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Synthesis of surfactant-modified ZSM-5 nanozeolite for the removal of nickel (II) from aqueous solution

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ABSTRACT

Removal of nickel ions from aqueous solutions using modified ZSM-5 nanozeolites was investigated. Experiments were conducted in terms of different solute concentrations, temperatures, and pH. Mesoporous Na-ZSM-5 zeolite was modified with tetrapropylammonium bromide (TPABr) and sodium dodecylsulfate (SDS) by using the impregnation method. The modified zeolites were characterized by X-ray diffraction, Fourier transform infrared spectroscopy, Brunauer–Emmett–Teller, and scanning electron microscope techniques. According to the results, SDS-ZSM-5 revealed a higher adsorption capacity than Na-ZSM-5 and TPA-ZSM-5. Langmuir and Freundlich adsorption models were used for the mathematical description of the adsorption equilibrium. The analyses revealed that the sorption of Ni(II) could be considered an endothermic and spontaneous process.

Keywords: Nanozeolites; Surfactants; Characterization; Adsorption; Nickel removal

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1. Introduction

Heavy metals such as lead, copper, nickel, cobalt, and zinc are naturally occurring elements. Small amounts of these elements which are actually necessary for our health could be found in the environment. However, large dosage of these metals may cause sickness or have hard toxicity [1,2]. Nickel, as well as lead, cadmium, chromium, and other heavy metals are categorized among serious toxic heavy metals. They tend to cumulate in the living organisms, causing innumerable diseases and disorders. Presence of heavy metals in human body may lead to damaged or diminished mental and central nervous function. Also, they might alter the blood composition, harm lungs, kidneys, and livers [3]. In the case of heavy metal removal from water, many different methods and techniques such as chemical precipitation, ultra filtration, adsorption and ion-exchange, reverse osmosis and electro dialysis have been tested and developed. Although chemical precipitation could be considered the most extensively used method, it has the obstacles of difficult sludge disposal and more importantly being poorly beneficent in cases of treating waters with low heavy metal levels [4,5]. However, these methods are usually very expensive and have high operation costs. Other methods such as electrodialysis, membrane electrolysis, and electrochemical precipitation have also been used; however, due to high consumption of energy in such methods, their

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applications have been limited [6]. On the other hand, ion exchange process simply involves convenient operations. It has been applied as a useful and effective procedure for the removal of pollutants such as ammonia and heavy metals from water [7]. Moreover, the ion exchange seems specifically effective in removal of heavy metals with low concentrations which is the most common case [8]. Numerous materials such as activated carbon, clay minerals, biomaterials, and zeolites were synthesized and used widely for the ions sorption in the wastewater by the ion exchange method. Zeolites have been recently studied due to their applicability in removing trace quantities of heavy metal ions from aqueous solutions using the ion exchange phenomenon [9–11].

The applications of surfactants have been widely used to modify the surface properties of the swelling clays and other materials to improve the sorption capacity [12–16]. Most of the previous studies focused on the use of cationic surfactants to sorb organic materials or metallic anions; e.g. the sorption of phenol and alkyl phenols on HDTMAB (hexadecyltrimethyammonium bromide)-modified montmorillonite [14] and anion–cation organobentonite [12], removal of BTEX (benzene, toluene, ethylbenzene, and xylenes) from aqueous solutions by HDTMA-modified Y zeolite [17], and sorption of chromate anions from aqueous solutions by HDTMA-exchanged zeolites [18]. On the other hands, few studies have been made for the sorption of heavy metal cations on adsorbents modified with anionic surfactants such as sodium dodecylsulfate (SDS). Removal of Cu(II) and Zn(II) from aqueous solutions by sorption on the montmorillonite modified with SDS was carried out by Lin and Juang [19]. Since zeolites have surface adsorption due to their negative charge surface, the effect of alteration of surface charge could be specified by these surfactants.

In the present study, ZSM-5 nanozeolites were prepared and used as the absorbent for removal of nickel ions from aqueous solutions. In order to study their activities, they have been modified by tetrapropylammonium bromide (TPABr) and SDS as surfactant. The experiments were carried out in a batch system. The influence of different variables such as pH, solute concentration, and temperature on the adsorption capacity of ZSM-5 nanozeolites was investigated. Kinetic studies have been performed in which the parameters were determined at ambient temperature. Furthermore, equilibrium and thermodynamic parameters of Ni(II) adsorption were calculated at three different temperatures.

2. Materials and methods

2.1. Materials

For the conducted experiments, tetraethylorthosilicate (TEOS, 98 wt.%, Merck), aluminumisopropoxide (AIP, Merck), tetrapropylammonium hydroxide (TPAOH, 40 wt.%, Merck), tetrapropylammonium bromide (TPABr, Merck), sodium hydroxide pellets (Aldrich 99.5%), acetone (Merck, 99 wt.%), and HCl (Merck, 99%) were purchased and used. Tetraethylorthosilicate and aluminum isopropoxide were used as Si and Al sources, respectively. Also, tetrapropylammonium hydroxide, TPABr, and sodium dodecylsulfate (SDS, Merck) were applied as template and surfactant sources, respectively. In order to adjust the pH of the solutions, concentrated sodium hydroxide and HCl were used.

