pH, some microorganisms are able to use ferric ion as an electron acceptor in anaerobic respiration. In addition, both oxidative and reductive reactions are complementary elements of the iron cycle in the biosphere (Malki et al., 2006). Based on these facts, it is aimed in this manuscript to throw light on the efficiency of SCB to act as a benign biosorbent for selective removal of trace amounts of Fe(III) spiked natural water samples prior to determination by flame atomic absorption spectrometry (FAAS).

2. Materials and methods

All chemicals and reagents used were of analytical grade and were purchased from E. Merck, India/Germany. Sugar cane bagasse (SCB) was obtained from Abou-Korkas Sugar Factory, El-Minia, Egypt. Water samples including: Nile River water (NRW), ground water (GW) and drinking tap water (DTW) were collected from El-Minia governorate, Egypt. Doubly distilled water (DDW) and natural drinking water (NDW) were obtained from our lab and a local company for natural water, respectively.

2.1. Development of the sorbent SCB

SCB was first washed thoroughly with distilled water to remove the dust particles, then soaked over night in 0.1 N NaOH solution and again washed well with DDW. SCB was then soaked in 0.1 N CH₃COOH for a period of 2–3 h to remove the traces of NaOH (Rao et al., 2002). It was thoroughly washed again with DDW till the wash water became colorless and then filtered, well dried, powdered and sieved before use. The average particle size was 0.75 mm.

2.2. Metal binding capacities of SCB

The metal uptake capacities of SCB towards Fe(III), Co(II), Cu(II), Zn(II), Cd(II) and Pb(II) ions were determined in triplicate under static conditions by the batch equilibrium technique. SCB (100 mg) was added to a mixture of 100 µl of

0.1 M of the tested metal ion and a buffer solution of pH 1.0–7.0 – except with Fe(III) the pH used were in the range 1.0–4.0 – 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. The SCB was separated by filtration, washed with DDW and the unretained metal ion in the filtrate was determined by complexometric EDTA titration or FAAS (Soliman et al., 2004). For pH adjustment, solutions of 0.1 M HCl and 0.1 M NaOH were used. The equation of metal uptake capacity could be obtained as follows:

$$M_c = (X - Y)/Z$$

where X refers to the initial concentration of metal ion in μmol , Y equals concentration of the unadsorbed metal ion in the filtrate in μmol , Z = mass of the SCB in g, M_c = metal capacity value in $\mu\text{mol g}^{-1}$.

Moreover, the effect of contact time on Fe(III) uptake was determined under the same batch conditions, but at different shaking periods (10, 30, 45, 60, 90, 120 and 150 min) and at the pH 3.0 (Soliman et al., 2004). The effects of Fe(III) concentration (10.0–100.0 μmol) and weight of phase (25.0–150.0 mg) on its uptake efficiency by SCB were also systematically investigated.

2.3. Instrumentation

Infrared spectra of SCB before and after Fe(III) sorption were obtained using FT-IR model 410 JASCO (Japan). A Fisher Scientific Accumet pH-meter model 825 calibrated against two standard buffer solutions at pH 4.0 and 9.2 was used for all pH-measurements. Atomic absorption measurements were performed with Aquanova-Genway spectrometry.

3. Results and discussions

3.1. FT-IR analysis of SCB before and after Fe(III) sorption

SCB as a lignocellulosic compound is generally considered as structures built by cellulose molecules, organized in microfibrils and surrounded by hemicellulosic materials (xylans, mannan, glucomannans, galactans, and arabogalactans), lignin and pectin along with small amounts of protein (Ashih and Duvnjak, 1997). The FT-IR spectra of SCB before and after sorption of Fe(III) were performed to determine the vibration frequency changes in their functional groups within the range of 4000–400 cm^{-1} . The spectral measurements support the complex nature of the examined adsorbent. SCB before Fe(III) sorption showed an absorption peak around 3403.7 cm^{-1} indicates the existence of free and intermolecular bonded hydroxyl groups. The peaks observed at 2918.7 cm^{-1} can be assigned to stretching vibration of the C–H group. The presence of strong C–O band at 1058.7 cm^{-1} due to $-\text{OCH}_3$ group in addition to the peaks at 613.2 and 833.1 cm^{-1} related to bending modes of aromatic compounds confirm the presence of lignin structure incorporated sugarcane bagasse (Garg et al., 2008). Moreover, a weak intensity band located at 1704.8 cm^{-1} was argued to stretching vibration of carboxylic groups of galactouronic acid (Pehlivan et al., 2008). Comparing and assignments of SCB before and after Fe(III) sorption is too important to indicate the functional groups responsible for Fe(III) binding. Generally, the binding of metal ions to biosorbents may be proceed via

