

## Nickel ion removal using nanoporous poly(styrene-co divinyl benzene) copolymer

Abbas Bagherian\*, Mohsen Ghorbani\*\*,†, and Seyed Nima Mirzababaei\*

\*Chemical Engineering, Babol University of Technology, Babol, Iran

\*\*Faculty of Chemical Engineering, Babol University of Technology, P. O. Box 484, Babol, Iran

(Received 7 November 2014 • accepted 27 January 2015)

**Abstract**—To achieve a suitable porous structure and high mechanical strength that is extremely valuable properties in adsorbent polymeric particles, poly(styrene-co-divinylbenzene) with high amounts of cross-linker and diverse proportions of diluent agent (porogen) were synthesized according to the methodology of the suspension polymerization technique. The structural characteristics of the particles and their adsorption properties for adsorption of Nickel ions were studied. Effect of solvent type and monomeric fraction on particles morphology and porosity was discussed. The solvents including n-heptane (HEP) and acetonitrile and monomer fraction was 50% and 30% of divinylbenzene (DVB). From the results obtained, we decided to apply an adsorbent with high mechanical strength and a porous structure appropriate for absorbing the Ni(II). The copolymer was characterized by Fourier transform infrared (FT-IR) analysis. We used scanning electron microscopy (SEM) and transmission electron microscopy (TEM) tests to study the morphology and particle size of the nanoparticles. According to the results, the copolymers synthesized with n-heptane have more porosity. Also an increase in the percentage of DVB caused finer pores. After synthesis of copolymer the applicability of these polymer beads to separation and concentration of Ni(II) is discussed. In separation of Ni(II) from aqueous solution, the effects of pH, temperature and time are discussed and thermodynamic and kinetic calculations are done and its isotherm are fitted with various equations.

Keywords: Copolymer, Styrene, Divinylbenzene, Adsorption, Kinetic, Thermodynamic

### INTRODUCTION

Polymer colloids have received much attention due to their vast application areas including conventional and recently emerged electronic and biotechnology fields such as coatings, adhesives, inks, toner binders, immunoassay and so forth [1-3]. At certain stages of industrial processes, the compounds of a given mixture must be separated or purified, and an adsorption procedure is often the best alternative for accomplishing this task. The separation or adsorption of heavy metals through an adsorption process requires continuous research aimed at the development and optimization of adsorbents with properties suitable for specific applications. Once it has been decided to use the adsorption method for a separation process, the next step is to choose the most suitable solid adsorbent. Their applications are dominated by the chemical and/or physical properties of the polymers, and some of the most important physical properties are the size and size distribution of the final particles. In particular, one of the most frequently studied systems is cross linked poly styrene (PS) beads, due superior thermal and mechanical resistance, applicability of surface modification, adaptability in a wide pH range, and susceptibility to deposition of inorganic materials on the surface [4,5] etc.

An ideal adsorbent for the adsorption of heavy metals should have a high adsorption capacity, fast kinetics in the adsorption-

desorption process, and good mechanical and chemical stability. Additionally, the desorption process should be simple and complete to recover the chemical compounds that have been separated in order to reuse the adsorbent. Nanoparticles [6-10] can increase the chemical and physical cross-linking of the system, thus enhancing the strength. There are many types of adsorbent materials such as alumina, silica gel, zeolites, active carbon, and natural and synthetic polymers. Many separation processes are based on the selective adsorption of the components of a mixture on polymeric adsorbents. In recent years, nanoparticles, in particular those based on poly(styrene-co-divinylbenzene), have been widely used as adsorbents owing to their high physical and chemical stability, and their permanent porous structure [11-15]. In many cases, spherical polymeric adsorbent particles are synthesized by suspension polymerization.

