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Removal of Ni(II), Cd(II) and Cr(III) from industrial wastewater by raw and modified cotton stalk

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Key words: Biosorption, Real Wastewater, Cotton stalk, Surfactant, Isotherms.

Abstract

Waste cotton stalk (CS) and surfactant modified CS (SMCS) biosorbents were evaluated for their ability to remove Ni(II), Cd(II), and Cr(III) ions from wastewater. Sodium dodecyl sulfate (SDS), a commonly used surfactant, was used to modify the raw biomass. The CS and SMCS biosorbents were characterized with Fourier transform infrared (FTIR) spectroscopy and scanning electron microscopy (SEM). The effects of several parameters, such as initial heavy metal (HM) concentration, pH of the solution, charge and concentration of the surfactant, on the sorptive properties of the SMCS were also investigated. The results showed that surfactant modification improved HM removal by the biosorbents, especially when concentration was below the critical micelle concentration (CMC). The trend of HM ions uptaken by the SMCS followed the order of Cr(III) > Ni(II) > Cd(II). Maximum HM removal efficiency of 100% was achieved for Cr(III) and ≥ 90% for Ni(II) and Cd(II) in concentration range of 1-100 mg L^{-1}. Sorption equilibrium data of HM on the biosorbents were analyzed and the results demonstrated that the most appropriate models to simulate the isotherms were Langmuir and Freundlich equations.

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Introduction

The direct discharge of heavy metal (HM) ions into sewage systems has become one of the most serious environmental problems today. Wastewater containing different HMs is released from a variety of sources, such as metal plating, mining, battery manufacturing, pigment and chemical industries. Various HM treatment methods for the purification of water and wastewater have been developed, including chemical precipitation (Djedidi, 2009), chemical oxidation/reduction (Naumczyk, 2014), filtration (Martinez, 2014), ion-exchange (Dharnaik, 2014) and solvent extraction (Çetin, 2011), However, application of these methods may be limited because of high operational costs and low removal efficiency, especially when HM concentration is lower than 100 mg L^{-1} (Krauter, 1996, Lodeiro, 2006). These disadvantages have led to the initiation of a large number of studies to develop more efficient and cost-effective methods for the removal of HMs. Among them, the application of biosorbents (i.e., biomass based sorbents) in controlling and removing metal pollution has received much attention, and has gradually become a hot topic in the field of HM remediation.

In recent years, agricultural by-products have been widely viewed as inexpensive, convenient, and effective adsorbents for the treatment of HM ions. The surfaces of agricultural materials often contain a variety of functional groups that can attract metal ions to sequester them. Previous studies have revealed that agricultural waste materials, such as rice bran, bark of trees, groundnut shells, coconut shells, cotton seed hulls, waste tea leaves, orange peels, soybean hulls, sugar beet pulp, sunflower stalks, and cotton stalks can effectively remove HMs from aqueous solutions (Sud, 2008).

Agricultural waste materials have been used not only in their natural forms but also after some physical or chemical modifications (Chen, 2011, Arief, 2008). In general, raw lignocellulosic biosorbents can be modified by various methods to improve their sorptive properties (Miretzky, 2010). These treatments can modify the surface characteristics of the raw materials either by removing or masking some of the functional groups or by adding more metal binding sites (Wang, 2009, Martín-Lara, 2010). For example, base treatment of biomasses may significantly increase their metal uptake capacity. While, acid treatment of biomass had almost no influence on metal sorption onto biomasses (Martín-Lara , 2008, Ofomaja, 2010). To the best of our knowledge, however, there is no systematic study in the literature to determine the effect of surfactant modification on the sorption of HMs onto cotton stalk in real industrial wastewaters. Hence, the main objects of this work were: i) to study the feasibility of using raw and surfactant-modified cotton stalks as alternative adsorbents for the removal of HM ions (i.e., Ni(II), Cd(II) and Cr(III)), ii) to compare the effectiveness of different types of surfactant including anionic, cationic and nonionic on heavy metal removal iii) to evaluate various physiochemical conditions (e.g., pH, concentration, and surfactant charge) affecting the sorption, and iv) to test the applicability of various isotherm models (Langmuir, Freundlich, and Sip's models) for the experimental data.

Materials and methods

Reagents and materials

Sodium dodecyl sulfate (SDS), Hexadecyltrimethylammonium (HDTMA), sodium lauryl sulfate, nonyl phenol and ethoxylated lauric acid were bought from Merck Chemicals (Darmstadt, Germany). Ultra-purified water was used for preparing all solutions. Cotton stalks (CS) used in this work were obtained from a cotton field in Isfahan, Iran.

Preparation of biomass

After collection, cotton stalks were separated from impurities, and washed thoroughly several times with tap water. After the scrap and leaves were removed, the samples were sun-dried and then coarsely chopped. They were further grinded and washed with deionized (DI) water until the pH stabilized. The obtained biomass was oven-dried at 70˚C for 24 h and then crushed and sieved to obtain particles of 0.5-0.7 mm diameter for subsequent studies.

