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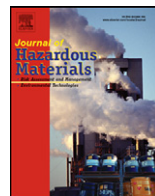
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Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Utilization of carbon derived from mustard oil cake (CMOC) for the removal of bivalent metal ions: Effect of anionic surfactant on the removal and recovery

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ARTICLE INFO

Article history:

Received 17 June 2009

Received in revised form 18 August 2009

Accepted 18 August 2009

Available online 25 August 2009

Keywords:

Sodium dodecyl sulfate

Chemical adsorption

Pore diffusion

Film diffusion

ABSTRACT

Effect of sodium dodecyl sulfate (SDS) on the adsorption of Zn(II) and Ni(II) on CMOC was investigated. Addition of SDS favored the adsorption process. Adsorption process was found to be dependent on concentration, pH, dose, contact time and temperature. Thermodynamic studies showed that the process is endothermic and spontaneous. The spontaneity increases with increase in temperature. *D-R* isotherm suggests that the adsorption is chemical in nature. Kinetics studies showed better applicability of pseudo second order model. Reichenberg equation showed that pore diffusion was not only the rate determining step but some other process like film diffusion was also involved in the adsorption. These metals could be desorbed (75–80%) with 0.1 M HCl as eluent.

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1. Introduction

The extent of heavy metal adsorption is a critical component in the evaluation of their fate in natural water systems. Heavy metals discharged from civil and industrial wastewater streams have become an ecotoxicological hazard of prime interest. Heavy metals represent a major problem for the environment since they are non-biodegradable and have the tendency to accumulate in vital organs of humans and animals, thereby posing a threat to flora and fauna.

Various techniques have been employed for the treatment of heavy metals such as chemical precipitation, electrolysis, ion exchange, reverse osmosis and adsorption [1–5]. Surfactant based separation processes [6] such as micellar enhanced ultra filtration (MEUF) have shown to be an effective alternative in removing the multivalent metal ions from waste streams [7]. A disadvantage of MEUF is the relatively large concentration of surfactant that must be used for effective separation. Often the economic viability of the MEUF process is strongly dependent on the ability to recover or recycle a substantial expense to the separation [8] or makes the processed effluent environmentally unacceptable.

Adsorption technique using a number of organic, inorganic, natural, synthetic, activated or modified adsorbents is the most widely employed procedure in the wastewater treatment. Low cost alternatives or cheaper and effective adsorbents are still needed. Use

of oil cakes as an adsorbent for the removal of heavy metals is an effective alternative [9,10] as they are cheaper than other materials such as activated carbon and zeolite and are abundantly available. The other advantage of using oil cakes as an adsorbent is the low C/N ratio therefore their degradation is rapid [11].

The aim of this work was to study the effect of sodium dodecyl sulfate (SDS) on the adsorption of Zn(II) and Ni(II) on carbon derived from mustard oil cake (CMOC). Surfactants, surface-active agents can be synthetic but are also naturally produced by plants, animals and many different microorganisms. These molecules reduce surface and interfacial tensions in both aqueous and hydrocarbon mixtures.

2. Material and methods

2.1. Adsorbent preparation

Mustard oil cake (MOC) was burnt in a furnace at 700 °C for about 15 min in absence of air in order to remove organic matter. The carbon obtained by burning MOC was named as carbonized mustard oil cake (CMOC). CMOC was crushed to a desired mesh size (300–100 µm). The CMOC was washed several times with double distilled water (DDW) and then dried at 65 °C for 24 h in an oven.

2.2. Preparation of adsorbate solution

Single-component stock solution of Ni(II) and Zn(II) and were prepared (1000 mg/L) by dissolving the desired quantity of their nitrate salt (CDH, India, A.R. grade) in DDW. Stock solu-

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tion of anionic surfactant (0.1 M) sodium dodecyl sulfate (SDS) ($C_{12}H_{25}OSO_3Na$) was prepared by dissolving the desired quantity of SDS (Merck Co. Ltd., India, A.R. grade) in DDW.

2.3. Characterization of adsorbent

FT-IR spectra of completely dried blank sample before and after the metal ions adsorption with and without SDS were recorded using KBr technique with a spectrum GX series 49387 spectrometer in the range $4000\text{--}600\text{ cm}^{-1}$. The surface morphology of aforesaid samples was also recorded by using scanning electron microscope (SEM) after gold sputter coatings on a desired membrane samples.

2.4. Determination of active sites

Active sites present on the surface of the biosorbent were determined by acid–base titration method [12]. Acidic sites were determined by adding 50 mL of 0.1N titrating solution and 1 g of biosorbent to 100 mL of stopper corked conical flask. The flask was slowly agitated at room temperature (30°C) in a shaker and was left for 5 days. Afterwards, a sample of 10 mL was titrated with 0.1N HCl solution to its neutralization point. The titration was done in triplicate [12].

2.5. Characterization of the surfactant

The critical micelle concentration (CMC) of SDS used is 8 mM [13]. In aqueous solution without electrolysis, the reported micelles aggregation number for SDS is 64 [14]. That gives the micelles equivalent molecular weight of $\approx 18\text{ kDa}$.

2.6. Adsorption/desorption studies

Adsorption studies were carried out by batch process. 0.25 g adsorbent was placed in conical flask with 25 mL solution of metal ion of desired concentration. The mixture was shaken in temperature controlled shaker incubator for 24 h at 120 rpm. The mixture was then filtered using Whatman filter paper number-41 and final concentration of metal ion was determined in the filtrate by atomic absorption spectrophotometer (AAS) (GBC 902, Australia). The % removal of adsorbate and equilibrium adsorption capacity (q_e), were calculated using the following relationships.

$$\% \text{ Removal} = \left[\frac{(C_0 - C_e)}{C_0} \right] \times 100 \quad (1)$$

$$\text{Adsorption capacity } (q_e) (\text{mg/g}) = [(C_0 - C_e)] \times \frac{V}{W} \quad (2)$$

where, C_0 initial concentration of adsorbate (mg/L); C_e equilibrium adsorbate concentration (mg/L); V volume of the solution (L); W mass of the adsorbent (g).

Desorption studies were also carried out by batch process. 50 mL solution of Ni(II), Zn(II) and each of 50 mg/L metal ions concentration in presence of (2 mM) SDS was treated separately with 0.5 g of adsorbent in temperature controlled shaker incubator at 120 rpm for 24 h. The adsorbent in each flask was washed several times with DDW to remove excess of metal ions. The adsorbent after washing was treated with 50 mL of water and kept for 24 h. The water was then analyzed for leaching of metal ions. The adsorbents in other flasks were treated with 50 mL of various eluents. The flasks were shaken in temperature controlled shaker incubator at 120 rpm for 24 h. The solutions were then filtered by using Whatman filter paper number-41 and filtrates were analyzed for the metals desorbed.

2.7. Effect of pH

The effect of pH in the range 2–10 for the adsorption of metal ions on CMOC was studied by batch process as follows: 50 mL of metal ions solution (50 mg/L initial concentration) was taken in a beaker. The pH of solution was adjusted by adding 0.1N HCl or 0.1N NaOH. The concentration of metal ions in this solution was then determined (initial concentration). 25 mL of this solution was taken in conical flask and treated with 0.25 g adsorbent and after equilibrium, the final concentration of metal ions was determined.