Suspension polymerization is a process in which water-insoluble monomers are dispersed as liquid droplets by stirring, to produce polymeric particles as a dispersed solid phase. Poly(styrene-co-divinylbenzene) particles, with structural characteristics ranging from the gel to the porous type, have been synthesized through a free-radical cross linking copolymerization of styrene (St) and DVB monomers using the suspension polymerization method, the divinylbenzene monomer being used as the cross-linker [16-18]. Gel-type particles do not have permanent pores, so they cannot adsorb heavy metals and their use in separation or purification in biotechnology is very limited. In contrast, nanoporous and nanoparticles, which usually have a higher degree of cross-linking than the gel type, have a permanent porous structure and can therefore

†To whom correspondence should be addressed.

E-mail: m.ghorbani@nit.ac.ir

Copyright by The Korean Institute of Chemical Engineers.

be used in a broader range of applications. They are synthesized by adding an organic diluent, inert with regard to the polymerization reaction, which is miscible with the monomers but is a poor solvent for the copolymer, to the mixture of monomers.

There are several methods for preparing a wide range of sizes using different particle formation mechanisms. In synthesizing polymer colloids, it is quite important to endow stability on individual particles to prevent coagulation among the particles. In general, individually stable, spherical polymer beads are obtained by electrostatic stabilization in emulsion polymerization [19], steric stabilization in suspension, dispersion and seeded polymerization [20], and self-stabilization by cross-linking in precipitation polymerization. The porous structure of nanoparticles is due to the hollow space that is left after the removal of the inert organic diluent added to the monomeric mixture during the polymerization reaction. Depending on the thermodynamic affinity between the diluent and the copolymer molecules, and on the proportions of diluent and cross-linker (divinylbenzene) in the organic phase, particles with different porous structures can be obtained [15]. Studies by Abrams and Millar [21] have determined the values of the synthesis conditions under which the onset of macro porosity of poly(styrene-co divinylbenzene) micro particles occurs. These adsorbents display different structural characteristics, which depend on their synthesis conditions.

In this work, nanoporous poly(styrene-co-divinylbenzene) nanoparticles from mixtures with several DVB and porogene concentrations were synthesized. The goal was to determine, within the range of these synthesis conditions, the operating conditions which would lead to the synthesis of an adsorbent with the best compromise between its adsorption equilibrium and kinetic properties. This paper deals with the adsorption of Ni(II) on several kinds of poly(styrene-co-divinylbenzene) polymer beads prepared by the copolymerization of styrene (st) and DVB. Once the porous structures of the nanoparticles synthesized had been characterized, experiments addressing the adsorption of a heavy metal on these nanoparticles were carried out. The adsorption isotherms allowed us to determine the maximum adsorption capacity of the heavy metal on each adsorbent by fitting the adsorption model to the isotherm data. Also, thermodynamics and kinetics study of the absorption, the optimum conditions for nickel ions by copolymer network is determined. Therefore, in addition to the economic comparison of this method, the proper scope of the adsorbed Ni(II) could be determined.

## EXPERIMENTAL

### 1. Materials

#### 1-1. Organic Phase

The monomers to be polymerized were styrene (St, 99%) and divinylbenzene (DVB, containing 55% DVB isomers, the remainder mainly being 3- and 4-ethylvinylbenzene), which were supplied by Merck. Prior to polymerization, both monomers were first washed with a 5% aqueous NaOH solution to remove the inhibitor, p-tert-butylcatechol, and then with deionized water until neutralization. The initiator, benzoyl peroxide (BPO, 70%, remainder water), was supplied by Merck and used as received. The inert dilu-

ent (porogen) was n-heptane (HEP, synthesis grade) and acetonitrile which was obtained from Merck.

#### 1-2. Aqueous Phase

The suspension agent was poly vinyl alcohol (PVA, having a weight-average molar mass of 72000 and a degree of hydrolysis of 98%) from Merck. It was used without further purification. All the other reagents were of synthesis grade and used as obtained. Aqueous solutions were prepared from deionized water.

The adsorption experiments were carried out with salt-sulfate buffer solutions, which were prepared from  $\text{NiSO}_4 \cdot 6 \text{H}_2\text{O}$ , of reagent grade and all obtained from Merck.