Modification of CS

An anionic surfactant, sodium dodecyl sulfate (SDS) ($NaC_{12}H_{25}SO_4$, molecular weight of 288.38 g mol^{-1}, CMC of 8.0 mmol L^{-1}, Merck Co.), was used to make the surfactant-modified cotton stalks (SMCS). Modification was carried out by treating 10.0 g of CS with 500 ml of the SDS solution of 4.0 mmol L^{-1} (0.5 CMC), 8.0 mmol L^{-1} (CMC), or 16.0 mmol L^{-1} (2CMC). All of the samples were shaken at 180 rpm (Orbital shaker, Edmund Buhler, M-30 control) under room temperature (25 ˚C) for 6 h. The suspensions were left undisturbed to be separated into two phases. The liquid phase was discarded and the solid phase (i.e., SMCS) was washed with DI water several times to remove superficially-held surfactants. The obtained samples were oven-dried at 70˚C for 8 h.

Preparation of metal ions solutions

Real wastewater from a plating factory was used for the experiments. The solution contained 3653, 1848, and 2312 mg L^{-1} Ni(II), Cd(II) and Cr(III), respectively. Test solutions of the HMs used in this work were prepared by diluting the real wastewater with DI water to the required concentrations. Metal ions concentrations in the solutions were measured with an inductively coupled plasma (ICP) spectrometer (Optima 7300 DV, PerkinElmer 2009). The instrument's operating conditions were optimized according to the expected range of metal concentrations in the samples as stated in the operations manual. Each sample was read twice to get an average value. Initial pH of the solution was near 2.0. The pH was measured using a pH-meter (Metrohm 827, pH Lab).

Adsorption equilibrium experiments

All biosorption experiments were performed using the diluted real wastewater solutions, which contained mixture of the Ni(II), Cd(II) and Cr(III). The pH of the solutions was adjusted to 7.0 by adding NaOH (1.0 M) and HCl (1.0 M) solutions. Batch-mode experiments were done at different initial concentrations ranging from 30-360 mg L^{-1} for Ni(II), 15-180 mg L^{-1} for Cd(II) and 17-230 mg L^{-1} for Cr(III). The adsorption isotherms were obtained by shaking plastic bottles containing 0.5 g of CS or SMCS and 100 ml of the solution with the above-mentioned concentrations at 180 rpm and 25 ˚C. Each experiment had two replications. At the end of the adsorption period (2 h), supernatant solutions were separated by being passed through Whatman paper No. 42. Afterwards, the concentrations of the remaining Ni(II), Cd(II) and Cr(III) in the solutions were determined by the ICP. The amount of each HM adsorbed by the biomass was calculated by the difference between the original and final concentrations (Reddy, 2011),

$$q_e = \frac{V\left(C_0 - C_e\right)}{W} \qquad (1)$$

Where q_e is the amount of adsorbed Ni(II), Cd(II) or Cr(III) on CS or SMCS (mg g^{-1}), W is the CS or SMCS mass (g), C_0 and C_e are the initial and equilibrium concentrations of HMs in the solution (mg L^{-1}), respectively, and V is the volume of the solution (L). The removal efficiency was calculated with following equation:

$$\%RE = \frac{\left(C_0 - C_e\right)}{C_0} \times 100 \qquad (2)$$

Where RE is removal efficiency of each HM.

Characterization of sorbents

Fourier transform infrared spectroscopy (FTIR; Tensor Bruker, Germany) was used to determine the functional groups on the two adsorbents. In general, the sites responsible for the HM adsorption process are surface functional groups, such as carboxyl (–C=O), amine ($–NH_2$), and hydroxyl (–OH) groups. The surface morphology of the raw and surfactant modified biomass samples were recorded using scanning electron microscope (SEM) (Stereo Scan

LEO, Model-400).

Results and discussion

Effect of contact time

The data obtained from the adsorption of Ni(II), Cd(II) and Cr(III) ions on the two CS based adsorbents showed that a contact time of 2 h was sufficient to achieve equilibrium and the adsorption did not change with further increase in contact time (data not shown).

Table 1. Adsorption isotherm parameters for adsorption of Ni(II), Cd(II) and Cr(III) by CS and SMCS.

	Ni(II)		Cd(II)		Cr(III)	
Isotherm model	CS	SMCS	CS	SMCS	CS	SMCS
Langmuir						
q_{max} (mg g-1)	31.91	38.23	19.58	24.93	38.29	43.33
b (L mg-1)	0.035	0.064	0.120	0.160	0.117	3.145
R^2	0.955	0.912	0.940	0.926	0.958	0.944
Freundlich						
	4.57	8.91	5.36	7.13	6.91	21.76
n	2.86	3.59	3.62	3.95	2.43	5.05
R^2	0.852	0.938	0.907	0.968	0.946	0.945
Sip's						
q_{max} (mg g-1)	33.21	37.72	20.10	25.43	34.46	47.66
b (L mg-1)	0.010	0.012	0.099	0.006	0.063	1.042
n	0.951	0.390	0.932	0.041	0.862	0.423
R^2	0.957	0.944	0.940	0.969	0.963	0.971