2.8. Point of zero charge (PZC)

The zero surface charge characteristics of CMOC were determined by solid addition method [15] using 0.1 M KCl and $2 \times 10^{-3}\text{ M}$ SDS solutions. 40 mL of KCl and SDS solution of desired strength was transferred to a series of 100 mL stoppered conical flasks. The initial pH (pH_i) values of the solutions were roughly adjusted between 2 and 12 by adding either 0.1N HCl or 0.1N NaOH. The total volume of the solution in each flask was adjusted exactly to 50 mL by adding the KCl and SDS solution of the same strength. The pH_i of the solutions was then accurately noted. 0.5 g of CMOC was added to each flask, and the flask was securely capped immediately. The suspensions were then manually shaken and allowed to equilibrate for 48 h with intermittent manual shaking. The final pH values of the supernatant liquid were noted. The difference between the initial and final pH (pH_f) values ($\Delta pH = pH_i - pH_f$) was plotted against the pH_i . The point of intersection of the resulting curve with abscissa, at which $\Delta pH = 0$, gave the PZC.

2.9. Effect of contact time

A series of 100 mL conical flasks, each having 0.25 g adsorbent and 25 mL solution of 50 mg/L initial concentration of metal ions were shaken in temperature controlled shaker incubator at 120 rpm and at the predetermined intervals, the solution of the specified flask was taken out and filtered. The concentration of metal ions in the filtrate was determined by AAS. The amount of metal adsorbed in each case was then determined as described earlier.

The rate constants were calculated by pseudo-first-order and pseudo-second-order models. The pseudo-first-order kinetic model as expressed by Lagergren [16]. The values of pseudo-first-order rate constant (K_1) for Zn(II) and Ni(II) in presence and absence of SDS were calculated from slope the linear plot of $\ln(q_e - q_t)$ vs. t . The values of pseudo-second-order kinetic rate constant (K_2) [17] for Zn(II) and Ni(II) in presence and absence of SDS were calculated from the slope of the linear plot of t/q_t vs. t .

The nature of adsorption was also verified by Reichenberg equation [18]. The linearity test of βt vs. time (t) plots is employed to distinguish between film and particle diffusion controlled rates of adsorption.

2.10. Effect of adsorbent dose

A series of 100 mL conical flasks each containing 25 mL of metal ions solution (50 mg/L) were treated with varying amount of adsorbent (0.1–1.0 g). The flasks were shaken in shaker incubator at 120 rpm and after equilibrium (24 h) the solutions were filtered. The amount of metal ions in filtrate was then determined by AAS. The amount of metal adsorbed in each case was calculated as above.

2.11. Quality assurance and quality control

To make sure that no metal ions were released to the solution from the adsorbent, an equilibrium test was performed using

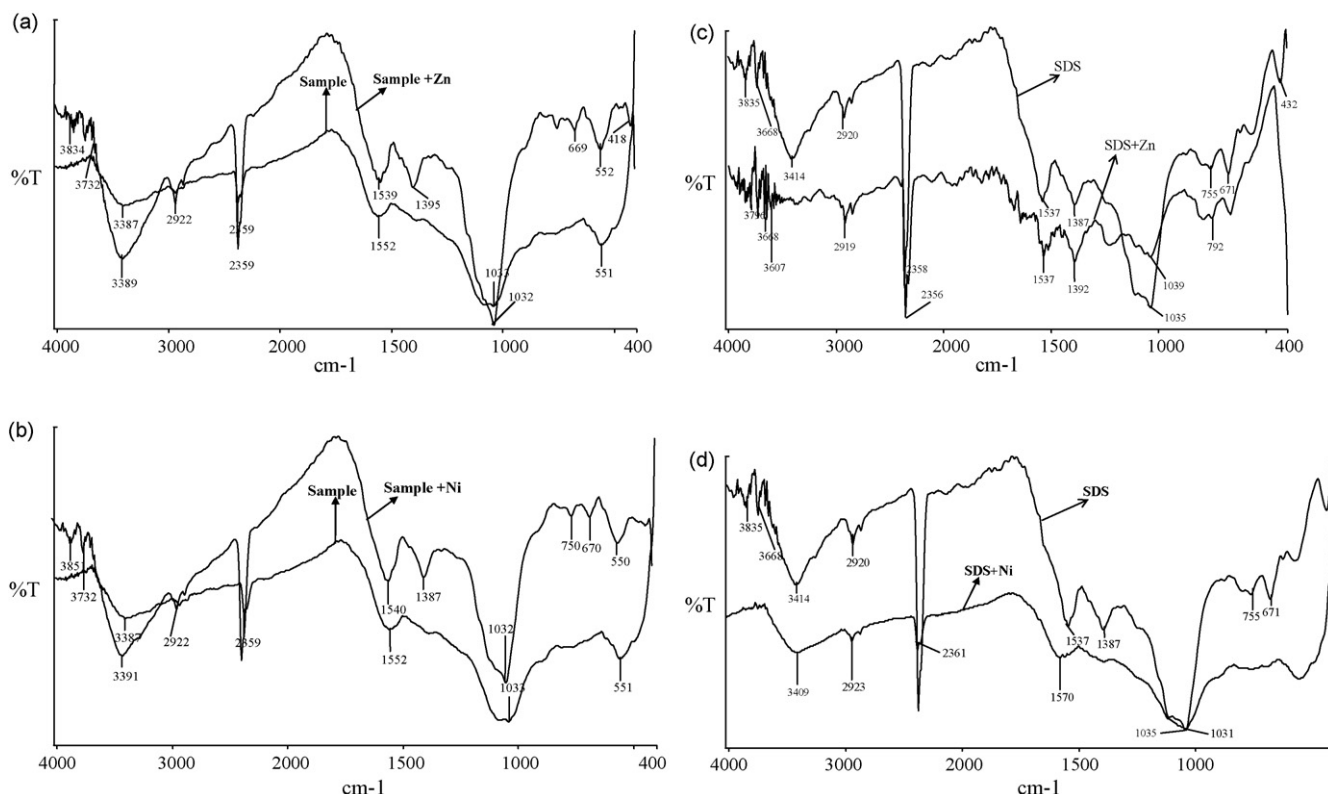


Fig. 1. (a) FTIR spectrum of sample (CMOC) before and after adsorption of Zn(II). (b) FTIR spectrum of sample (CMOC) before and after adsorption of Ni(II). (c) FTIR spectrum of sample (CMOC) loaded with SDS before and after adsorption of Zn(II). (d) FTIR spectrum of sample (CMOC) loaded with SDS before and after adsorption of Ni(II).

adsorbent CMOC in DDW. For assuring quality in the adsorption studies distilled water blank and two duplicates were included in the experiment. To ensure accuracy after each set of five samples, a standard was run to ensure that drift had not occurred.