2.2. Characterization techniques

The Brunauer–Emmett–Teller (BET) surface area (S_{BET}), total pore volume (V_{p}), and average pore diameter (d_{p}) were measured using a N_2 adsorption–desorption isotherm at liquid nitrogen temperature (−196˚C), using a NOVA 2200 instrument (Quantachrome, USA). The Fourier transform infrared spectroscopy (FT-IR) spectra were recorded by a Shimadzu spectrometer at ambient conditions, using the KBr pellet method over a wavenumber range from 500 to 4,000 cm^{-1}. The structure morphology and particle size of the prepared catalysts were examined by scanning electron microscope (SEM, TESCAN-VEGA), operated at 15 kV. The zeolite was dried at 105˚C for 12 h and then coated with a thin gold film to increase electrical conduction on the zeolite external surface. Powder X-ray diffraction (XRD) patterns of the calcined samples were obtained using a EQUINOX 3,000 automated diffractometer (Cu Kα radiation, $\lambda = 1.5{,}406$ Å) operated at 40 kV and 30 mA, in the 2θ range of 2–60˚ and at a scanning rate of 0.05˚/s. Also, Adsorption studies were performed by UV–Vis spectrophotometer (Cary 50 Conc, Varian).

2.3. Preparation of zeolites

The Na-ZSM-5 sample was prepared using a synthetic solution with initial molar composition of Al_2O_3: 29.16 SiO_2: 10.153 TPAOH: 0.12 Na_2O: 480.91 H_2O. In this synthesis, 1.93 g aluminumisopropoxide was slowly added to 23.94 g TPAOH solution. Stirring was followed by consecutive addition of 25.57 g double distilled water. 28.43 g TEOS as an organic silica source which is supposed to dissolve in aqueous phase was slowly added dropwise during 2 h. The components were well mixed with constant stirring. After addition of all the mentioned components, the resulting mixture was aged for 30 min in a microwave oven which also made the hydroxylation occur. The hydrolysis of TEOS led to a concentrated gel. The obtained gel was then charged into Teflon-lined stainless steel autoclaves and crystallized using hydrothermal treatment at 180˚C for 40 h without stirring. Afterward, the product was separated by a centrifugation speed of 15,000 rpm, washed several times using double distilled water, dried overnight at 120˚C, and then calcinated at 500˚C for 5 h in air as proposed by Kulkarni et al. [20]. Samples of 100 ml of SDS and TPABr 5% solutions were prepared separately in conical flasks and 5 g of zeolite was added to each flask. The mixtures were shaken at 200 rpm in a 25˚C water bath for 24 h. Then, the modified zeolites were recovered by centrifuging and washed several times with distilled water to remove extra surfactants, they were then dried in an oven at 120˚C and stored in a desiccator for later use [21,22].

2.4. Batch adsorption experiments

Adsorption experiments were performed at ambient temperature by using batch method. In order to consider the interaction between Ni(II) and Na-ZSM-5, the effect of pH and initial concentration on adsorption capability were studied. During the experiments, only one parameter was changed at a time while others were kept constant. The amount of removal of Ni(II) was investigated at various pH values (2, 4, 6, 8, and 10), adsorbent dosage of 1 g/l, initial Ni(II) concentration of 15 mg/l, and a predetermined time of 90 min. Series of clean 100 ml conical flasks were put on a shaker at a speed of 200 rpm. After determination of optimum pH, the effect of Ni(II) concentration (5, 10, 15, 20, and 25 mg/l), temperature and contact time were studied.

Each experiment was carried out three times and the average results were reported. The relative standard deviation values of the results were relatively low and of the order of ±3%, which shows the good reproducibility and accuracy of the experiments. The percentage removal of Ni(II) ($R\%$) and the amount of Ni(II) removed per unit mass of adsorbent (q) were calculated according to the following equations:

$$R(\%) = \frac{(C_{\mathrm{i}} - C_{\mathrm{e}})}{C_{\mathrm{i}}} \times 100 \tag{1}$$

$$q(\mathrm{mg/g}) = (C_{\mathrm{i}} - C_{\mathrm{e}}) \times \frac{V}{m} \tag{2}$$

where V is the volume of nickel solution (l), m is the amount of adsorbent (g), and C_{i} and C_{e} are the initial and equilibrium Ni(II) concentrations (mg/l), respectively.

2.5. Analysis of Ni(II)

The analysis of Ni(II) was performed calorimetrically; absorbance values were obtained at the wavelength which provides the maximum absorbance ($\lambda_{\max}$ = 445 nm) by making a red colored complex of Ni(II) with dimethylglyoxime. These absorbance values were then converted into concentration data using calibration relation which was predetermined at the wavelength of interest as illustrated by Gazda et al. [23].

3. Results and Discussion

3.1. Characterization of ZSM-5 nanozeolites

3.1.1. XRD patterns

Fig. 1 provides data on the XRD analysis of Na-ZSM-5, TPABr modified ZSM-5, and SDS-ZSM-5. XRD patterns were calculated using the characteristic peaks at $2\theta = 7–9$ and $2\theta = 22.5–24.5^\circ$ to identify the phases and to calculate crystallinity for each sample as proposed by Kim et al. [24]. The results confirm that all the samples were single phase formed, no other phase apart from ZSM-5 was found, and the crystallinity of all of the samples was appeared to be at high amounts. Since the samples are single phase, it