Effect of surfactant charge

Most substances acquire a surface electric charge when brought into contact with a polar medium such as water. The adsorption of ionic surfactants could be one mechanism for this phenomenon. It may be possible that surfactant adsorption causes increasing, decreasing or not significantly changing the electric charge of the surface. Surfactant adsorption is a transfer process of surfactant molecules from bulk solution phase to the surface/interface that most commonly occurs in porous media. Adsorption of surfactants onto substrates, such as cotton in neutral solution, is mainly performed by a combination of hydrogen bonding and adsorption via dispersion forces (Rosen, 2004). The orientation of the surfactant molecules at the surface of the adsorbent is an important issue in terms of determining how hydrophilic or hydrophobic the surface will become. The surface functional groups of the adsorbent almost have the ability to form the hydrogen bond with water. Surface equilibrium in solid–liquid interface creates a surface charge which can be positive, negative or neutral. Cotton stalk that composed primarily of cellulose is a negative charged in neutral and alkali aqueous solutions (Nigmatullin, 2004), Ionic surfactants tend to adsorb onto opposite-charged solid surfaces due to electrostatic interactions. When the charge of the cotton surface would be negative, the cationic surfactants have more tendencies to be adsorbed on the cellulose surface. It has been shown that in these situations, the kinetic rate of adsorption of cationic surfactant is very fast and the amount of cationic surfactant adsorbed at the cellulose–water interface is higher than the anionic and non-ionic surfactant. In summary, the order of rate of adsorption would be as follows: cationic > anionic ≈ non-ionic (Paria, 2004). In this work, the effect of the charge of the surfactant on cotton stalks for heavy metal removal efficiency was studied using three kinds of surfactant containing cationic, anionic and nonionic surfactants.

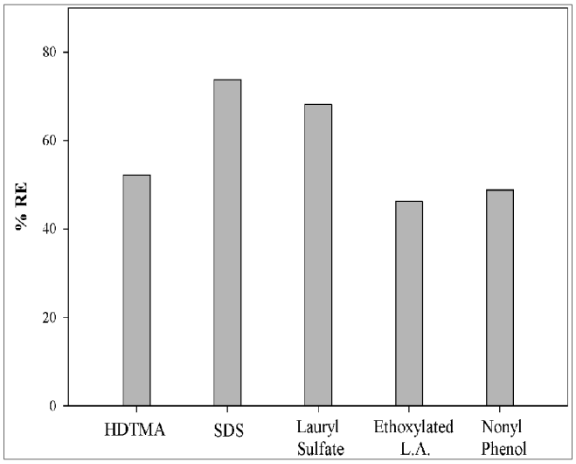

Fig. 1. Effect of the different surfactants on removal efficiency of surfactant-modified cotton stalks. Adsorption experiments: surfactant concentration, CMC (SDS, 8.0 mM) was used for each of the surfactant types, heavy metal concentration, 200 mg L^{-1}; SMCS dose, 0.5 g/100 mL; pH, 7.0; contact time, 120 min.

Hexadecyltrimethylammonium (HDTMA) was used as a cationic surfactant, sodium dodecyl sulfate (SDS) and sodium lauryl sulfate as anionic surfactants and nonyl phenol and ethoxylated lauric acid as nonionic surfactants. The results of the addition of these three kinds of surfactant into cotton stalks are shown in Fig. 1. As it can be seen in this figure that cationic and nonionic surfactants have nearly the same effect, but the most efficient surfactant in increasing the removal efficiency are SDS and lauryl sulfate which are the anionic surfactants.

When the charge of the surfactant would be the same sign as the surface, then the repulsion of the charges cause to prevent the adsorption. This situation will exist for anionic surfactant onto negatively charged surface and cationic surfactant onto positively charged surface. Adsorption of ionic surfactants onto the surface with the same charge can occur rarely via hydrogen bonding or attractive dispersion forces (Rosen, 2004), as is the case for nonionic surfactants. On a cellulose substrate, previous studies have indicated that nonionic surfactants can be adsorbed, at least partly, by hydrogen bonding between the hydroxyl groups of the cellulose and the ether linkages of the hydrophilic chain of nonionic surfactants (Rosen, 2004). Adsorption of the surfactant onto the cellulose substrate in this mode makes the latter more hydrophobic and impedes the removal of heavy metals. This may also account for the poor performance of cationic surfactant modified cotton stalks. Since cotton stalk residue acquires a negative charge at neutral pH, cationic surfactants may be adsorbed onto it by electrostatic attraction between the negatively charged sites on the fiber and the positively charged hydrophilic groups of the surfactant, with the hydrophobic groups of the adsorbed surfactant molecules oriented toward the solution. This orientation of the cationic surfactant onto the cotton residue will make it more hydrophobic and thus impede the removal of heavy metals.

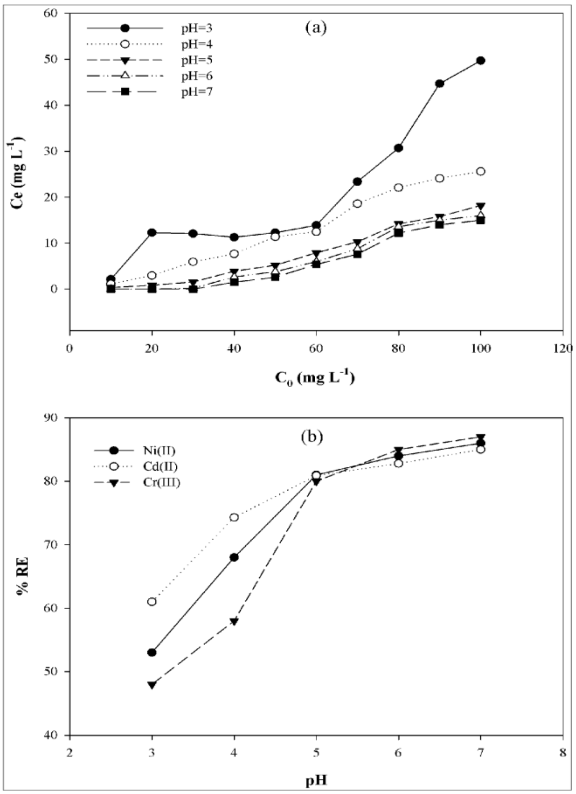

Fig. 2. a) The effect of pH on removal efficiency of Cd(II) in different initial concentrations of Cd(II) using SMCS (SDS, 8.0 mM) b) The effect of pH on removal efficiency of Ni(II), Cd(II) and Cr(III), initial concentration of 80 mg L^{-1} of each metal ion, using SMCS (SDS, 8.0 mM).