complexation with functional groups, ionic exchange, surface precipitations and chemical reaction with surface sites (Torresdey et al., 2004). Regarding FT-IR for SCB after Fe(III) uptake, it was found that, oxygen containing functional groups vis, methoxy $-\text{OCH}_3$, carboxy $-\text{COOH}$ and phenolic $-\text{OH}$ groups are affected after uptake process. This is judging from shifts in their position, shape or band intensity from 1058.7, 1704.8 and 3403.7 cm^{-1} to 1046.2, 1682.6 and 3406.6 cm^{-1} of $\nu(-\text{O}-\text{C})$, $\nu(-\text{COOH})$ and $\nu(-\text{OH})$ for SCB before and after Fe(III) sorption, respectively. The results indicate the participation of these groups via oxygen for Fe(III) binding to SCB in agreement with Person principal for hard-soft acids and bases (Pearson, 1963).

3.2. Effect of pH on metal ion binding capacities using SCB

SCB mainly contains cellulose (45%), hemi-cellulose (28%) and lignin (18%). This variety of chemical composition and consequently functional groups make SCB shows different efficiencies for removal of heavy-metal ions over a wide range of pH (Garg et al., 2008). This is clear as shown Fig. 1 for the uptake of the studied metal ions as a function of pH (1.0–7.0). Therefore, at low pH values (pH < 2.0) SCB showed very low tendency for uptake of all the investigated metal ions due to protonation of its functional groups or competition of H^+ with metal ions for binding sites (Mohan and Singh, 2002). These uptake values increased with increasing pH from 2.0 to 7.0. The binding capacities reached their maximum values around pH 6.0 and then retained almost constant. Maximum sorption capacities were 15.5 $\mu\text{mol g}^{-1}$ at pH 5.0 for Co(II), 86.0, 70.0 and 87.0 $\mu\text{mol g}^{-1}$ at pH 6.0 for Cu(II), Cd(II) and Pb(II), respectively, and 81.0 $\mu\text{mol g}^{-1}$ at pH 7.0 for Zn(II). The predominant metal species at pH between 2.0 and 7.0 are positively charged [M^{n+} and $\text{M}(\text{OH})^{(n-1)+}$], therefore, uptake of metals may proceed through M^{n+} exchange process with acidic sites H^+ , complexing with functional groups and/or chelation (Rengaraj et al., 2001).

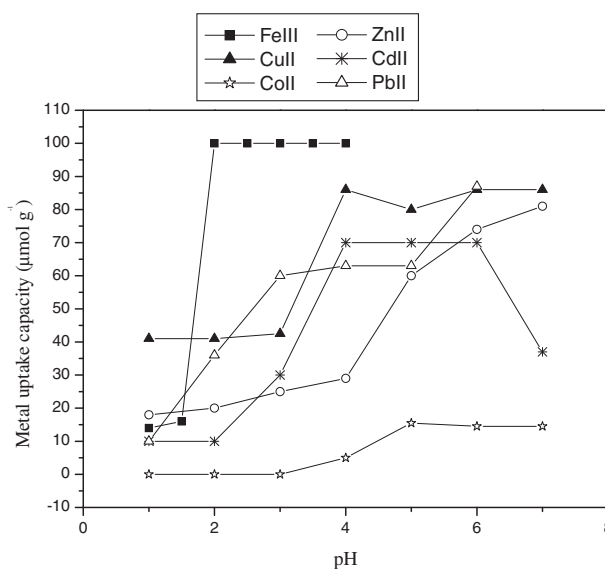


Figure 1 Metal uptake capacity ($\mu\text{mol g}^{-1}$) as a function of pH using SCB.