### 2. Preparation of Copolymers

Poly(styrene-co-divinylbenzene) nanoparticles were prepared by the suspension polymerization technique, using n-heptane or acetonitrile as the porogen. Benzoyl peroxide was used as the initiator, and poly(vinyl alcohol) was used as the suspension agent. The DVB concentration in the monomeric mixture (% DVB, w/w, the weight percentage of DVB isomers in the monomeric mixture) and the monomeric fraction in the organic phase ( $F_m$ , v/v, the volume fraction of the monomers in the organic phase) were synthesis conditions. So their effects were considered on the structural characteristics of the nanoparticles. In a typical polymerization, the reaction was in a 500 mL three-necked round bottomed jacketed glass reactor fitted with a mechanical stirrer, a condenser, and a thermometer. At first, a solution of 0.5% wt PVA in 250 mL of water at 70 °C was prepared into the reactor and heated to 85 °C. The monomers (St and DVB) were mixed well to form the monomeric mixture. Then 0.5% wt BPO initiator was added. The diluent was added to this monomeric mixture to form the organic phase as porogen followed by transfer the mixture into the reactor. The volume ratio between the two phases (organic/aqueous) was 1/5 for all reactions. Polymerization was performed at a temperature of 80 °C for 8 hr with stirring; the stirrer speed was 400 (rpm). After polymerization, the resulting copolymer were washed with double distilled water at 65 °C and than these products were vacuum-filtered to dissolve the PVA surrounding them. To remove progeny and residual monomers the products were stirred in acetone for at least 6 h in a Soxhlet apparatus, then they were washed with methanol in order to remove impurities. Finally, the beads were dried under vacuum in an oven at 45 °C for 24 h and then sieved.

Also this procedure was carried out with using acetonitrile as diluent and monomer ratio of 50% and 30%.

### 3. Characterization of the Copolymers

#### 3-1. SEM

The surface morphology of the copolymer beads was examined by scanning electron microscopy using a KYKY EM 3200 microscope. Some beads were broken to disclose their inner structure.

#### 3-2. TEM

TEM images were acquired using a Zeiss - EM10C transmission electron microscope with an accelerating voltage of 80 KV. The samples were first prepared to suspension by ultrasonic dispersion and then were drought at ambient temperature from a droplet on carbon-coated copper grids. The relevant size data of nanoparticles was obtained by averaging the values from TEM measurements.

#### 3-3. FTIR Analysis

Fourier transform infrared spectra of polymeric beads were

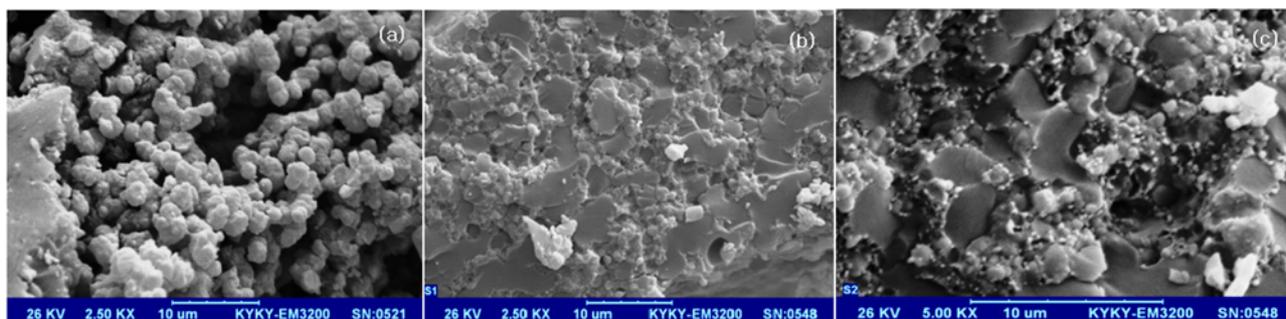


Fig. 1. Scanning electron microphotographs of the external surface of the styrene-divinylbenzene copolymers: (a) 30% DVB with n-heptane, (b) 50% DVB with n-heptane and (c) 30% DVB with acetonitrile.

recorded on a Bruker-Tensor 27 series spectrophotometer.