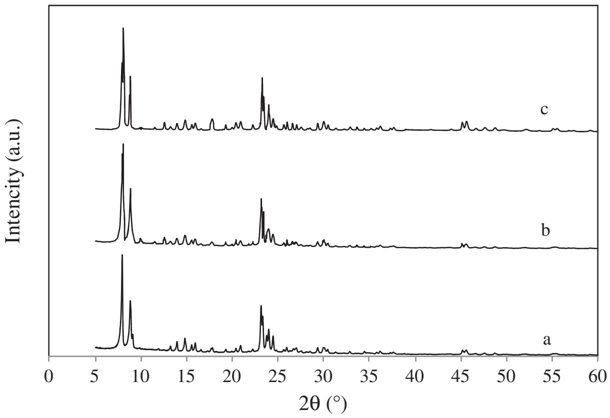

Fig. 1. X-ray diffractograms of (a) NaZSM-5, (b) TPA-ZSM-5, and (c) SDS-ZSM-5.

can be concluded that they are pure. The XRD patterns for TPA-ZSM-5 and SDS-ZSM-5 were approximately the same as Na-ZSM-5 and no significant differences were noted. A very low intensity peak at 9° was found for TPA-ZSM-5.

The peaks in all patterns broadly indicate the formation of nanocrystallites. The average crystallite size of each sample was calculated using the Scherrer equation [25] and was estimated to be about 42 nm.

3.1.2. SEM characterization

Morphology and microstructure of samples were investigated by SEM. Fig. 2 shows SEM micrographs of three synthesized samples. The micrographs demonstrated uniform distribution of the crystal size and almost regular morphology of the crystals for each sample. According to this figure, the smooth spherical surfaces can be seen for the crystals obtained from the synthesis procedure and the average particle size of all samples is identical. This may be due to the presence of TPAOH which acts as a suitable template for ZSM-5 zeolite and could be attributed to the high alkalinity of the TPAOH media [26]. Moreover, it can be observed in Fig. 2 that amorphous materials or very small crystallites are absent; crystals are indeed clear in this arrangement, while the gel and small crystallites are black and opaque.

3.1.3. FT-IR analysis

Todorova and Su [27] and Sazama et al. [28] suggested that the bands around 808, 1,120–1,250 cm^{-1} in the FT-IR analysis are characteristic of SiO_4 tetrahedron units. The presence of absorption bands at 1,219 and 565 cm^{-1} supply information on the difference between ZSM-5 nanozeolite and other types of nanozeolites. The external asymmetric stretching vibration near 1,219 cm^{-1} is due to the presence of structures containing four chains of five-member rings of ZSM-5. The band near 790 cm^{-1} is assigned to the symmetric stretching of external linkages and the one near 542 cm^{-1} is attributed to a structure-sensitive vibration caused by the double five-member rings of the external linkages.

In the present study, the FT-IR spectra analysis of the Na-ZSM-5 zeolite, TPA-ZSM-5, and SDS-ZSM-5 were carried out in order to demonstrate that TPABr and SDS have been completely adsorbed on the Na-ZSM-5 zeolite surface which depicted in Fig. 3. It can be seen that the absorbance near 3,500 cm^{-1} represents the surfaces of Na-ZSM-5 zeolite, TPA-ZSM-5, and SDS-ZSM-5 possessing OH^- groups. The peak at around 1,300 cm^{-1} indicates the stretching vibration of C-H on TPA-ZSM-5. The presence of a sharp peak at 1,722 cm^{-1} indicates the stretching vibration of N-H on TPA-ZSM-5, while no such a peak was observed on the ZSM-5 and SDS-ZSM-5 spectra. The external stretching vibration of Ar–H at 3,047 cm^{-1} is due to the aromatic rings of SDS-ZSM-5.

Generally, all of the zeolite bonds are identical after modification by the surfactant, suggesting that the core crystal structure of ZSM-5 remains.

3.1.4. Surface texture

The adsorption–desorption of N_2 for Na-ZSM-5, TPA-ZSM-5, and SDS-ZSM-5 followed the BET isotherm, indicating that all of the samples have mesoporous diameters. The BET surface areas, pore volume (V_p), and average pore diameter (d_p) for Na-ZSM-5, TPA-ZSM-5, and SDS-ZSM-5 are presented in Table 1. The S_{BET} of Na-ZSM-5 was 482 $\mathrm{m}^2\,\mathrm{g}^{-1}$, higher than the BET surface area of TPA-ZSM-5 and SDS-ZSM-5. The decrease in the surface area in TPA-ZSM-5 and SDS-ZSM-5 could be due to the effect of surfactant adsorbed on the Na-ZSM-5 zeolite surface. In addition, the decrease in pore volume of SDS-ZSM-5 and TPA-ZSM-5 showed the adsorption of TPABr and SDS on the surface of zeolite. As depicted in Fig. 4, N_2 adsorption–desorption isotherms of three samples were approximately the same. Then, generally no structural change occurs during the modification using surfactants.