The uptake behavior of Fe(III) by SCB as a function of pH was unique compared to the other metal ions (Fig. 1). Its uptake reached to maximum value ($100 \mu\text{mol g}^{-1}$) at pH 2.0 and then retained constant at pHs 2.5, 3.0, 3.5 and 4.0. This behavior reflects the pronounced capability of Fe(III) ions to overcome the competition arisen by H^+ ions at low pH values for binding to oxygen donor sites in SCB.

Finally, the decreasing affinity of SCB for binding to the studied metal ions can be arranged based on their uptake values according to the following order: $\text{Fe(III)} > \text{Cu(II)} > \text{Pb(II)} > \text{Zn(II)} > \text{Cd(II)} > \text{Co(II)}$.

3.3. Optimum conditions for binding of Fe(III) using SCB

Considering the biological important of Fe(III), the study will be directed to optimize the uptake properties of Fe(III) after choosing pH 3.0 for this purpose.

3.3.1. Effect of shaking time

Shaking time is an important factor in the process of evaluation of the SCB. The batch experiments were carried out at different contact times 10, 30, 45, 60, 90, 120 and 150 min using mechanical shaker with a fixed sorbent mass (100 mg), Fe(III) concentration ($100 \mu\text{l}$) at a pH of 3.0 and 50.0 ml contact solution. Results of percentage extraction of Fe(III) as a function of shaking time intervals is represented in Fig. 2. The equilibrium is reached within the first 60 min of contact and reached a saturation level. In the beginning, the ions adsorbed, occupied selectively the active sites on SCB. As the contact time increased the active sites on the sorbent were filled. The results which plotted in Fig. 2 clearly indicate that the equilibrium for Fe(III) is attained in 60 min of contact, (100.0%). These results of percentage extraction and time of attained equilibrium are higher and faster, respectively, than the values reported by other authors (Bansode et al., 2003).

3.3.2. Effect of initial Fe(III) concentrations

The effect of initial concentration of Fe(III) on its percentage extraction was studied at concentrations of 10.0–100.0 μmol at fixed sorbent weight of 100.0 mg, pH 3.0 and contact time 60 min. The results showed that the percentage extraction of

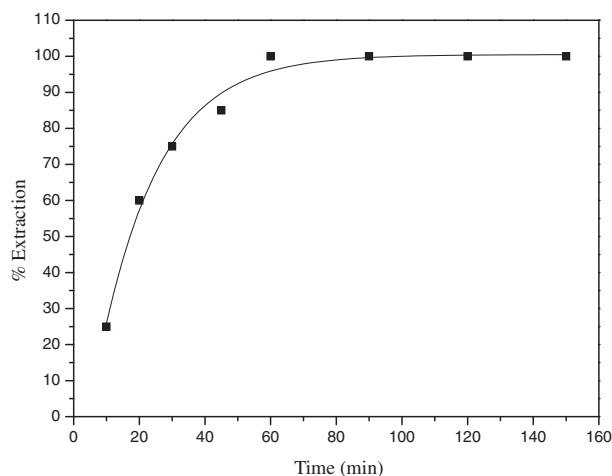


Figure 2 % Extraction of Fe(III) as a function of shaking time using SCB.

Fe(III) ions initially increased with concentration of 10.0 μmol . As the concentration was increased from 40.0 to 100.0 μmol , the percentage extraction decreased indicating that the metal uptake is highly dependent on the initial concentration of Fe(III) in solution. At lower metal concentration, the ratio of number of moles of Fe(III) in solution to the available surface area is low and hence binding is independent of initial concentration. At higher concentration the available sites for binding is less and hence metal removal is dependent on the initial concentration.