#### 4. Adsorption Experiments

After adsorption time, the Ni(II) concentration in the supernatant ( $C_e$ , mg/mL) was determined with a UV-vis spectrophotometer (Varian, Cary 50) at 280 nm. The amount of Ni(II) adsorbed per unit dry weight of adsorbent ( $q_e$ , mg/g of dry adsorbent) was obtained from a mass balance.

#### 5. Batch Adsorption Experiments

Adsorption experiments were performed by batch method at ambient temperature. To consider the interaction between Ni(II) and poly(styrene-co-divinylbenzene) the effects of pH, initial concentration and temperature on adsorption capability were considered. During the experiments only one parameter was changed at a time while others were kept constant. At the beginning of each experiment, the amount of removal was considered at various pH values (2, 3, 4, 6, 8) at adsorbent dosage of  $10 \text{ g}\cdot\text{L}^{-1}$ , initial Ni(II) of  $100 \text{ mg}\cdot\text{L}^{-1}$  and a predetermined time (200 min) in a shaker at a speed of 200 rpm using series of clean 10 mL conical flasks. After determination of optimum pH, the effects of Ni(II) concentration (10, 50 and  $100 \text{ mg}\cdot\text{L}^{-1}$ ), temperature and time contact were measured.

The percentage removal of Ni(II) was calculated according to the following equation:

$$\%R = \frac{C_o - C_t}{C_o} \times 100 \quad (1)$$

where  $C_o$  and  $C_t$  are the Ni(II) concentrations in  $\text{mg}\cdot\text{L}^{-1}$  initially and at a given contact time  $t$ , respectively. The amount of Ni(II) removed per unit mass of adsorbent ( $q$ ) was calculated according to:

$$q_e = \frac{(C_o - C_e) \times V}{m} \quad (2)$$

where  $v$  is the solution volume (L),  $m$  is the amount of adsorbent (g), and  $C_o$  and  $C_e$  are the initial and equilibrium Ni(II) concentrations ( $\text{mg}\cdot\text{L}^{-1}$ ), respectively.

#### 6. Analysis of Ni(II)

The analysis of Ni(II) was performed calorimetrically; absorbance values were obtained at the wavelength for maximum absorbance ( $\lambda_{max}=445 \text{ nm}$ ) by making a red colored complex of Ni(II) with dimethylglyoxime which was converted into concentration data using calibration relation predetermined at the wavelength of interest as illustrated by Gazda et al. [22].

## RESULTS AND DISCUSSION

### 1. Structural and Mechanical Characterization of the Adsorbents

#### 1-1. SEM Photographs

Fig. 1(a), (b) and (c) shows the scanning electron microphotographs of the external surface and inner structure of the particles obtained with n-heptane and 30% DVB, n-heptane and 50% DVB and also acetonitrile and 30% DVB respectively.

The adsorbents synthesized with the n-heptane (Fig. 1(a)) have the most open structure, confirming the conclusions obtained from the pore size distributions of the adsorbents. N-heptane is a poor solvent. Therefore, due to structural differences with the monomers the phase separation in copolymer synthesis is well done. As seen in Fig. 1(c) copolymer synthesized using acetonitrile as the solvent has a dense structure with less porosity and surface area and smaller pore size. We can say because the phase separation during the synthesis of copolymers with acetonitrile will be slower than n-heptane, so the network will be expanded and has gel-like structure.

As seen in Fig. 1(b) the copolymer synthesized with high amounts of DVB (50%) has small pores and low porosity. Increasing the DVB led to high density of network crosslinking, and it reduced the distance between fitting and causing small pores.

Among the synthesized copolymers, copolymer with n-heptane as progeny and 30% DVB is more suitable for the adsorption process, due to the porous structure and uniform spherical particles. Since, in this case, adsorption capacity will be increased and also particles shape is more suitable for the deposition of functional group. Thus, we choose the copolymer synthesized with n-heptane as porogen and 30% DVB for adsorption process.