3.2. Effect of pH

The effect of pH on the removal of Ni(II) was studied by performing equilibrium sorption experiments at different pH values from 2 to 10 as shown in Fig. 5. The uptake efficiency of Na-ZSM-5 zeolite gradually was gradually increased as the pH was increased from 2 to 6 in Ni(II) solution. However, at pH values above 6, the removal of Ni(II) was declined. At $pH > 6.0$, the concentration of Ni(II) ions remained constant. This could be explained by the adsorption surface becoming less positive as the pH value increases to 6. The Ni(II) ions may be covered by OH^- which lead to decreasing adsorption tendency onto the anionic surface of zeolite at $pH > 6.0$. It seems that the OH^- effect on removal was constant at $pH > 6.0$. Thus, the removal was constant too in this range of pH. Therefore, the adsorption of metal ions on the surface of adsorbent could be explained by H^+–Ni^{2+} exchange reaction at around 6 values of pH. In the acidic range of pH from 2 to 6, H^+ ions compete with Ni^{2+} ions for

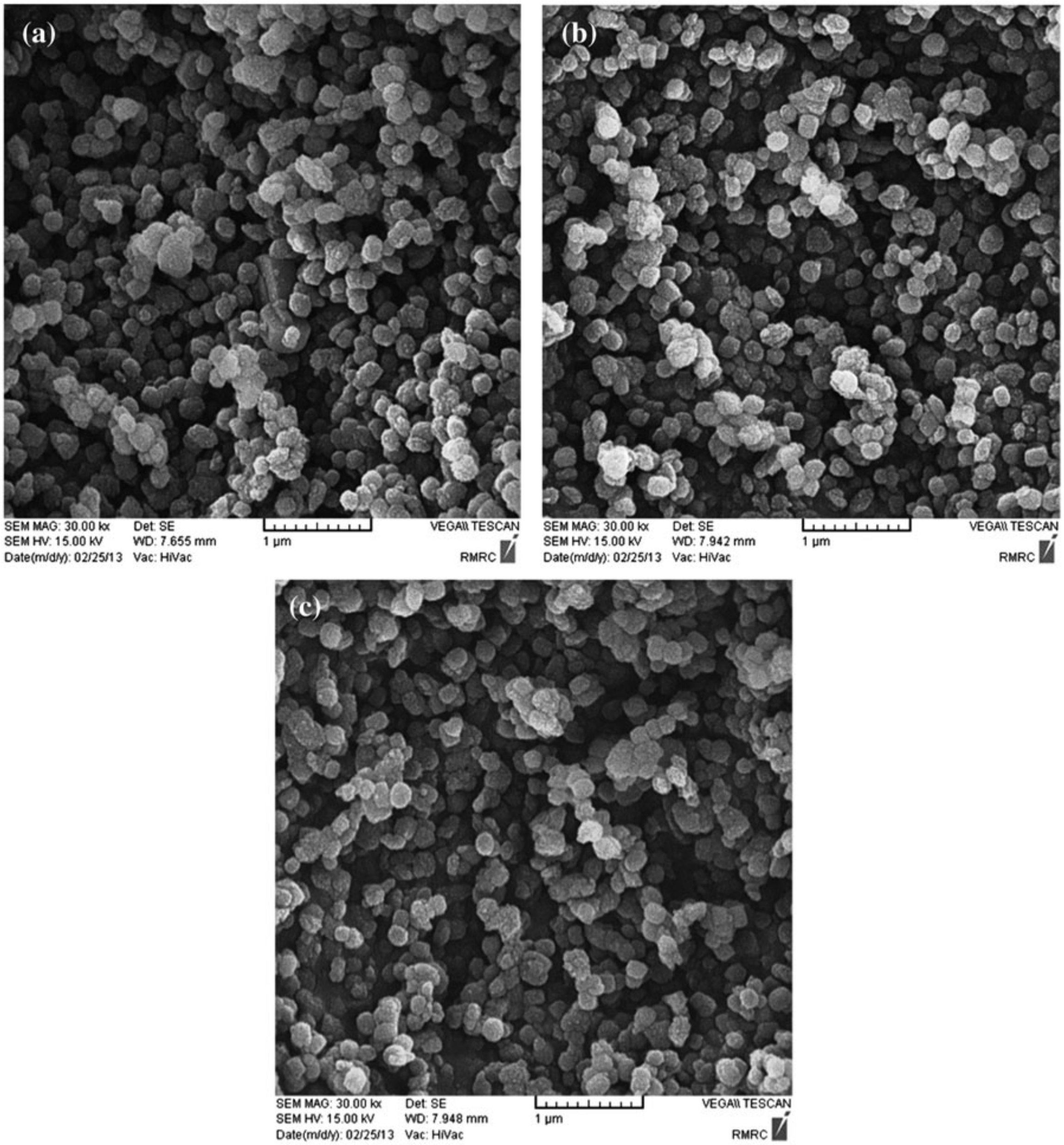

Fig. 2. SEM images of (a) NaZSM-5, (b) TPA-ZSM-5, and (c) SDS-ZSM-5.

the surface of the adsorbent, so the repulsive forces would prevent Ni(II) ions from binding sites of the sorbent. Therefore, optimum pH range for the removal of Ni(II) was found to be 6 which was also reported by Hasar [29] and Panneerselvam et al. [30].

3.3. *Adsorption of Ni(II) on Na-ZSM-5, TPA-ZSM-5, and SDS-ZSM-5*

The removal percentage of Ni(II) by different zeolites treated by different surfactants at optimum pH is presented in Fig. 6. As depicted, SDS-ZSM-5 showed the highest removal percentage which may be related to the increase in zeolite surface adsorption due to the growth of zeolite surface negative charge density caused by sodium dodecylsulfate.