3.3.3. Effect of weight of SCB

The weight of SCB adsorbent was varied from 50.0 to 150.0 mg keeping all the other experimental variables, viz., pH 3.0 initial concentration (10.0 μmol), and contact time 60 min. Fig. 3 presents the adsorbent weight profile versus Fe(III) adsorbed per unit mass. It may be observed that on increasing the adsorbent weight, the percentage extraction of Fe(III) increased up to a weight of 100.0 mg remained constant.

3.3.4. Effect of medium

The study of medium effect on the stability of the SCB phase is important from practical application point of view. It was performed in different buffer solutions pH 1.0–10.0 for 10 h contact time in order to assess the possible leaching or hydrolysis processes (Soliman et al., 2004). The results showed that the SCB is stable after long time of contact in the pH range from 1.0 to 10.0. So, a decomposition or hydrolysis of SCB was found at high hydrogen ion concentration judging from the percentage decrease of efficiency of Fe(III) uptake as found to be 0.9%, 0.54% and 0.43% at pHs 1.0, 2.0 and 3.0, respectively. On the other hand, at pH range 4.0–10.0 the percentage of hydrolysis not exceed than 0.1%.

3.4. Binding performance (sorption isotherms)

The purpose of the adsorption isotherms is to relate the adsorbate concentration in the bulk and the adsorbed amount at the interface (Demirbas et al., 2002). The simplest adsorption isotherm is based on the assumptions that every adsorption site is equivalent and the ability of a particle to bind is independent

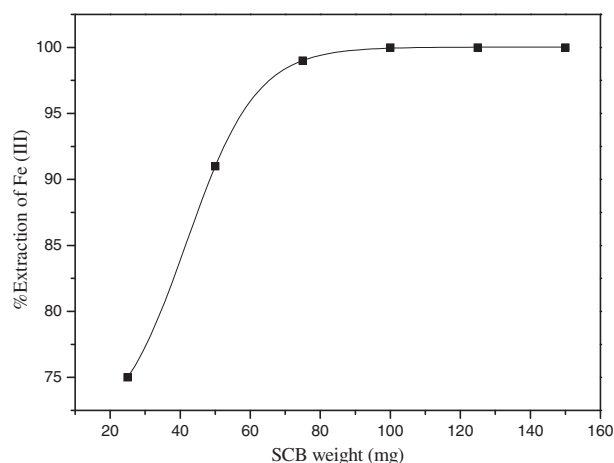


Figure 3 Effect of SCB weight on % extraction of Fe(III).

of whether or not adjacent sites are occupied (Shukla et al., 2005). To find out the mechanistic parameters associated with Fe(III) sorption, the results obtained by the adsorption experiments were analyzed by the well-known models given by Freundlich and Langmuir models. The sorption isotherms for binding of Fe(III) with SCB were determined by the batch technique at pH 3.0. Thus, solutions of iron(III) in the concentration range: $(4.0 \times 10^{-4} - 2.0 \times 10^{-3} \text{ M})$ were shaken for 60 min with a constant weight 100.0 mg of SCB.

The basic assumption of Freundlich isotherm is that if the concentration of the solute in the solution at equilibrium, C_e was raised to the power $1/n$, the amount of solute sorbed being q_e , then $C_e^{1/n} q_e$ was a constant at a given temperature. This model is more widely used but provides no information on the monolayer biosorption capacity (Pehlivan et al., 2008) and it assumes neither homogeneous site energies nor limited levels of sorption. The non-linear form (Fig. 4) of Freundlich equation expressed as follows:

$$q_e = K_f \cdot C_e^{1/n} \quad (\text{non-linear form}) \quad (1)$$

where K_f and $1/n$ are Freundlich constants (indicators of sorption capacity and intensity, respectively). Taking logs and rearranging of Eq. (1), it can give the linear form of Freundlich model which expressed as:

$$\log q_e = \log K_f + 1/n \log C_e \quad (\text{linear form}) \quad (2)$$

The constants (K_f) and ($1/n$) can be calculated from the intercept and slope of this linear equation, respectively (Table 1). From Table 1, it is clearly shown that the data is not fitting very well to the Freundlich model (Delle Site, 2001).