Anionic surfactants, by contrast, may not be adsorbed well onto negatively charged CS residue; however, they can adsorb onto it only with their negatively charged hydrophilic groups oriented away from the similar charged substrate, and toward the solution (Rosen, 2004). Therefore, its hydrophilic character increased and facilitated cationic HMs deposition on the surface of cotton residues. In addition, surface chemical heterogeneities of negatively charged surfaces can be masked by the addition of an anionic surfactant (Litton, 1994, Hull, 1969) which results in a more uniform distribution of negative surface charge (Litton, 1994). By adding anionic surfactants, there would be more negative charge sites on cotton stalk surface and consequently cationic heavy metals will be adsorbed more effectively. That explains why SDS, an anionic surfactant, showed the highest removal efficiency to HMs tested in this work. In this study, SDS was thus selected as the most efficient surfactant to modify CS for further investigation.

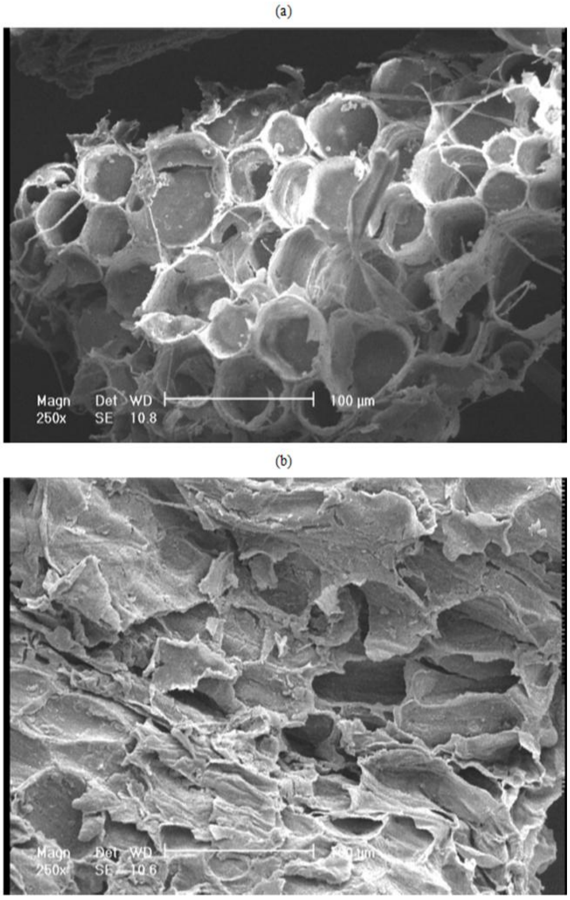

Fig. 3. SEM micrograph of a) cotton stalk and b) surfactant modified cotton stalk.

Effect of pH

pH of the solution has a significant impact on the uptake of HMs because it determines speciation of the adsorbate and the charge of the adsorbent surface. Removal of the metal ions as a function of pH is presented in Fig. 2 (a). These studies were carried out using 0.5 g SMCS (using SDS, 8.0 mM) in 100 mL solutions at different initial concentration of Cd(II). The adsorption of Cd(II) on the prepared cotton stalks increases with the increase in pH. The removal of Cd(II) is found to increase as the pH increases beyond 3.0 and at pH of 7.0 the uptake has maximum level. Adsorption of Cd(II) is low at pH lower than 3.0; it increases from 80% to 90% at pH 5.0–7.0. At the pH values more than 7.0, Cd(II) hydroxide starts precipitating which means that removing of Cd(II) from aqueous solution is accomplished via precipitation process. This mechanism may lead to inaccurate results about sorption studies. This type of behavior has also been observed for other hydrolysable metals (Mathialagon, 2002).

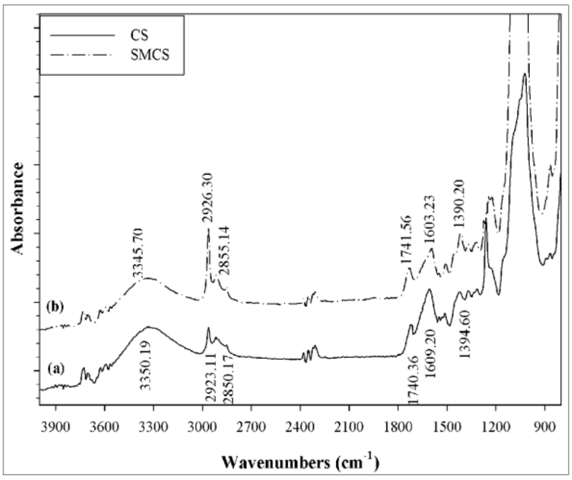

Fig. 4. FTIR spectra of (a) cotton stalk and (b) surfactant modified cotton stalk.