Applying SDS-ZSM-5 could be considered a major mechanism for the removal of Ni(II) ions whereby the ion-exchange and adsorption processes occurred in the zeolite structure [31,32]. The removal percentage of Ni(II) by TPA-ZSM-5 was observed to be lower than Na-ZSM-5. It seems that TPABr molecules may

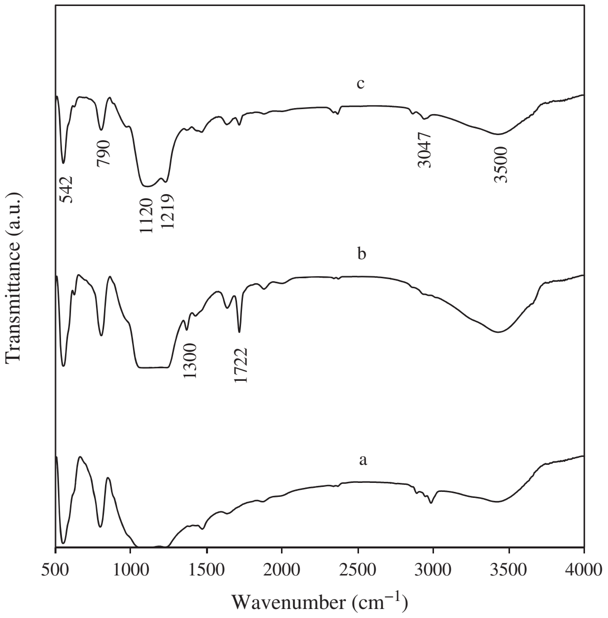

Fig. 3. FT-IR spectra of (a) NaZSM-5, (b) TPA-ZSM-5, and (c) SDS-ZSM-5.

Table 1
Elemental and textural properties of the samples

Sample name	S_{BET} (m^2/g)	V_p (cm^3/g)	d_p (nm)
ZSM-5	482	0.353	3.82
SDS-ZSM-5	465	0.264	2.8
TPA-ZSM-5	428	0.182	2.7

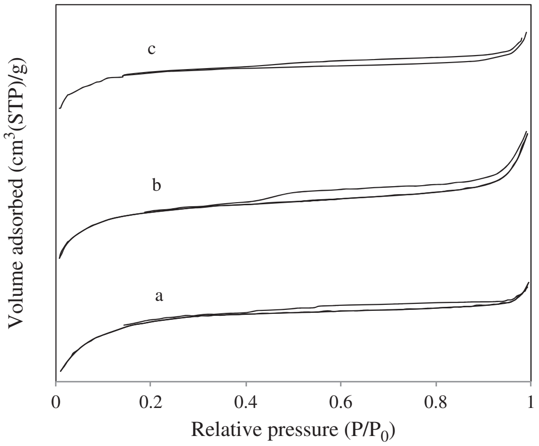

Fig. 4. N_2 adsorption isotherms of (a) NaZSM-5, (b) SDS-ZSM-5, and (c) TPA-ZSM-5.

slightly exceed the width of zeolite channel apertures of ZSM-5 zeolite. Consequently, TPA-ZSM-5 does not have any access to the channels due to the steric obstacle [33].

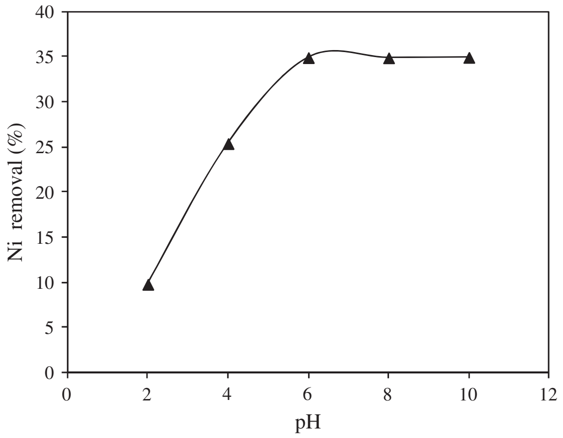

Fig. 5. Effect of pH on the adsorption of Ni(II) on NaZSM-5 at 20˚C.

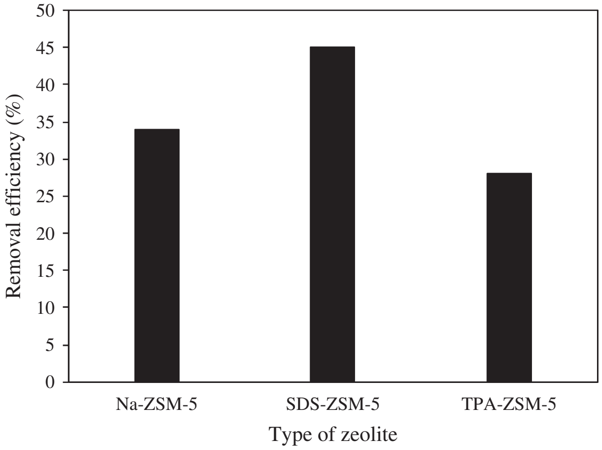

Fig. 6. Adsorption of Ni(II) on different type template modified zeolites (contact time = 120 min, pH 6, and C_i = 15 mg/l).