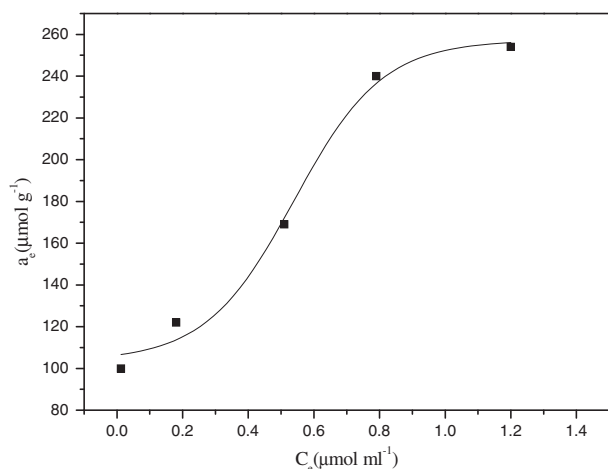


Figure 4 Adsorption isotherm of Fe(III) using SCB phase.

The Langmuir equation, which is valid for monolayer sorption onto a completely homogeneous surface with a finite number of identical sites and with negligible interaction between adsorbed molecules is given by the following equation:

$$C_e/q_e = (1/Q_o)C_e + (1/Q_o b) \quad (\text{linear form}) \quad (3)$$

where C_e and q_e are the equilibrium concentrations of adsorbate in the liquid and adsorbed phases in $\mu\text{mol ml}^{-1}$ and $\mu\text{mol g}^{-1}$, respectively (Rao et al., 2009). Q_o and b are Langmuir constants, which are related to maximum Fe(III) sorption capacity ($\mu\text{mol g}^{-1}$) and affinity parameter ($\text{ml } \mu\text{mol}^{-1}$), respectively, and 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. 5. The correlation coefficient ($r^2 = 0.985$) showed that the Langmuir model fitted the results better than Freundlich model. 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 sorption 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 as follows:

R_L value	Type of isotherm
$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$0 < R_L < 1$	Favorable
$R_L = 0$	Irreversible

The R_L for Fe(III) sorption (0.8) supports a highly favorable sorption process based on Langmuir model.

The different parameters of Freundlich and Langmuir isotherms constants are collected in Table 1. Data were fitted with non-linear regressions using a least-square fitting program (origin 6.0) to obtain the best estimate of all constants for the Freundlich and Langmuir isotherms.

3.5. Kinetic studies

The sorption kinetic data of Fe(III) measured on SCB was analyzed in terms of pseudo-second-order sorption equation (Reddad et al., 2002). This equation can be written as:

$$dq_e/dt = k_2(q_e - q_t)^2 \quad (4)$$

where k_2 ($\text{g}/\mu\text{mol}/\text{min}$) is the rate constant. Integration of Eq. (4) and application of the conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, give:

$$1/q_e - q_t = 1/q_e + k_2 t \quad (5)$$

Table 1 Parameters of Freundlich and Langmuir isotherms constants for binding of Fe(III) using SCB at room temperature.

Sorbent	Metal ion	Freundlich constants			Langmuir constants		
		K_f	$1/n$	r^2	Q_o^a	b^b	r^2
SCB	Fe(III)	161.1	12.9	0.934	331.1	2.52	0.985

^a $\mu\text{mol g}^{-1}$.

^b $\text{ml } \mu\text{mol}^{-1}$.