At low pH values, surface of the adsorbent would be surrounded by hydronium ions which decrease the cationic metal interaction with binding sites of the cotton residues by greater repulsive forces. Thus, it may be concluded that at low pH values, ion-exchange reaction involving metals are in competition with the high concentrations of H^+ in the solution. Considering the fact that cellulose surface would be negative charged in neutral and alkali aqueous solutions (Myllytie, 2009), as the pH increased, the overall surface on the cotton residues became negative and adsorption increased. Thus for further studies the optimum initial pH chosen for studied heavy metals was 7.0, to correlate the removal with the adsorption process. The results of the effect of pH in removal efficiency of Ni(II) and Cr(III) which are shown in Fig. 2 (b), also demonstrate that the pH of 7.0 is proper for removal experiments.

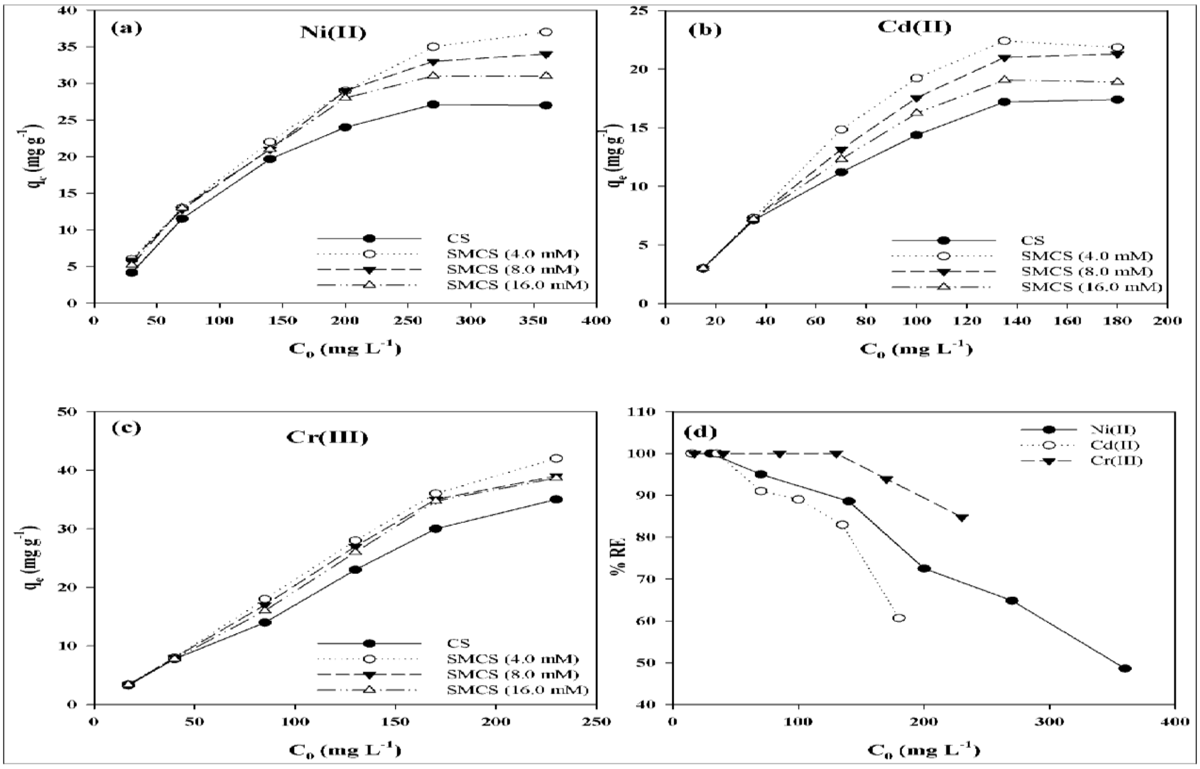

Fig. 5. Effects of initial ion concentration and surfactant concentration on biosorption of a) Ni(II), b) Cd(II), c) Cr(III) ions by CS and SMCS biosorbents d) Effect of initial ion concentration on removal efficiency of Ni(II), Cd(II) and Cr(III) using SMCS. (pH 7.0; biomass dose, 0.5 g/100 mL; contact time, 2 h).

Characterization of CS and SMCS

The morphological characteristic of the CS and SMCS was investigated by scanning electron microscopy. The results of SEM analysis for CS and surfactant modified CS (SMCS) are shown in Fig. 3. The structure of CS surface, as shown in Fig. 3a, is highly porous and sponge-like. The CS biosorbent has some cavities on the external surface capable of uptaking heavy metals. This structural feature of the biomass may be important since it increases the total surface area (Sud, 2008), Comparison of the SEM images indicates that the surface morphology of SMCS (Fig. 3b) is different from that of the natural CS. The SEM image of SMCS shows that the surface architecture of SMCS is much smoother and more homogeneous in comparison to CS, indicating that surfactant may be homogeneously dispersed throughout modification onto the surface of CS. Infrared spectra can provide useful information concerning chemical groups of biosorbents. In the present work, the main effective binding sites of CS and SMCS biosorbents have been compared using FTIR. CS is mainly comprised of cellulose but also includes other compounds, such as phenolics and organic acids. Figure 4a shows IR spectrum of CS. The vibrational modes in the 3500 to 2800 cm^{-1} region are mainly due to stretching the O-H and C-H (Silverstein, 1998, Himmelsbach, 2003). The broad and strong bond at about 3350 cm^{-1} is indicative of $-OH$ and $-NH_2$ groups. The peaks at 2923 and 2850 cm^{-1} are attributed to the stretching vibrations of $-CH_2$ groups. The modes in the 1800 to

1500 cm^{-1} region are from the carbonyl functional group, as well as some overlapping involvements of C-H bending vibrations (Himmelsbach, 2003). The band at 1609 cm^{-1}, which is caused due to olefinic, C═C vibrations, indicates the olefinic, C═C bonds or phenyl groups. The absorption band at 1740 cm^{-1}, which is ascribed to C═O vibrations in carbonyl groups, shows the presence of acetyl derivative group, aldehyde groups, etc. The region below 1500 cm^{-1}, the fingerprint region, is made up of additional bands that correlate mainly to carbohydrates and other bio-constituents (Boeriu, 2004, Chung, 2004). The FTIR spectrum of SMCS is shown in Fig. 4b.