The samples were analyzed in triplicate by AAS. Average of the values obtained gives mean concentration of the sample. In order to compare quantitatively the applicability of different models in fitting to data, the percent relative deviation (P), was calculated by equation:

$$P = \frac{100}{N} \sum \left\{ \frac{q_{e(\text{exp})} - q_{e(\text{theo})}}{q_{e(\text{exp})}} \right\} \quad (3)$$

It is generally accepted that when P value is less than 5, the fit is considered to be excellent [19].

3. Result and discussions

3.1. Characterization of adsorbent

3.1.1. Fourier transform infrared spectroscopy (FT-IR) analysis

FT-IR spectrum of CMOC before and after the adsorption of metal ions (Ni(II) and Zn(II)) in presence or absence of SDS were obtained and presented in Fig. 1(a–d). Some of the bands were originated from the blank sample and can be assigned. The broad and strong absorption peaks at 3387 cm^{-1} was the characteristics of $-\text{OH}$ stretching vibration (Fig. 1a and b). The strong and intense peaks at 2919 – 2923 cm^{-1} were aroused due to the $-\text{CH}_2$ and CH_3 asymmetric and symmetric stretching vibrations (Fig. 1c and d). The very intense peaks in the region 1537 – 1570 cm^{-1} were obtained, which were the characteristics of stretching mode of carbonyls and their salts (Fig. 1c and d). In addition, the peaks at 1387 – 1392 cm^{-1} were aroused due to the stretching vibration of $\text{O}=\text{S}=\text{O}$ of sulphate, which was observed in carbon samples in presence SDS adsorption

along with metal ions and were attributed to the contribution from the surfactant (Fig. 1c and d) [20].

3.1.2. Scanning electron microscope (SEM) analysis

The surface studies of CMOC shows smooth and clear surface with no preoccupation (Fig. 2a). Adsorption of Zn(II) and Ni(II) on CMOC leads to the surface coverage with irregular and non-uniform particles all over the surface (Fig. 2b and c). Adsorption of SDS on CMOC shows heterogeneous surface coverage with pores (Fig. 2d). The adherence of Zn(II) and Ni(II) in presence of SDS on CMOC leads to the formation of an agglomerative mass like structures showing strong binding of Zn(II) and Ni(II) in presence of SDS on CMOC (Fig. 2e and f).

3.2. Determination of active sites

The total numbers of acidic sites matching carboxylic, phenolic, and lactonic sites were neutralized using alkaline solutions (0.1 N NaOH , 0.1 N NaHCO_3 , $0.1 \text{ N Na}_2\text{CO}_3$). The carboxylic and lactonic sites were titrated with $0.1 \text{ N Na}_2\text{CO}_3$ solution, the carboxylic sites were determined with 0.1 N NaHCO_3 solution and the phenolic sites were estimated by the difference [12] (Table 1).

Table 1
Concentration of active sites on CMOC surface.

Sites	Concentration (mequiv./g)
Acidic sites	
Total sites	2.82
Carboxylic and lactonic	1.41
Carboxylic	0.45
Phenolic	0.96
Basic sites	0.62

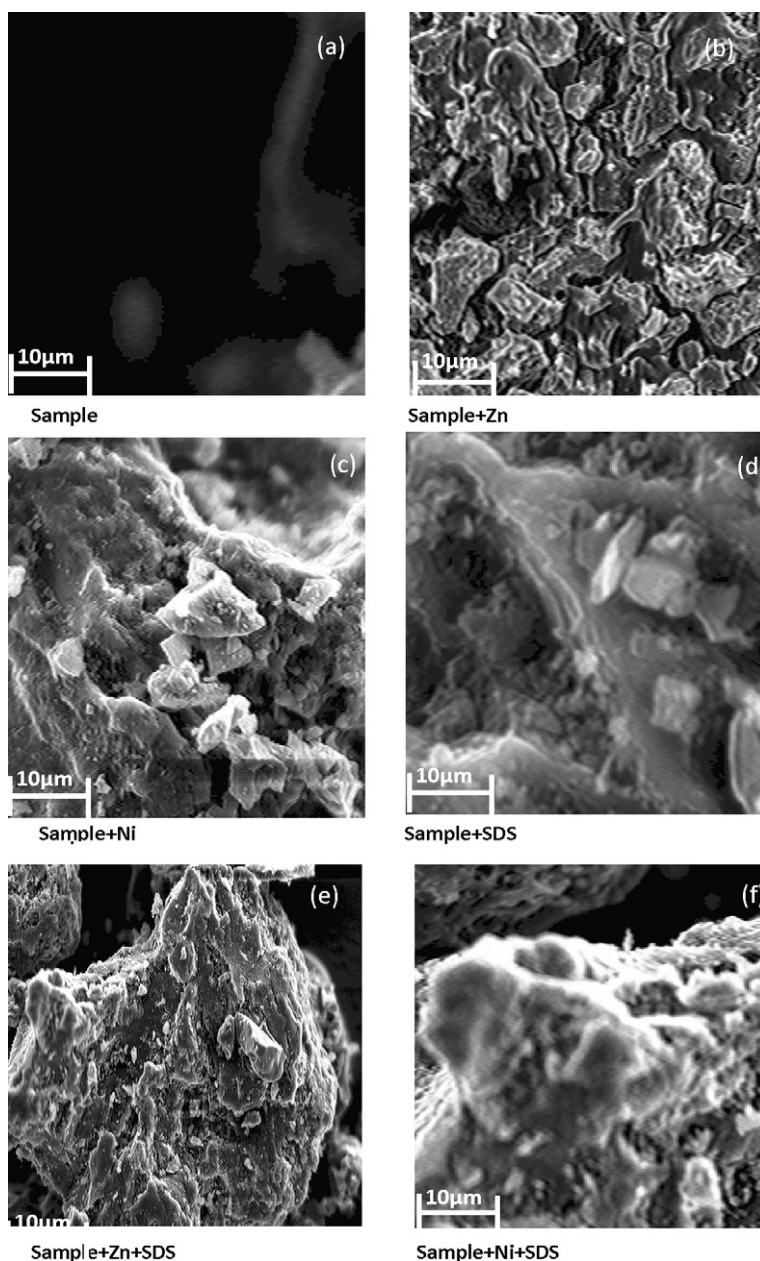


Fig. 2. (a–f) SEM images of CMOc (sample) before and after adsorption.