3.4. The effect of contact time at different temperatures

The effect of contact time on the removal of Ni(II) using SDS modified nanozeolite was studied at different temperatures (20, 40, and 60˚C) at optimized pH 6. From Fig. 7, as it could be inferred from the slope of the curve, the adsorption of Ni(II) was significantly increased at 20˚C during the first 90 min of the experiment, afterward adsorption of Ni(II) onto the SDS-ZSM-5 was remained constant without any remarkable change. The contact time of 90 min was considered the optimal time for removal of Ni(II). The same experiment was also carried out for temperatures of 40 and 60˚C at optimal contact time. The uptake removal efficiency of Ni(II) under the optimal conditions (contact time = 90 min, and pH 6) for a concentration of 5 (mg/l) reached to these percentage of removal 50, 80, and 99 at 20, 40, and 60℃, respectively.

3.5. Adsorption kinetics

Adsorption kinetics provides exquisite information regarding the mechanisms of process. The kinetics of Ni(II) adsorption on SDS-ZSM-5 were fitted to pseudo-first-order and pseudo-second-order models. The similarity between experimental data and the model prediction was reflected by the determination correlation coefficients (R^2). A relatively high R^2 value demonstrated the fact that the model can successfully describe the kinetics of Ni(II) adsorption.

3.5.1. The pseudo-first-order equation

The pseudo-first-order adsorption kinetic rate equation is explained as [34]:

$$q_t = q_e(1 - e^{-k_1 t}) \tag{3}$$

where q_e and q_t are the amounts of adsorbed Ni(II) (mg/g) at equilibrium and time t, respectively and k_1 is the rate constant of the pseudo-first-order adsorption (min^{-1}). The kinetic curves for three concentrations (5, 15 and 25 mg/l) were obtained by plotting q_t against time at ambient temperatures, as shown in Fig. 8.

3.5.2. The pseudo-second-order equation

The pseudo-second-order adsorption kinetic rate equation is expressed as [34]:

$$q_t = \frac{k_2 q_e^2}{1 + k_2 q_e t} t \tag{4}$$

where q_e and q_t are the sorption capacity (mg/g) at equilibrium and time t, respectively, and k_2 is the rate constant of the pseudo-second-order sorption (g/mg min). Fig. 9 plots the q_t values vs. time for three concentrations at given temperature.

The values of the determination correlation coefficient (R^2) of pseudo-first- and second-order kinetic equation models are presented in Table 2. The results revealed that between the two models considered, pseudo-second-order kinetic equation provided higher R^2 values, thus, the removal of Ni(II) ions from aqueous solutions by SDS-ZSM-5 were found to appropriately follow the pseudo-second-order kinetic equation.

3.6. Adsorption isotherm studies

Chemical interaction between adsorbate and adsorbent may cause an increase in adsorption capacity as indicated by Thamilarasu et al. [35]. To explain the relationship between the amount of adsorbed Ni(II) (q_e) and concentration (C_e) at equilibrium, two adsorption isotherm models called Langmuir and Freundlich were implemented at three different temperatures (20, 40, and 60℃).

The Langmuir adsorption isotherm equation is mathematically expressed as [36]:

$$q_e = \frac{b q_m C_e}{1 + b C_e} \tag{5}$$

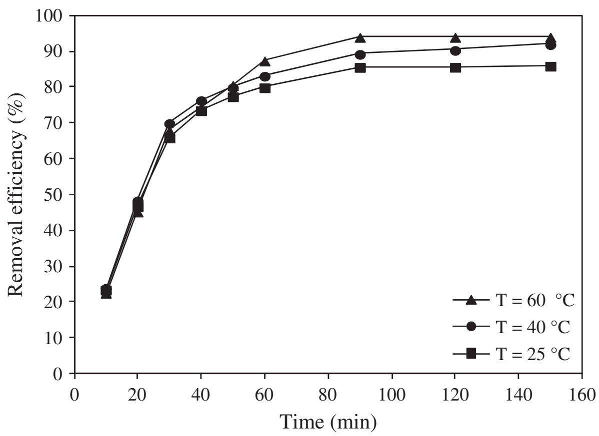

Fig. 7. Removal of Ni(II) by SDS-ZSM-5 at different temperatures (C_i = 5 mg/l, pH 6).

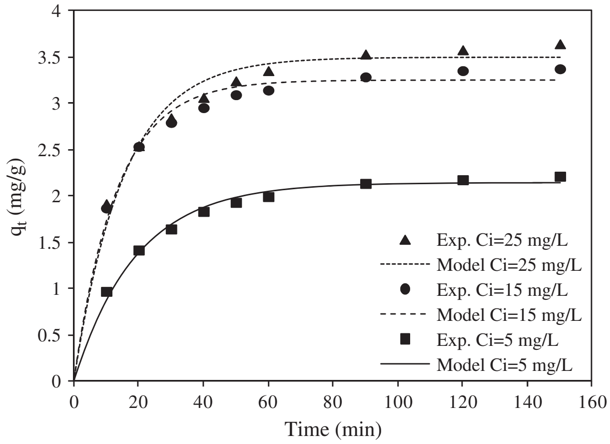

Fig. 8. Pseudo-first-order kinetics for adsorption of Ni(II) on SDS-ZSM-5 at three initial concentrations.