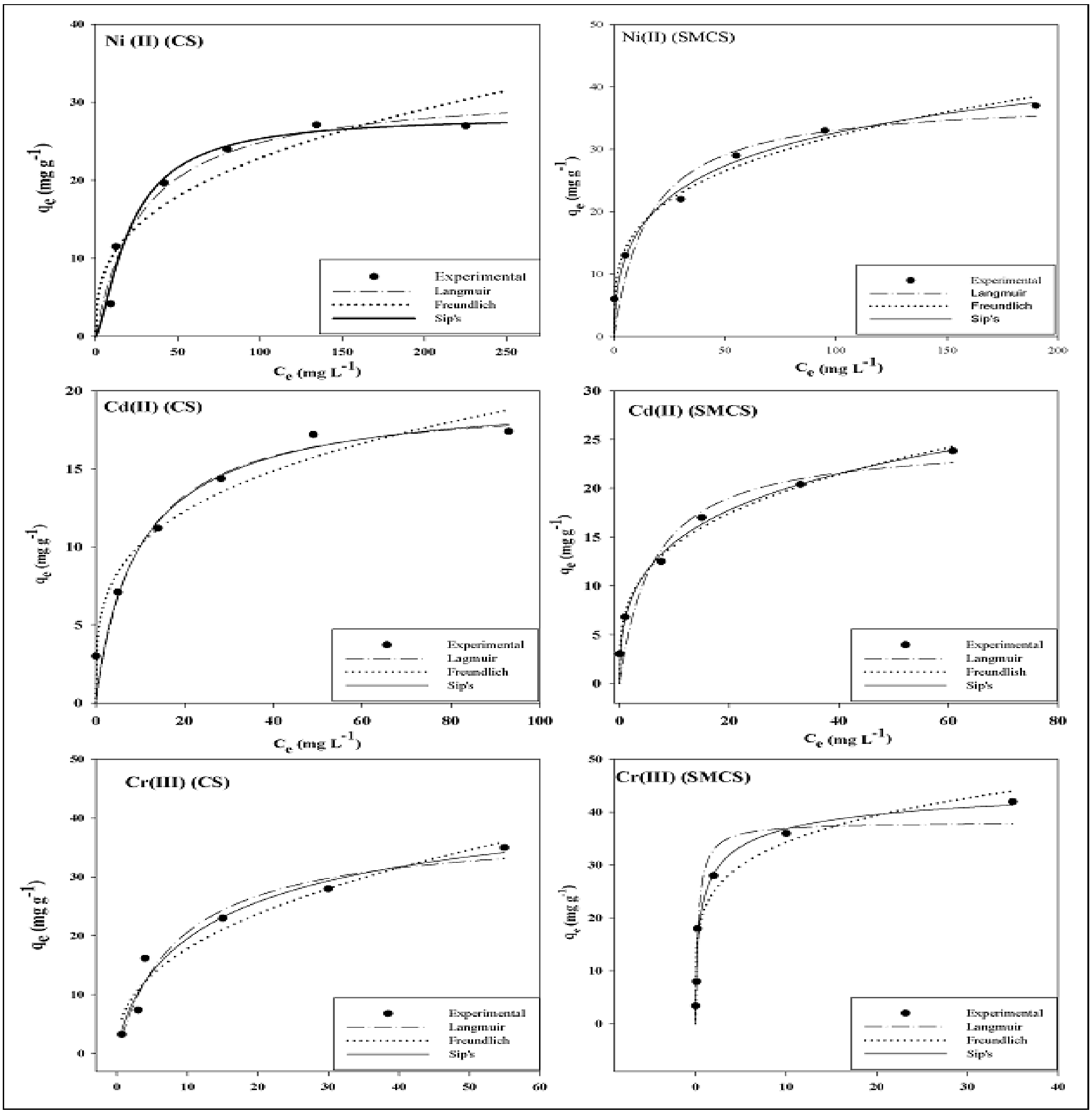

Fig. 6. Biosorption isotherms of Ni(II), Cd(II) and Cr(III) ions on CS and SMCS.

In comparison with spectrum of CS, that of SMCS shows more intense absorption bands at 2926 and 2855 cm^{-1} attributing to $-CH_3$ and $-CH_2$ groups. Furthermore, the peak at 1390 cm^{-1} ascribed to C–H bending vibration also significantly increased. These clearly indicate that natural CS has been successfully modified by surfactant. On the whole, other characteristic peaks of the CS sample do not change after modification, which implies that most likely the surfactant molecules is present on the surface of CS particles through dispersion forces between adsorbate and adsorbent.