#### 1-2. TEM Images of Copolymers

Fig. 2 shows the TEM images and the size distribution of the poly(styrene-co-divinylbenzene) nanoparticles. These copolymers had a good size monodispersity (mean particle size: 50 nm) and were free from non-spherical by-products.

In fact, every particle in the SEM images is composed of nanoparticles that we see this particle size range in TEM images.

#### 1-3. FTIR Analysis

The infra-red spectrum of the poly(styrene-co-divinylbenzene)-based nanoparticles is shown in Fig. 3. By observing Fig. 3, the presence of aromatic rings in the polymer can be confirmed by the presence of several characteristics bands of these structures, such as the characteristic absorption bands of unsubstituted styryl residues at

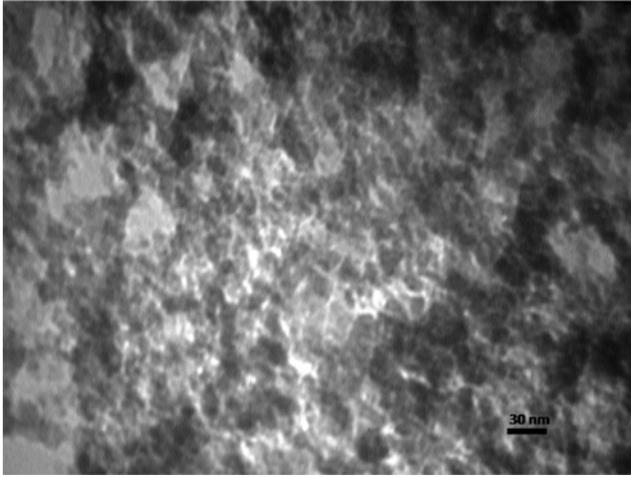


Fig. 2. TEM image of styrene-divinylbenzene copolymer synthesis with 30% DVB with n-heptane and their particle size distribution.

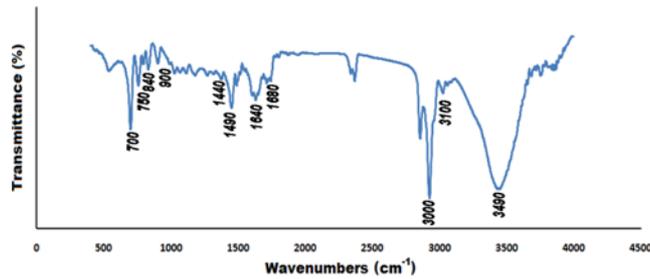


Fig. 3. FT-IR spectra of poly(styrene-co-divinylbenzene).

700 and 750  $\text{cm}^{-1}$ , those of the vinyl aromatic bonds at 1,440 and 1,490  $\text{cm}^{-1}$ , and those that match the skeletal vibration at 1,603  $\text{cm}^{-1}$ .

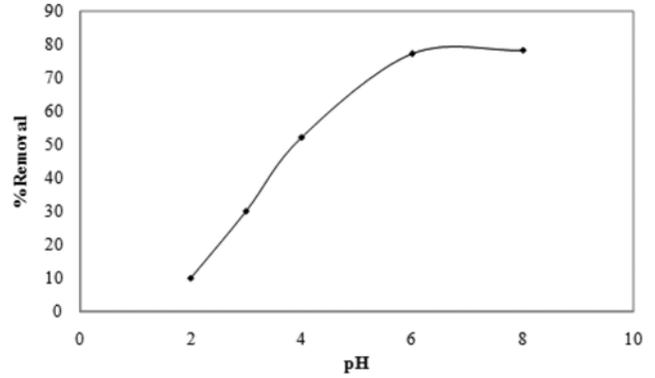


Fig. 4. Effect of the solution pH on the nickel ions adsorption onto poly(styrene-co-divinylbenzene).