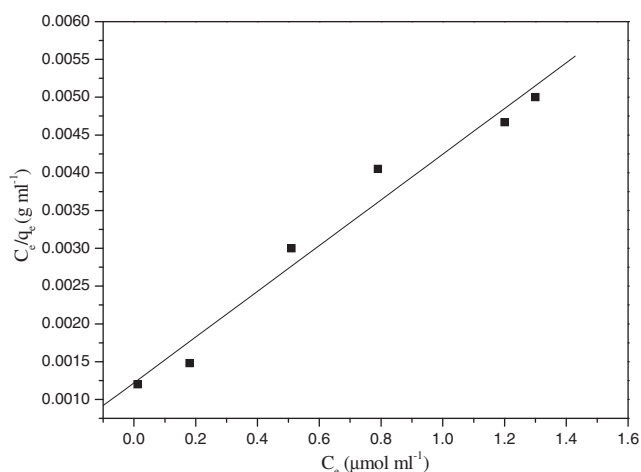


Figure 5 Langmuir plot for the sorption of Fe(III) on SCB at constant temperature.

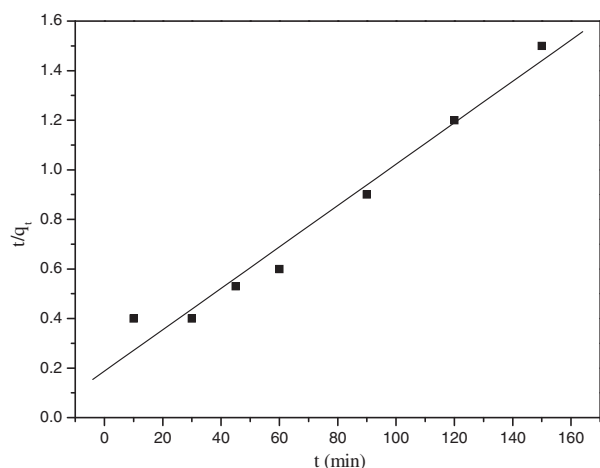


Figure 6 Pseudo-second-order kinetic plot for the sorption of Fe(III) on SCB.

The following equation can be obtained on rearranging Eq. (5) into a linear form as follows:

$$t/q_t = 1/v_o + (1/q_e)t \quad (6)$$

$v_o = kq_e^2$ is the initial sorption rate ($\mu\text{mol g}^{-1} \text{min}^{-1}$), v_o and q_e can be obtained from the intercept and slope of plotting t/q_t vs t (Fig. 6), respectively. They were calculated to be $v_o = 5.35$,

$q_e = 119.7 \mu\text{mol g}^{-1}$ and $k_2 = 3.7 \times 10^{-4} \text{min}^{-1}$. Since, the kinetic of the uptake has to be determined in order to establish the time course of the uptake process; the previous results showed that the adsorption kinetics data were best fitted with the pseudo-second-order model, which give a correlation factor (r^2) of 0.99. Time dependent (30–150 min) adsorption of Fe(III) on SCB is shown in Fig. 2, the uptake increased sharply over 60 min, and after that it increases slowly till reaching equilibrium within 1 h.

3.6. Separation and selectivity studies

The values of distribution coefficients $K_d = (\text{amount of the metal ion sorbed by the SCB in } \mu\text{mol g}^{-1})/(\text{amount of the metal ion unsorbed in solution in } \mu\text{mol ml}^{-1})$ and selectivity parameter $S = \log K_{d_{\text{Fe(III)}}} - \log K_{d_{\text{M}^{n+}}}$, where M^{n+} [Co(II), Cu(II), Zn(II), Cd(II) and Pb(II)], for separation of Fe(III) from the investigated metal ions are given in Table 2. It can be deduced that the separation process is possible and successful at pHs 2.0 and 3.0 ($K_{d_{\text{Fe(III)}}} = 49,950$, $S \geq 2.0$). As the S value increase the separation process is favorable with minor or no interferences. The order of increasing interference is as follows: at pH 2.0, Co(II) < Cd(II) < Zn(II) < Pb(II) \cong Cu(II) and at pH 3.0, Co(II) < Zn(II) < Cd(II) < Cu(II) < Pb(II).