Effect of SDS treatment and initial metal ion concentration

The effect of initial concentration on the removal capacity of heavy metals by the CS and SMCS is shown in Fig. 5. These adsorption curves were obtained from experiments where adsorptions of Ni(II), Cd(II) and Cr(III) HMs in wastewater aqueous solution were studied simultaneously. The adsorption of Ni(II), Cd(II) and Cr(III) by CS and SMCS biomass was studied at different ion concentrations in the range of 30-360 mg L^{-1} of Ni(II), 15-180 mg L^{-1} of Cd(II) and 20-230 mg L^{-1} of Cr(III). As shown in Fig. 5 (a, b, c), while the dosage of CS remains constant (5.0 g L^{-1}), the removal capacity increases with increasing initial concentrations of the HM ions till the metal ions' uptake value reached the state of equilibrium saturation. This may be due to the fact that a higher initial HM ion concentration increases driving force to overcome the mass transfer resistance of HM ions between the aqueous and solid phases resulting in higher chance of collision between the ions and the adsorptive sites on the surface of adsorbent. This figure also shows the effect of different concentration of SDS surfactant used for modification of CS. Figure 5 (a, b, c) shows that the adsorption capacity of the SMCS biosorbent was increased for metal ions compared to CS biosorbent. This means that additional binding sites were provided for metal ions by incorporation of surfactant into CS natural support material. This may be attributed to creation of uniform negative charge on CS surface by adding SDS which increased the affinity of HM cations into the sorbent surface. The results also show that the most increment in adsorption capacity is related to 4.0 mM of SDS which is below the CMC. Further increase in the concentration of SDS, 8.0 mM and 16.0 mM, decreased the removal percentage of three ions. Similar results were reported by Rao *et al.* Rao, 2010, They reported that addition of SDS at the concentration of 2.0 mM favored the adsorption process of Zn(II) on carbon derived from mustard oil cake (CMOC). The critical micelle concentration (CMC) of SDS is 8.0 mM. The percentage adsorption increases in presence of SDS below its CMC value (8.0 mM) Lin, 1990, A decrease in adsorption above CMC may be due to slow transfer of micelles–metal complex from bulk to the surface of the biosorbent (Das, 2012).Therefore all further biosorption experiments were carried out using 4.0 mM SDS.

The effect of initial concentration on the percentage of removal efficiency of HMs by the SMCS is shown in Fig. 5d. On this figure, it can be seen that percent removal decreases with the increase in initial HM concentration. These results may be due to increase in the number of ions competing for available binding sites and also because of the lack of active sites on the biomass at higher concentrations. Therefore, at higher initial HM ion concentration levels more ions were left unadsorbed in solution. Furthermore, it can be observed that the uptake capacity for Cr(III) ions was significantly higher than other metal ions evaluated. The percentage removal of Cr(III) is almost complete (nearly 100%) at initial metal ions concentration range of 10-130 mg L^{-1} for 5.0 g L^{-1} adsorbent dose, at pH 7.0 and a contact time of 2 h. The results also show that removal efficiency of Ni(II) and Cd(II) is higher than 90% using SMCS at ions concentration of 1-100 mg L^{-1}. According to Fig. 5d, adsorption capability of CS and SMCS for these HM ions can be ordered as Cr(III) >Ni(II) >Cd(II).

Isotherms

Biosorption isotherms describe the interaction of adsorbate with biosorbents and equilibrium which is established between adsorbed metal ions on the biosorbent and the residual metal ions in the solution during surface biosorption process. A biosorption isotherm, characterized by certain constant values, expresses the surface properties and affinity of the biosorbents Senturk, 2010, and can be used to compare biosorptive capacity of the biosorbent for various HMs. In this work, simultaneous biosorption of Ni(II), Cd(II) and Cr(III) ions by CS and SMCS (using 4.0 mM of SDS) was studied using wastewater solutions. Three well-known adsorption isotherms were chosen to fit the experimental data regarding the sorption of metal ions on the surface of the biomass. The biosorption isotherm was characterized by Langmuir, Freundlich and Langmuir-Freundlich isotherm (also known as Sip's model), to describe the equilibrium between adsorbed metal ions and metal ions in the solution. The Langmuir model assumes monolayer coverage of sorption of adsorbate onto a homogeneous surface containing finite number of identical sorption sites with homogeneous adsorption energy. Generally-used Langmuir isotherm is represented by the following equation (Yusan, 2010).

$$q_e = \frac{\left(q_{\max} b C_e\right)}{1 + b C_e} \qquad (3)$$

Where q_e is the amount of biosorbed (mg g^{-1}) at equilibrium, $q_{\max}$ is the Langmuir constant (mg g^{-1}) reflecting the maximum adsorption capacity of the metal ion per unit weight of the biosorbent to form a complete monolayer on the biosorbent surface, C_e is the equilibrium metal ion concentration in the solution (mg L^{-1}) and b is the biosorption constant (L mg^{-1}) which represents the affinity of the metal toward the binding sites present on the biosorbent surface (Zeng, 2010).

The Freundlich isotherm equation is also used to describe adsorption from a solution and is given by (Rosales, 2012).

$$q_e = K_f\, C_e^{1/n} \qquad (4)$$

Where K_f [(mg g^{-1})(mg L^{-1})^n] is a constant for relative adsorptive capacity and n is an affinity constant. The Freundlich isotherm interpreted to be used in the case of sorption of heterogeneous surfaces or surfaces supporting sites of different affinities. Freundlich isotherm supposes a multilayer biosorption on a heterogeneous surface with a nonuniform distribution of heat of biosorption over the surface.