3.3. Effect of SDS concentration

The adsorption of Zn(II) and Ni(II) (initial concentration 50 mg/L) on CMOc in absence of SDS is 85.6% and 60.4%, respectively (Fig. 3). The percentage adsorption increases in presence of SDS below its critical micelle concentration (CMC) value (8 mM), above CMC value of SDS the percentage adsorption decreases. The percentage adsorption of Zn(II) and Ni(II) on CMOc is 96% (maximum) and 85.8% (maximum), respectively at 2 mM SDS concentration. Further increase in the concentration of SDS decreases the percentage adsorption (Fig. 4). Therefore below CMC value, metal cations are preferentially adsorbed as compared to large negatively charged SDS ions. A decrease in adsorption above CMC may be due to slow transfer of micelles–metal complex from bulk to the surface of the adsorbent. The physico-chemical properties of surfactants vary markedly above and below the CMC values. Below the CMC values, the physico-chemical properties of ionic surfactants (SDS) resemble those of a strong electrolyte [21]. Above CMC, surfactant

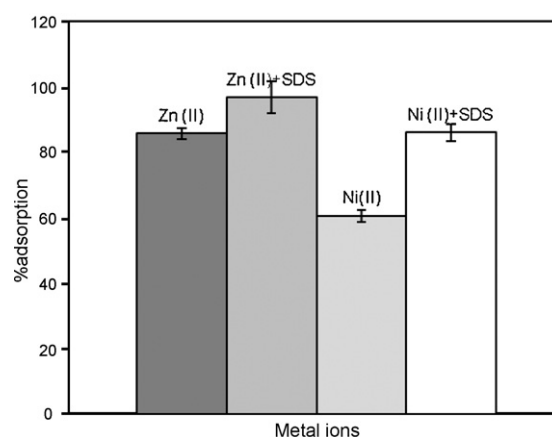


Fig. 3. Adsorption of Zn(II) and Ni(II) on CMOc in presence and absence of SDS.

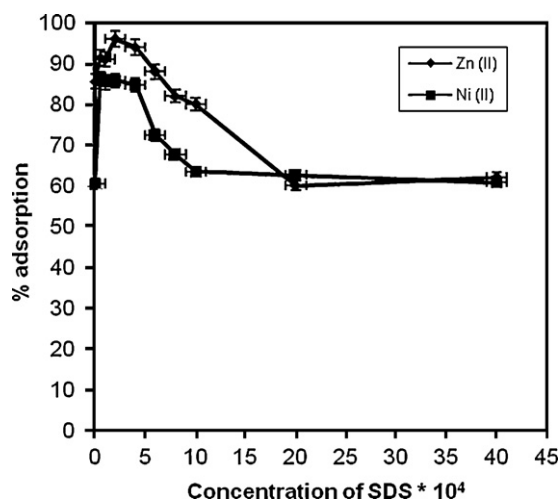


Fig. 4. Effect of concentration of SDS of on the adsorption of Zn(II) and Ni(II) on CMOC.

molecules form dynamic aggregation (micelles). These micelles possess a hydrophobic interior and hydrophilic exterior, causing them to behave like dispersed oil drops. The interaction between the micelles and ionic species is mainly through hydrogen bonding and electrostatic forces [22]. Therefore further studies were carried out at 2 mM concentration of SDS.

3.4. Effect of concentration of metal ions

The adsorption isotherms (Figs. 5 and 6) are regular, smooth, positive and concave towards concentration axis. The adsorption capacities of Zn(II) and Ni(II) on CMOC at lower equilibrium concentration in absence of SDS are almost equal (Figs. 5 and 6) but in presence of SDS, adsorption goes on increasing with increase in metal ion concentrations. This may be because more and more form ion pair with SDS which are easily adsorbed on the surface of CMOC. The equilibrium is attained early in absence of SDS (Figs. 5 and 6). The discharge of wastewater from commercial and domestic sectors may cause the contamination of natural water by surfactants and other substances. It is, therefore necessary to examine the interference due to the presence of surfactants, for the removal of Zn(II) and Ni(II). The effect of ionic interaction on the adsorption may be interpreted, using the ratio of the adsorption capacity of the

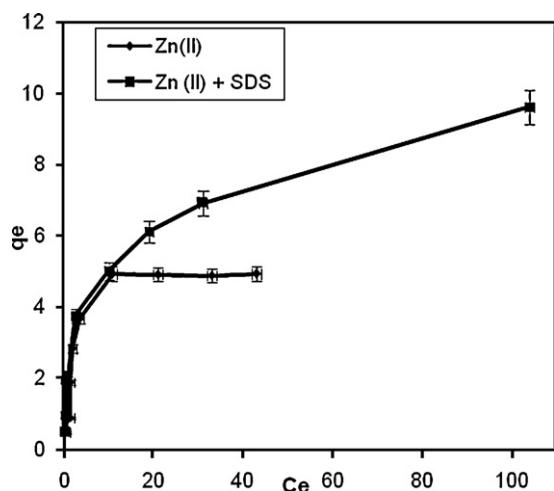


Fig. 5. Effect of concentration of Zn(II) on the adsorption on CMOC in presence/absence of SDS.

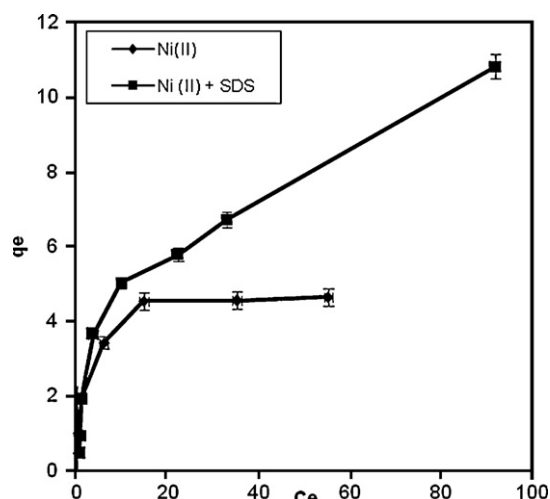


Fig. 6. Effect of concentration of Ni on the adsorption on CMOC presence/absence of SDS.

ion in multicomponent system (q_M) to that in a single-component system (q_0) [23] such that

- $q_M/q_0 > 1$: adsorption is promoted by the presence of other metal ions/surfactants.
- $q_M/q_0 = 1$: no observable net interaction effect.
- $q_M/q_0 < 1$: adsorption is suppressed by the presence of other metal ions/surfactants

The competitive adsorption of Zn(II) and Ni(II) was studied in presence of SDS. Conclude that the scavenging efficiency is $q_M/q_0 > 1$ for the adsorption of Zn(II) and Ni(II) on CMOC in the presence of SDS (2 mM) indicating that adsorption is promoted due to the presence of SDS as evident from Figs. 5 and 6.

3.5. Effect of pH

The adsorption of Zn(II) is negligible at pH 2 (Fig. 7) when pH of the solution is increased the adsorption of Zn(II) increases and reaches to a maximum value at pH 4 and then remains constant up to pH 9. This is the general trend observed in many cases at lower pH because H^+ ions compete with metal ions (high H^+ ions concentration) rendering the adsorption of meal ions. When pH is increased (H^+ ions concentration is lowered) the metal ions compete and are

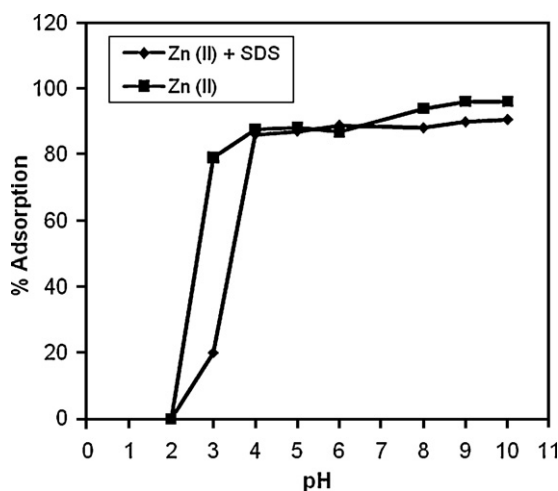


Fig. 7. Effect of pH on the adsorption of Zn(II) on CMOC presence/absence of SDS.