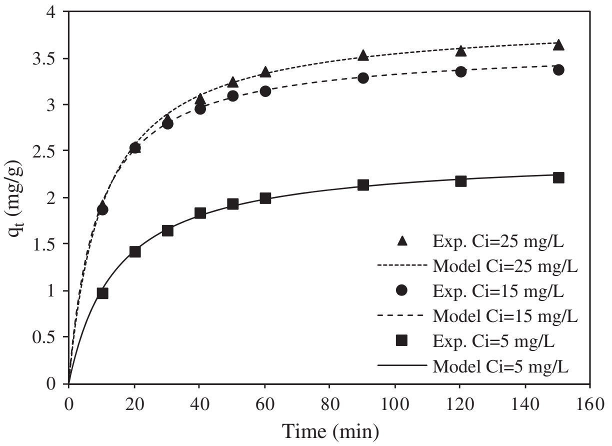

Fig. 9. Pseudo-second-order kinetics for adsorption of Ni (II) on SDS-ZSM-5 at three initial concentrations.

where q_e is the amount adsorbed per gram of adsorbent (mg/g) and C_e is the concentration of Ni(II) (mg/l) in the aqueous solution at equilibrium. q_m and b are both constants related to the maximum adsorption capacity (mg/g) and the adsorption energy (l/mg), respectively, which were calculated from the isotherm curves of q_m vs. C_e given in Table 3 along with determination correlation coefficients (R^2).

In addition, the Freundlich isotherm could be described by the following equation [36]:

$$q_e = K_f C_e^{\frac{1}{n}} \tag{6}$$

where K_f ((mg/g) (l/mg)$^{1/n}$) is related to the relative adsorption capacity and n is the intensity of the adsorption.

The equilibrium isotherms for the adsorption of Ni(II) onto SDS-ZSM-5 nanozeolite at various temperatures (20, 40, and 60°C) and optimum pH of adsorption are depicted in Fig. 10(a) and (b). The relationship between the amount of Ni(II) adsorbed (q_e) and its equilibrium concentration (C_e) was provided using these isotherms. It could also be concluded from these figures that as temperature elevated, the adsorption of Ni(II) was increased. This indicated that the adsorption of Ni(II) from aqueous solutions on SDS-ZSM-5 was an endothermic process.

As represented in Fig. 10, the adsorption of Ni (II) obeyed the Freundlich isotherm better than Langmuir isotherm model. Values of Freundlich constants and determination correlation coefficient (R^2) are illustrated in Table 3. It is also apparent from the determination correlation coefficient (R^2) values that the Freundlich isotherm model is in better agreement with experimental data-sets.

The comparison of the experimentally obtained values with both isotherm models, provided reasonable results for explanation of Ni(II) adsorption by SDS-ZSM-5. Moreover, some other studies proved that

Table 2
Kinetic constant parameters obtained for Ni (II) adsorption on SDS-ZSM-5 nanozeolite at 20°C

	Pseudo-first-order				Pseudo-second-order			
C_i (mg/l)	k_1 (min^{-1})	q_e (mg/g)	R^2	RMSE[a]	k_2 (g/mg min)	q_e (mg/g)	R^2	RMSE
5	0.052	2.151	0.9934	0.056	0.0277	2.471	0.9991	0.022
15	0.0756	3.251	0.9902	0.103	0.0313	3.613	0.9995	0.024
25	0.0651	3.492	0.9852	0.135	0.0238	3.923	0.9995	0.026

[a] Root mean square error.

Table 3
Isotherm constants of the Langmuir and Freundlich models for Ni(II) ions uptake by SDS-ZSM-5 nanozeolite

		Langmuir				Freundlich		
T (°C)	b (l/mg)	q_m (mg/g)	R^2	RMSE	K_f ((mg/g) (l/mg)$^{1/n}$)	n	R^2	RMSE
20	0.5701	4.601	0.9717	0.246	2.2807	5.163	0.9922	0.129
40	1.304	4.905	0.9351	0.419	2.7886	5.834	0.9960	0.104
60	0.5397	5.739	0.7799	0.837	3.5938	8.539	0.9925	0.218

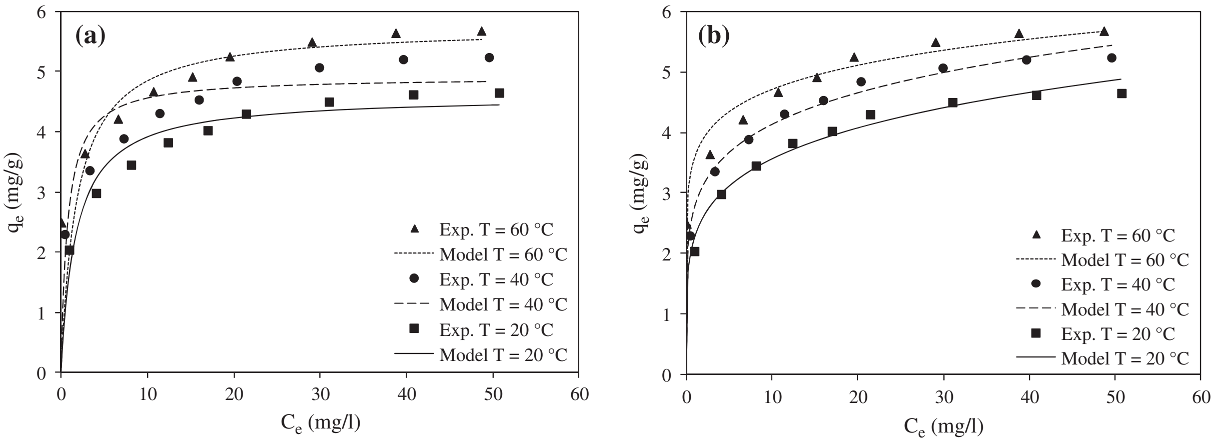

Fig. 10. Adsorption isotherms models for removal of Ni(II) by SDS-ZSM-5 at different temperatures (a) Langmuir (b) Freundlich.