The three-parameter Sip's model (Sips, 1948, Witek-Krowiak, 2011) is combination of Langmuir and Freundlich models and is given by:

$$q_e = \frac{q_{\max} \left(b C_e\right)^n}{1 + (b C_e)^n} \qquad (5)$$

Where, q_e is the amount of biosorbed (mg g^{-1}) at equilibrium, $q_{\max}$ is the constant (mg g^{-1}) reflecting maximum adsorption capacity of the metal ion per unit weight of the biosorbent, C_e is the equilibrium metal ion concentration in the solution (mg L^{-1}) and b is the affinity constant (L mg^{-1}) for adsorption. In this equation, n is dissociation parameter. If $n = 1$, the Sip's model reduces to Langmuir model (Chabani, 2009), Figure 6 represents the experimental biosorption isotherm of Cd(II), Ni(II) and Cr(III) ions on CS and SMCS. It could be seen that q_e increased initially with an increase in C_e until equilibrium was reached, after which q_e remained constant with further increase in C_e. The Langmuir, Freundlich and Sip's biosorption constants evaluated from the isotherms with the correlation coefficients related to CS and SMCS are listed in Table 1. Considering the results of Freundlich model, n values in the range of 1–10 indicated favorable adsorption. According to Table 1, the R^2 value of Langmuir isotherm attributed to biosorption of Ni(II) on the surface of CS (0.955), is much higher than the R^2 value of Freundlich model (0.852), indicated that biosorption of Ni(II) onto the surface of CS was a monolayer biosorption. The Sip's model is also perfect for describing the biosorption of nickel ions from aqueous solutions. Considering the results of Sip's model, value of n is closer to unity than zero, which implies that the isotherm is more approaching Langmuir than Freundlich isotherm. Hence, the monolayer coverage process of Ni(II) onto cotton residue approved by the best fit of equilibrium data in both sip's and Langmuir isotherm expressions.

The best correlation between the model and experimental data for Cd(II) into CS was obtained by using Langmuir model (R^2= 0.940) which illustrated that sorption of Cd(II) on the surface of CS was also a monolayer biosorption. The value of n from Sip's model (0.932) also shows that sorption behavior of cadmium ions into CS surface is much similar to Langmuir isotherm. The correlation coefficients (R^2) ranged from 0.946 to 0.963 for Cr(III) biosorption (Table 1) indicating that equilibrium data fitted well to the Langmuir, Freundlich and also sip's model. However, the n value of Sip's model (0.862) suggested that the best biosorption isotherm for Cr(III) into CS would be Langmuir model. According to Langmuir isotherm, the $q_{\max}$ value attributed to CS biosorbent for Cr(III) ions was 38.29 mg g^{-1}, and showed that biosorption uptake is higher than that observed for Ni(II) ions (31.91 mg g^{-1}) and also Ni(II) higher than Cd(II) ions (19.58 mg g^{-1}).

Adsorption constants in Table 1 show that the three-parameter Sip's model describes adsorption of metal ions into SMCS better than that of Langmuir and Freundlich models. The highest R^2 values were 0.944, 0.969 and 0.971 for Ni(II), Cd(II) and Cr(III), respectively. According to this table, the n values of Sip's model in SMCS biosorption for the three HM ions are closer to zero, which implies that the isotherms are more approaching Freundlich than Langmuir isotherm. It can be seen from the table that R^2 values of Freundlich model, which are higher than the Langmuir model, confirm this result. Therefore, it is indicated that sorption of Ni(II), Cd(II) and Cr(III) ions seems to be a multilayer sorption, and the adsorption takes place on a nonuniform SMCS surface. Maximum biosorption capacity ($q_{\max}$, mg g^{-1}), that is a measure of adsorption capacity into SMCR adsorbent, for Ni(II), Cd(II) and Cr(III) was found to be 33.21, 25.43 and 47.66 mg g^{-1}, respectively, which increases in the order: Cr(III) > Ni(II) > Cd(II). Comparison of $q_{\max}$ values also corresponds to CS and SMCS in Sip's model results shows that uptake of the studied HMs is higher into SMCS than the CS adsorbent.

Conclusions

This study confirms that raw and surfactant-modified cotton stalks can be successfully used as biosorbents for removal of Ni(II), Cd(II) and Cr(III) in industrial effluents. It was determined that optimum adsorption condition takes place for the surfactant concentration below CMC, pH, of 7.0 and contact time of 2 h. Comparison of the removal capacity of CS and SMCS demonstrated that SMCS sorbent is more effective than CS for biosorption of Ni(II), Cd(II) and Cr(III) ions. Experimental results were fitted by using two- and three-parameter equilibrium isotherm equations. Adsorption of these HMs onto the CS and SMCS was well described by the Sip's isotherm model. However, R^2 values of the models and n values of Sip's model imply that Freundlich isotherm describes HM sorption on SMCS in a greater degree, while Langmuir isotherm fits better HM sorption on CS. According to Sip's isotherm, maximum adsorption capacity of SMCS biomass for Ni(II), Cd(II) and Cr(III) was found to be 33.21, 25.43 and 47.66 mg g^{-1}, respectively. The results of the experiments also showed that maximum removal efficiency of 100% was achieved for Cr(III) and ≥ 90% for Ni(II), Cd(II) in concentration range of 1-100 mg L^{-1} of HM ions. Because of high surface area, low cost, non-toxicity and adsorption capacity of SMCS, this adsorbent can be considered as one of the most effective options to remove Ni(II), Cd(II) and Cr(III) from wastewater solutions. This, further proves that surfactant modification plays an important role in sorption processes and reflects a promising future for biosorbents in HM removal from wastewater solutions.

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