Interestingly, the presence of para-crosslinks from the DVB isomers is demonstrated by the peaks at  $840 \text{ cm}^{-1}$ . Furthermore, in this figure, one characteristic absorption band of monosubstituted vinyl groups can be recognized ( $900 \text{ cm}^{-1}$ ), likely due to unreacted double bonds during the polymerization reaction. Peaks of  $1,640\text{--}1,680 \text{ cm}^{-1}$  is related to C=C bonds and  $3,000\text{--}3,100 \text{ cm}^{-1}$  is related to =C-H bonds. Also humidity in the sample has created a peak in  $3,490 \text{ cm}^{-1}$ .

1-4. Molecular Weight

Synthesized copolymer has high percentage of crosslinking agent that its structure is very hard and cannot be solved in any solvent. There is a part of mysterious skeleton which is very compact for the hyper-cross-linked resin [23,24], and this very compact skeleton cannot be swollen by solvents. Although this feature is an advantage of the copolymer but dissolving in the solvent is necessary for calculating the molecular weight. Due to the lack of dissolving in a solvent, it was impossible to calculate the molecular weight.

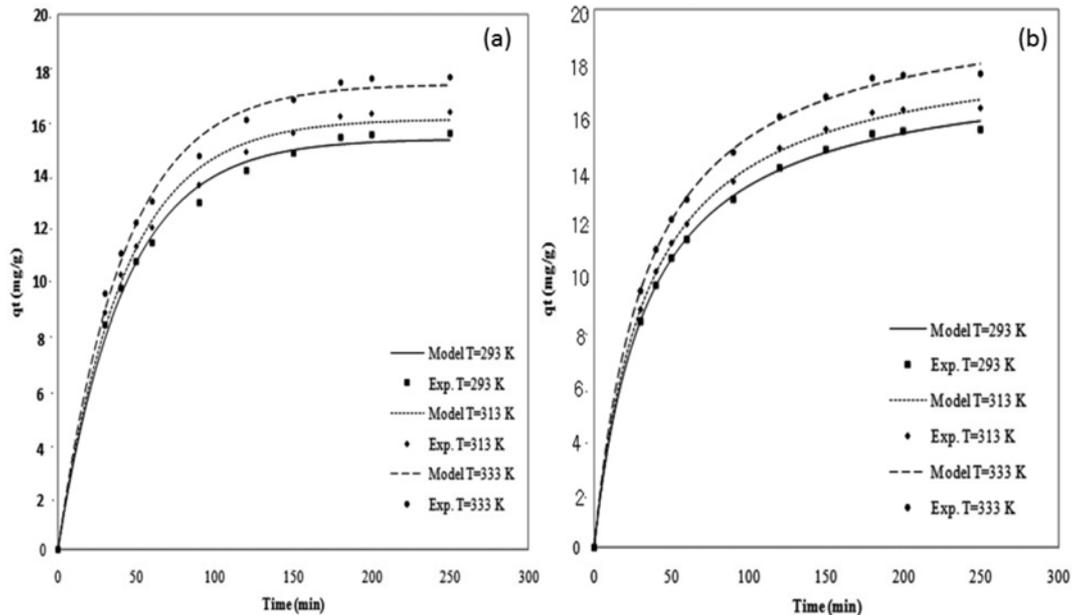


Fig. 5. Adsorption kinetic curves for the nickel ions adsorption onto poly(styrene-co-divinylbenzene): (a) The curve of the pseudo-first-order kinetics and (b) pseudo-second-order kinetics.

**Table 1. Kinetic parameters of nickel ions adsorption on poly(styrene-co-divinylbenzene)**

Second-order kinetics						
Temp.	C <sub>i</sub>	R <sup>2</sup>	a	B	q <sub>e</sub>	100*K <sub>2</sub>
20	100	0.999	1.3233	0.0293	45.16382	2.93
40	100	0.999	1.3894	0.0295	47.09831	2.95
60	100	0.999	1.5006	0.0297	50.52525	2.97
First-order kinetics						
Temp.	C <sub>i</sub>	R <sup>2</sup>	a	B	q <sub>e</sub>	100*K <sub>1</sub>
20	100	0.9945	38.3691	0.0241	38.3691	2.41
40	100	0.9952	40.2875	0.0242	40.2875	2.42
60	100	0.9956	43.5105	0.0247	43.5105	2.47

### 1-5. Effect of pH

The effect of the solution pH on the adsorption of Ni(II) from aqueous solution onto poly(styrene-co-divinylbenzene) is illustrated in Fig. 4.