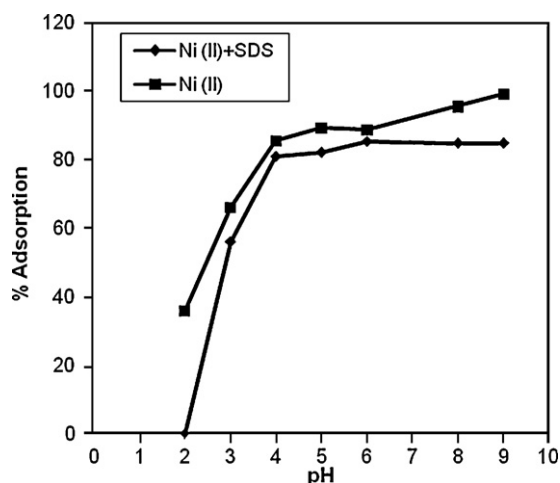


Fig. 8. Effect of pH on the adsorption of Ni(II) on CMOC in presence/absence of SDS.

adsorbed in the form of various species. At higher pH value (pH 4 and above) adsorption of Zn(II) remains constant. However, at pH > 8, adsorption of Zn(II) further increases (upto pH 10) which is probably due to the formation of metal hydroxide. Adsorption of Zn(II) in presence of SDS shows 20% at pH 3 and then increases rapidly above pH 3. Further increase in pH (pH > 4) does not affect the adsorption that remains maximum upto pH 10.

Adsorption of Ni(II) is 30% at pH 2 and increases with increase in pH (Fig. 8) reaches to maximum at pH 4 (80%). When pH is further increased from 4 to 6, adsorption of Ni(II) remains constant but above pH 6, adsorption further increases which is also due to the formation of Ni(OH)₂ at higher pH values. The adsorption of Ni(II) in presence of SDS is almost negligible at pH 2, 55% at pH 3 and maximum at pH ≥ 4 (78%). The adsorption remains constant when pH is increased above 4 (Fig. 8).

The variation in the adsorption of Zn(II) and Ni(II) on CMOC with respect to pH in presence and absence of SDS can be explained by considering the surface charge of the adsorbent. At lower pH value the number of negatively charged surface sites decreases which do not favor the adsorption of positively charged Zn(II) and Ni(II) ions. Lower adsorption of these metal ions in acidic pH is due to the presence of excess H⁺ ions competing with metal ions. The increased adsorption in the pH range 4–6 is due to the fact that solution pH influences the adsorbed surface charge. The point of zero charge (PZC) of CMOC (blank or control) is shown in Fig. 9. The first reversal of charge occurs at pH 1.5 and second reversal at pH 8.5. It means

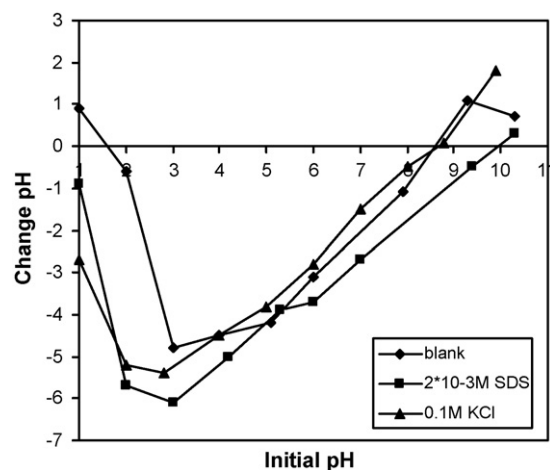


Fig. 9. Point of zero charge (PZC) of CMOC by soil addition method.

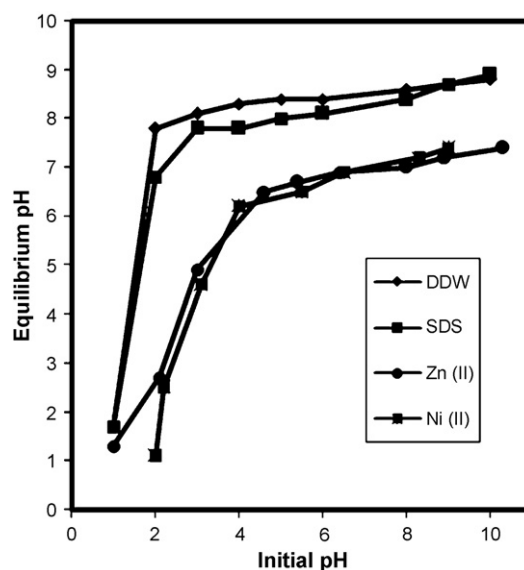


Fig. 10. Variation in pH at equilibrium (control).

that above pH 1.5, the decrease in H⁺ ions tends to increase final pH (pH_f) so that change in pH (ΔpH) decreases from 0 to −5. At pH ≥ 3, the ΔpH (pH_i − pH_f) increases showing that H⁺ ions are released from the adsorbent and at the same time adsorption of Zn(II) and Ni(II) increases rapidly (Figs. 7 and 8). However, presence of 0.1N KCl does no effect to the second charge reversal (pH 8.5) but the first charge reversal is not possible to determine pH_i goes below pH 0 (not possible to measure).

When SDS is added, again first charge reversal is impossible to determine. However, the ΔpH is minimum (−6.5) at pH_i 3, indicating the high value of pH_f at equilibrium (Fig. 10) (lower concentration of H⁺ ions). Therefore at pH ≤ 3, H⁺ ions are adsorbed maximum but when pH is increased above 3. The increase in ΔpH shows that H⁺ ions are released from the adsorbent and hence rapid adsorption of Zn(II) and Ni(II) occurs above pH 3 (Figs. 7 and 8). The second charge reversal or second PZC in presence of SDS occurs at pH 10. The shift in PZC in presence of SDS towards alkaline side may be due to the neutralization of some positively charged surface sites of the adsorbent through the adsorption of negatively charged SDS ions [24].

3.6. Effect of adsorbent doses

The adsorption capacity (mg/g) and percentage adsorption of Zn(II) and Ni(II) by varying the dose of CMOC are shown in Figs. 11 and 12. The percentage adsorption increases while adsorption capacity decreases as the dose of CMOC is increased. It may be concluded that by increasing the adsorbent dose, the removal efficiency of CMOC increases. The decrease in adsorption capacity may be due to the fact that some adsorption sites may remain unsaturated during the adsorption process where as the number of sites available for adsorption increases by increasing the adsorbent doses and that results an increase in removal efficiency [25]. The effect of SDS is more pronounced in case of Ni(II) as compared to Zn(II) (Fig. 12).