Table 4
Thermodynamic parameters for Ni(II) adsorption on SDS-ZSM-5 at $C_i = 5$ mg/l

T (℃)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol K)	R^2
20	−4.432	23.195	92.31	0.9836
40	−5.521			
60	−7.637			

Table 5
Comparison of maximum adsorption capacities with different types of zeolite for Ni(II) adsorption

Adsorbent	q_m(mg/g)	References
Na-montmorillonite	3.64	[40]
Zeolite	1.98	[41]
Ca-bentonite	6.3	[42]
Na-zeolite	1.3	[43]
Grdes (natural) zeolite	1.44	[43]
Vermiculite	0.229	[44]
Acid (H_2SO_4) treated vermiculite	0.139	[44]
Alkaline (NaOH) treated vermiculite	0.643	[44]
Modified zeolite (HCl + NaCl)	10.75	[45]
SDS-ZSM-5	5.739	This work

Langmuir and Freundlich adsorption isotherms corresponded well with the experimental results of other heavy metals [37–39].

3.7. Adsorption thermodynamics

The thermodynamic parameters such as Gibbs free energy(ΔG°), enthalpy(ΔH°),and entropy(ΔS°) change for Ni(II) adsorption on SDS-ZSM-5 nanozeolite was calculated by the following equation:

$$\ln K_C = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \tag{7}$$

where K_C is the distribution coefficient ($K_C = \frac{q_e}{C_e}\ l/g$), $R = 8.314$ J mol/K is the universal gas constant, and T (K) is the absolute temperature, respectively.

In addition, the Gibbs free energy change was calculated as follows:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{8}$$

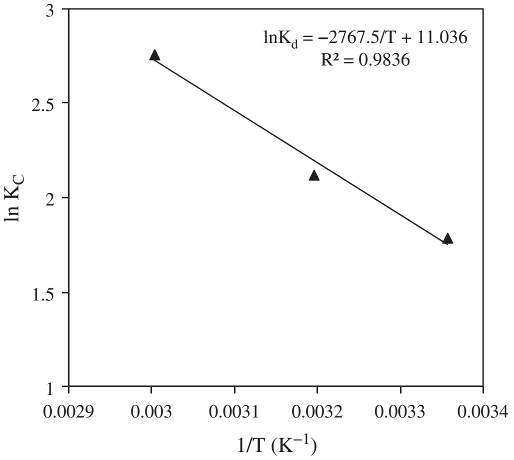

Fig. 11. Plot of ln K_C vs. $1/T$ for Ni(II) adsorption on SDS-ZSM-5.

Value of ΔH° and ΔS° were calculated from the slope and intercept of straight line obtained from the plot between ln K_C vs. $1/T$, respectively (Fig. 11). The obtained thermodynamic parameters for Ni(II) removal by SDS-ZSM-5 were listed in Table 4.

It may be observed from Table 4 that the positive value of enthalpy change ($\Delta H^\circ > 0$) indicated the endothermic process of adsorption, also the positive value of entropy change ($\Delta S^\circ > 0$) illustrated that Ni(II) adsorption caused disorderness in the system. The value of Gibbs free energy change ΔG° indicated the degree of spontaneity of the adsorption process and a more negative value stated that the adsorption process was favorably energetic. The elevation in ΔG° values with increase in temperature showed that the adsorption was favorable at higher temperatures. Comparisons between maximum uptake capacities (q_m) of SDS-ZSM-5 and other adsorbents for Ni(II) reported in the literature are presented in Table 5. The result shows that SDS-ZSM-5 exhibits a reasonable capacity for nickel adsorption from aqueous solutions.

4. Conclusions

The novel approach taken in this research is modification of ZSM-5 nanozeolites using surfactants in order to enhance the adsorption rate of nickel(II) from aqueous solutions. Hence, ZSM-5 nanozeolite was modified with SDS and TPABr as anionic and cationic surfactants, respectively. Thereafter, the surfactant-modified ZSM-5 nanozeolites were compared with bare zeolite for the sorption of Ni(II). SDS-ZSM-5 showed the highest adsorption for Ni(II) compared to other zeolites. In addition, it was observed that the amount of adsorption for bare zeolite was higher than TPA-ZSM-5. Ni(II) adsorption was found to be pH dependent. This influence on the adsorption of Ni(II) on SDS-ZSM-5 was investigated in a pH range of 2–10. The kinetics of Ni(II) adsorption on SDS-ZSM-5 followed the pseudo-second-order rate expression. The removal of Ni(II) was found to be dependent on the initial concentration as well. The removal percentage was increased with an increase in the initial concentration. Isotherm data were investigated according to Langmuir and Freundlich models, although the Freundlich adsorption isotherm model showed better agreement with experimental data than the Langmuir model in the studied temperature range. Ni(II) adsorption on SDS-ZSM-5 was found to be endothermic as adsorption capacity value was higher at higher temperatures. In terms of adsorption thermodynamics, negative values of ΔG° in the adsorption of Ni(II) on SDS-ZSM-5 indicated the spontaneity of the adsorption process, while positive value of ΔS° showed that Ni(II) adsorption causes disorder in the system.

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