4. Applications

4.1. Batch studies

Uptake experiments were carried out using different natural water samples: DDW, DTW, NRW, GW and NDW. A 100.0 mg of SCB was conditioned with 50.0 ml of water sample spiked Fe(III) at concentration of 2.5 and 5.0 ppm (adjusted at pH 2.0 by fine addition of concentrated HCl) with shaking for 60 min. Ten milliliters of the solution (free from the suspended solid phase) were taken at the end of the experiment where the residual concentration of metal ion was determined via FAAS. The percentage recovery values of Fe(III) are combined in Table 3.

4.2. Column studies

A glass column of 30 cm length and 2 cm internal diameter (ID) was used. SCB (100.0 mg) was put between two layers of glass wool, the first at the bottom to avoid loss of sorbent when the sample solution passes through the column and the second at the top to retain it. Then, 50 ml solution of each of the natural water sample (DDW, DTW, NRW, GW and

Table 2 Distribution coefficient (K_d) and selectivity parameter ($S = \log K_{d_{\text{Fe(III)}}} - \log K_{d_{\text{M}^{n+}}}$) for separation of Fe(III) from the investigated metal ions at pHs 2.0, 3.0 and 4.0 using SCB.

Metal ions	At pH 2.0		At pH 3.0		At pH 4.0	
	K_d	S	K_d	S	K_d	S
Fe(III)	49,950	–	49,950	–	49,950	–
Co(II)	1.00	4.7	1.00	4.7	26.3	3.3
Cu(II)	315.5	2.2	328.1	2.2	2147.8	1.4
Zn(II)	125.0	2.6	166.7	2.5	204.2	2.4
Cd(II)	47.32	3.0	202.8	2.4	1028.0	1.7
Pb(II)	264.8	2.3	682.3	2.0	767.4	1.8

Table 3 Recovery of Fe(III) spiked natural water samples with SCB using batch technique.

Sample	Added (ppm)	% Recovery
NRW	2.5	97.4 ± 0.1
	5.0	95.0 ± 0.1
GW	2.5	95.0 ± 0.05
	5.0	98.4 ± 0.1
DTW	2.5	95.0 ± 0.2
	5.0	98.0 ± 0.1
NDW	2.5	95.0 ± 0.05
	5.0	95.0 ± 0.2
DDW	2.5	97.2 ± 0.1
	5.0	98.2 ± 0.05

For $N = 3$, RSD% = 0.051–0.21.

Table 4 Recovery of Fe(III) spiked natural water samples with SCB using column technique.

Sample	Added (ppm)	% Recovery
NRW	2.5	98.15 ± 0.1
	5.0	99.07 ± 0.1
GW	2.5	98.80 ± 0.05
	5.0	99.40 ± 0.5
DTW	2.5	98.60 ± 0.1
	5.0	95.0 ± 0.1
NDW	2.5	97.06 ± 0.2
	5.0	96.08 ± 0.1
DDW	2.5	96.0 ± 0.05
	5.0	97.0 ± 0.05

For $N = 3$, RSD% = 0.051–0.503.

NDW) containing 2.5 and 5.0 ppm of Fe(III) (adjusted at pH 2.0 by fine addition of concentrated HCl) passed through the column with flow rate of 1.0 ml/min. Values of Fe(III) recovered are given in Table 4.

The quantitative recovery values of Fe(III) as shown in Tables 3 and 4 indicate the suitability and validity of using SCB for selective removal of Fe(III) from natural water samples either by batch or column techniques.

5. Conclusion

SCB as a natural solid phase extractor has the following advantages: (i) benign lignocellulosic material, inexpensive (sugar cane industry waste) and rich in oxygen containing functional groups. (ii) It has pronounced capability for uptake (in $\mu\text{mol g}^{-1}$) of Fe(III) in aqueous solution in the pH 2.0–4.0 compared to Co(II), Cu(II), Zn(II), Cd(II) and Pb(II) with no need to chemical modification. (iii) It was applicable for selective removal of Fe(III) from different natural water samples (percentage recovery >95.0%) using batch and column techniques. (iv) Its sorption performance was fitted well with Langmuir model with correlation factor $r^2 = 0.985$ and $R_L = 0.8$, along with fast kinetics obeying pseudo-second-order type $r^2 = 0.99$.

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