3.7. Effect of contact time

The adsorption increases with increase in contact time. The metal uptake (q_t) vs. contact time (t) curves for Zn(II) and Ni(II) in presence and absence of SDS shown in Figs. 13 and 14. The Zn(II) uptake on CMOC in presence and absence of SDS is 39 and

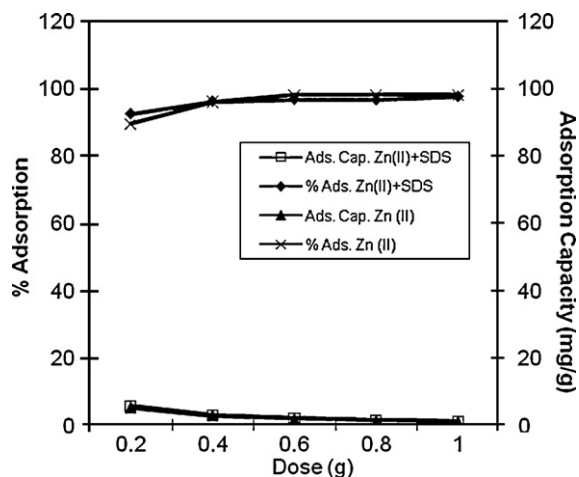


Fig. 11. Effect of doses on the adsorption of Zn on CMOC presence/absence of SDS.

28 mg/g, respectively within 15 min contact time, reaching 45.8 and 40 mg/g at equilibrium (Fig. 13). It is also observed that adsorption of Zn(II) in the presence of SDS is a fast process, with equilibrium being reached within 50 min when compared to the adsorption in absence of SDS.

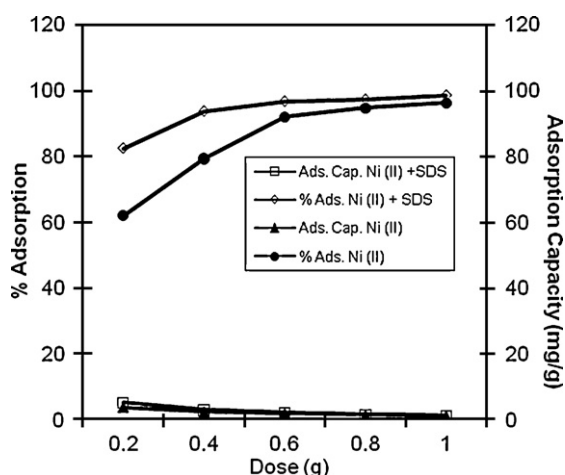


Fig. 12. Effect of doses on the adsorption of Ni on CMOC in presence/absence of SDS.

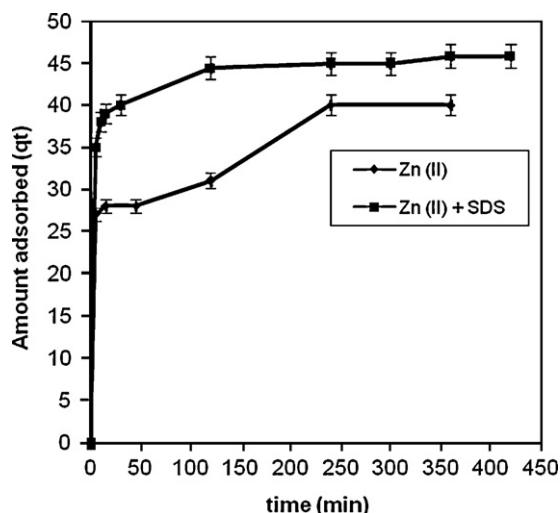


Fig. 13. Effect of contact time on the adsorption of Zn on CMOC in presence/absence of SDS.

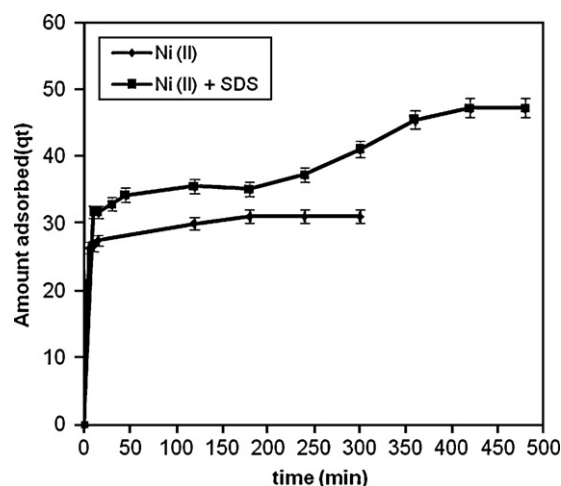


Fig. 14. Effect of contact time on the adsorption of Ni on CMOC in presence/absence of SDS.

The Ni(II) uptake on CMOC in presence and absence of SDS is 31.6 and 27.4 mg/g within 15 min contact time, reaching 47.2 and 31 mg/g at equilibrium (Fig. 14). The maximum amount of Ni(II) in presence of SDS is observed within 50 min. However, the initial rapid adsorption subsequently gives way to a very slow approach to equilibrium. The curves are single, smooth and continuous leading to saturation, suggesting possible monolayer coverage of metal ions on the surface of the adsorbent.

The values of pseudo-first-order rate constant (K_1) and pseudo-second-order rate constant (K_2) for the adsorption of Zn(II) and Ni(II) are higher in absence of SDS (Table 5). The $q_{e(\text{theo})}$ and $q_{e(\text{exp})}$ values for pseudo-first-order kinetic model differed appreciably. The percentage deviation (P) is also very high (Table 5). In pseudo-second-order kinetic model the values of $q_{e(\text{theo})}$ and $q_{e(\text{exp})}$ are found to be very close in case of Zn(II) in presence of SDS and Ni(II) in absence of SDS. The percentage deviation (P) values are well within the range and also the values of correlation coefficients (R^2) are very high as compared to pseudo-first-order model. It is therefore confirmed the adsorption of Zn(II) in presence of SDS and Ni(II) in absence of SDS follow pseudo-second-order rate equation.

Reichenberg equation plots (Figs. 15 and 16) for the adsorption of Zn(II) and Ni(II) on CMOC in presence and absence of SDS are linear and do not pass through the origin indicating that the pore diffusion is not only the rate limiting process but some other processes like film diffusion is also involved [18].

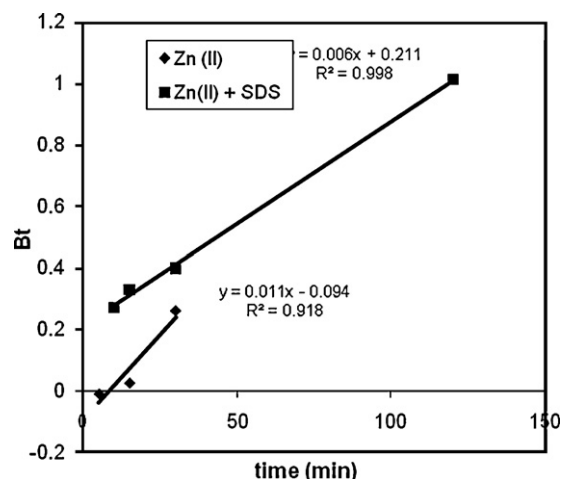


Fig. 15. Reichenberg plot for the adsorption of Zn(II) on CMOC in presence/absence of SDS.

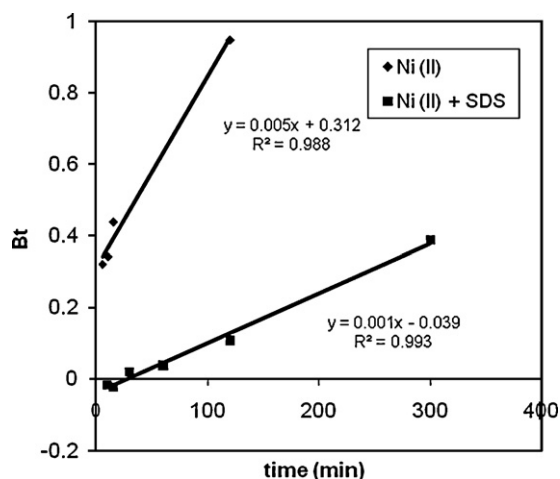


Fig. 16. Reichenberg plot for the adsorption of Ni(II) on CMOC in presence/absence of SDS.

3.8. Adsorption isotherms

Adsorption data for wide range of adsorbate concentration are most conveniently described by Langmuir and Freundlich adsorption isotherms. The values of Langmuir isotherm constants b and q_m were calculated from the slope and intercept of the linear plot of C_e/q_e vs. C_e (figure not shown). The coefficient b in Langmuir equation is a measure of the stability of the complex formed between metal ions and adsorbent under specified experimental conditions [26]. The $q_{m(\text{exp})}$ and $q_{m(\text{theo})}$ values for the adsorption of Zn(II) and Ni(II) in absence of SDS are very close (Table 2). The values of stability coefficient (b) of Zn(II) and Ni(II) in absence of SDS are higher than in presence of SDS showing more stable complex formation in absence of SDS.

The values of dimensionless constant (R_L) calculated for Zn(II) and Ni(II) in presence and absence of SDS are in between 0 and 1 showing favorable adsorption on CMOC (Table 2) [25].

The values of Freundlich isotherm constants K_f and n were calculated from intercept and slope of the Freundlich plots (figures not shown). These values are given in Table 2. K_f indicates the adsorption capacity of adsorbent. The values of K_f are higher for Zn(II) and Ni(II) in presence of SDS. The constant n is a measure of deviation from linearity of the adsorption. The values of n are greater than 1 in all cases indicating favorable adsorption on CMOC [27].

3.9. Thermodynamic studies

The thermodynamic parameters like enthalpy change (ΔH°) and entropy change (ΔS°) for the adsorption of Zn(II) and Ni(II) in presence and absence of SDS on CMOC were calculated from the Van't Hoff plot [28].

Free energy change (ΔG°) was calculated from the relation

$$\Delta G^\circ = -RT \ln K_c \quad (4)$$

Table 2
Langmuir and Freundlich constants for the adsorption of Zn(II) and Ni(II) in presence and absence SDS on CMOC.

Metal ions	Langmuir constants						Freundlich constants		
	$q_{m(\text{theo})}$ (mg/g)	$q_{m(\text{exp})}$ (mg/g)	b (L/mg)	R^2	R_L	P	K_f (mg/g)(L/mg) $^{1/n}$	n	R^2
Ni(II)	4.69	4.63	0.466	0.9961	0.021–0.300	1.29	1.622	2.487	0.9738
Ni(II) + SDS	7.16	10.8	0.279	0.9919	0.018–0.417	33.7	1.995	2.728	0.9738
Zn(II)	5.06	4.92	0.437	0.9858	0.022–0.186	2.84	2.340	3.020	0.9911
Zn(II) + SDS	10.13	9.6	0.142	0.9915	0.034–0.585	5.52	2.485	3.334	0.9832

Table 3

Thermodynamic parameters for the adsorption of Zn(II) and Ni(II) in absence and presence of SDS on CMOC.

Temperature ($^\circ\text{C}$)	K_c	ΔG° (kJ/mol)	ΔS° (J/mol)	ΔH° (J/mol/K)
Zn(II)				
25	30.25	−8.446		
45	49	−10.289	0.0919	0.0191
55	61.5	−11.232		
Zn(II) + SDS				
25	6.936	−4.799		
35	11.195	−6.184	0.0689	0.0057
55	49	−10.613		
Ni(II)				
25	4.102	−3.495		
45	5.25	−4.383	0.0708	0.0134
55	9.638	−6.179		
Ni(II) + SDS				
25	3.630	−3.193		
35	5.024	−4.133	0.0689	0.0096
55	14.625	−7.316		

Table 4

Dubinin–Radushkevich (D–R) parameters for the adsorption of Zn(II) and Ni(II) on CMOC in absence and presence SDS at 25 $^\circ\text{C}$.

Metal ions	β (mol/kJ) 2	$\ln q_m$	q_m (mol/g)	E (kJ/mol)	R^2
Ni(II)	−0.0023	−8.5556	0.0002	14.7	0.9801
Ni(II) + SDS	−0.0032	−7.9871	0.0003	12.5	0.9956
Zn(II)	−0.0026	−8.2729	0.0002	13.8	0.9915
Zn(II) + SDS	−0.0027	−8.1406	0.0003	13.6	0.9922

where T is the absolute temperature, R is the gas constant, ΔG° is the standard free energy change.

The positive values of ΔH° for the adsorption of Zn(II) and Ni(II) on CMOC in presence and absence of SDS (Table 3) suggest endothermic nature of adsorption. The increase in adsorption of Zn(II) and Ni(II) in presence and absence of SDS with temperature might have been due to dissolution of the adsorbing species, change in the pore size and enhanced rate of inter-particle diffusion [28]. The free energy change (ΔG°) of the process is spontaneous and spontaneity increases with increase in temperature. The positive value of entropy change (ΔS°) shows the increase in randomness at the solid/solution interface during the adsorption of Zn(II) and Ni(II) in presence and absence of SDS on CMOC [9].

To distinguish between the physical and chemical adsorption on CMOC, Dubinin–Radushkevich (D–R) isotherm based on the heterogeneous nature of the adsorbent surface is applied. The linear form of (D–R) isotherm equation is [29,30]

$$\ln C_{ad} = \ln q_m - \beta \varepsilon^2 \quad (6)$$

where β activity coefficient constant (mol 2 /J 2); q_m maximum adsorption (mol/g); C_{ad} adsorption capacity (mol/g); ε polanyi potential.

Polanyi potential (ε) can be calculated from the relation

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (7)$$

Table 5

Pseudo-first order and pseudo-second order kinetics constants for the adsorption of Zn(II) and Ni(II) in absence and presence SDS on CMOC.

Metal ions	Pseudo-first order kinetics					Pseudo-second order kinetics				
	K_1	$q_{e(\text{theo})}$	$q_{e(\text{exp})}$	R^2	P	K_2	$q_{e(\text{theo})}$	$q_{e(\text{exp})}$	R^2	P
Ni(II)	0.0124	4.79	31	0.9891	84.5	0.0052	31.5	31	0.9959	1.6
Ni(II) + SDS	0.0032	16.1	47.2	0.9959	65.8	0.0036	39.5	47.2	0.9925	16.2
Zn(II)	0.0212	13.7	40	0.6592	65.8	0.0490	28.7	40	0.9984	28.1
Zn(II) + SDS	0.0081	8.59	45.8	0.9585	81.2	0.0052	45.4	45.8	0.9993	0.8

where T Absolute temperature (K); R gas constant (kJ/mol/K); C_e concentration at equilibrium (mol/L).

Hence, by plotting $\ln C_{ad}$ vs. ε^2 (figure not shown), the values of q_m from the intercept and β from the slope are generated.

The mean free energy (E) for the adsorption can be calculated from the following equation:

$$E = \frac{1}{(-2\beta)^{1/2}} \quad (8)$$

The magnitude of mean free energy (E) (Table 4) for the adsorption of Zn(II) and Ni(II) in presence and absence of SDS is well within the range of chemical adsorption process i.e. 8–16 kJ/mol. The values of free energy (E) decreases in presence of SDS (Table 4). The values of ΔH° and ΔS° also decrease in presence of SDS (Table 3). The decrease in E , ΔH° and ΔS° values in presence of SDS indicate that adsorption of these metal ions is high in presence of SDS but interaction of metal with adsorbent is weak because of the simultaneous formation and adsorption of ion pair by the association of metal–SDS, since adsorption of hydrophobic species is more as compared to hydrophilic species but bond formation between hydrophobic species and adsorbent is weaker than hydrophilic species [31].

3.10. Desorption studies

In order to make the process economically feasible, it is important to desorb and regenerate the spent adsorbent. The desorption studies were carried out by batch process using HCl, KCl, NaOH and NaCl solutions of different concentration as eluents. Experiments were conducted in triplicate and standard deviation (SD) values were calculated for both adsorption (SD)_a and desorption (SD)_d studies (Table 6). Desorption of Ni(II) and Zn(II) in presence and absence of SDS by water is almost negligible. The percentage recovery of Ni(II) and Zn(II) in presence and absence of SDS is approximately 10–12% when different concentrations of KCl, NaOH and NaCl were used as eluents showing strong adsorption on CMOC. This is important because metal ions adsorbed by CMOC will not be desorbed by KCl, NaOH, and NaCl if CMOC is used to sequester metal ions in soil since appreciable amount of these salts are usually present in the soil. The recovery of Ni(II) by 0.1 M HCl in presence of SDS is 78.97%. While the recovery of Zn(II) is 75% by 0.1 M HCl in absence of SDS. The desorption of metal ions carried out by varying the concentration of acid (0.05 and 0.1 M HCl) indicate that desorption is not affected by varying the acid concentration. This indicates that adsorption of metal ions occurs most probably via ion-exchange process).

Table 6

Recovery of Ni(II) and Zn(II) in absence and presence SDS from CMOC by batch process.

Eluents used	Metal ions	Amount loaded (mg)	Amount adsorbed (mg)	(S.D.) _a	%Adsorption	Amount recovered (mg)	(S.D.) _d	%Recovery
H ₂ O	Ni(II)	2.5	1.97	0.029	78.8	0.015	0.003	0.75
	Ni(II) + SDS	2.5	2.09	0.048	83.6	0	0.000	0
	Zn(II)	2.5	2	0.021	80	0.02	0.004	0.88
	Zn(II) + SDS	2.5	2.4	0.038	96	0.01	0.002	0.42
0.1 M HCl	Ni(II)	2.5	1.97	0.030	78.8	1.3	0.024	65.9
	Ni(II) + SDS	2.5	2.09	0.052	83.6	1.65	0.031	78.97
	Zn(II)	2.5	2	0.019	80	1.5	0.071	75
	Zn(II) + SDS	2.5	2.4	0.040	96	1	0.011	41.67
0.05 M HCl	Ni(II)	2.5	1.97	0.029	78.8	1.3	0.023	65.9
	Ni(II) + SDS	2.5	2.09	0.057	83.6	1.55	0.127	74.16
	Zn(II)	2.5	2	0.023	80	1.5	0.281	75
	Zn(II) + SDS	2.5	2.4	0.040	96	1	0.032	41.67
0.05 M KCl	Ni(II)	2.5	1.97	0.025	78.8	0.14	0.032	7.11
	Ni(II) + SDS	2.5	2.09	0.052	83.6	0.125	0.100	5.98
	Zn(II)	2.5	2	0.027	80	0.05	0.001	2.5
	Zn(II) + SDS	2.5	2.4	0.038	96	0.04	0.020	1.67
0.1 M KCl	Ni(II)	2.5	1.97	0.027	78.8	0.17	0.010	8.63
	Ni(II) + SDS	2.5	2.09	0.055	83.6	0.17	0.022	8.63
	Zn(II)	2.5	2	0.023	80	0.1	0.002	5
	Zn(II) + SDS	2.5	2.4	0.039	96	0.05	0.006	2.08
0.05 M NaOH	Ni(II)	2.5	1.97	0.028	78.8	0	0	0
	Ni(II) + SDS	2.5	2.09	0.054	83.6	0	0	0
	Zn(II)	2.5	2	0.031	80	0.25	0.031	12.5
	Zn(II) + SDS	2.5	2.4	0.040	96	0.1	0.037	4.17
0.1 M NaCl	Ni(II)	2.5	1.97	0.027	78.8	0.135	0.002	6.85
	Ni(II) + SDS	2.5	2.09	0.049	83.6	0.14	0.005	6.7
	Zn(II)	2.5	2	0.022	80	0.05	0.031	2.5
	Zn(II) + SDS	2.5	2.4	0.036	96	0.04	0.009	1.67

4. Conclusions

CMOC is an ecofriendly adsorbent. Addition of SDS to Zn(II) and Ni(II) solutions leads to drastic increase in the adsorption capacity. The adsorption capacity for Zn(II) increases to 45.8 from 40 mg/g in presence of SDS and that for Ni(II) adsorption capacity increases to 47.2 from 31 mg/g. Adsorption process is chemical in nature and may proceed through ion-exchange process. The adsorption of Zn(II) and Ni(II) in presence of SDS indicates that film diffusion is also involved. The presence of SDS reduces the hindrance in the film diffusion process and makes easy transfer of Zn(II) and Ni(II) from bulk to the adsorbent surface. The percentage increase in the uptake of Ni(II) and Zn(II) increases by 5.54% and 16.67%, respectively in presence of SDS. This property of increase in the adsorption due to the addition of surfactant can be utilized for the effective removal Ni(II) and Zn(II) from waste streams containing surfactants. The recovery of Ni(II) is (78.97%). Adsorption of Zn(II) is 98% but its recovery is poor (41%). However 75% of Zn(II) can be recovered by 0.1 M HCl in absence of SDS.

Acknowledgement

The authors are thankful to the chairman department of applied chemistry for providing essential research facilities. Moonis Ali Khan is thankful to Brain Korea-21 (BK-21) program of Ministry of Education and Global Research Laboratory (GRL) project by Korean Institute of Geoscience and Mineral Resources (KIGAM), NP2008-019 for providing financial assistance. He is also thankful to Mr. Mahinder Kumar for his help in FT-IR and SEM analysis.

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