As shown, the pH values were verified in the range of 2 to 8. The removal of nickel had an increase trend from 2 to 8 pH value remarkably. Then the removal percentage was stable for higher than 6. Therefore removal of metal ions on the surface of adsorbent can be explained as H<sup>+</sup>-Ni<sup>2+</sup> exchange reaction. At the acidic range of pH from 2 to 6, H<sup>+</sup> ions compete with Ni<sup>2+</sup> ions for the surface of the adsorbent; thus the repulsive forces would prevent Ni(II) ions from binding sites of the sorbent. Therefore, the optimum pH range for the removal of Ni(II) was found to be 8, which was also reported by Hasar [25] and Panneerselvam et al [26].

### 1-6. Adsorption Kinetics

Fig. 5 displays the kinetic curves for the nickel ions adsorption onto poly(styrene-co-divinylbenzene) from aqueous solution. It is obvious that the nickel adsorption onto poly(styrene-co-divinylbenzene) can reach equilibrium within 250 min. Lower initial concentration of Ni(II) results in a shorter required time with a smaller adsorption capacity. The pseudo-first-order and pseudo-second-order kinetic models assume that the adsorption is a pseudo-chemical reaction and the adsorption rate can be determined as [27,28]:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (3)$$

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (4)$$

where q<sub>e</sub> and q<sub>t</sub> are the amounts of Ni(II) adsorbed (mg·g<sup>-1</sup>) at equilibrium and at time t, k<sub>1</sub> (min<sup>-1</sup>) and k<sub>2</sub> (g/(mg·min)) are the pseudo-first-order and pseudo-second-order rate constants, respectively.

Integrating Eqs. (3) and (4) will give:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (5)$$

**Table 2. Isotherm equation used in this study**

Plot	Parameters	Linear form equation	Equation	Isotherm
Log Q <sub>e</sub> vs log C <sub>e</sub>	K <sub>f</sub> , n	Log Q <sub>e</sub> = log K <sub>f</sub> + n log C <sub>e</sub>	Q <sub>e</sub> = K <sub>f</sub> C <sub>e</sub> <sup>n</sup>	Freundlich
1/Q <sub>e</sub> vs 1/C <sub>e</sub>	K <sub>L</sub> , Q <sub>m</sub>	1/Q <sub>e</sub> = [(1/K <sub>L</sub> Q <sub>m</sub> )(1/C <sub>e</sub> )] + (1/Q <sub>m</sub> )	Q <sub>e</sub> = K <sub>L</sub> Q <sub>m</sub> C <sub>e</sub> / (1 + K <sub>L</sub> C <sub>e</sub> )	Langmuir

**Table 3. Isotherm parameters of nickel ions adsorption on poly(styrene-co-divinylbenzene)**

Freundlich parameters						
Freundlich	Temp.	R <sup>2</sup>	A	B	K <sub>f</sub>	n
	20	0.9941	12.9262	0.3577	12.9262	2.795639
Langmuir parameters						
Langmuir	Temp.	R <sup>2</sup>	A	B	K <sub>L</sub>	Q <sub>max</sub>
	20	0.9705	12.8229	0.3071	0.3071	41.7548

$$\frac{t}{q_t} = \frac{1}{k_2 \cdot q_e^2} + \frac{t}{q_e} \quad (6)$$

If the adsorption follows the pseudo-first-order rate equation, a plot of ln(q<sub>e</sub> - q<sub>t</sub>) versus t should be a straight line. On the other hand, t/q<sub>t</sub> should change linearly with t if the adsorption obeys the pseudo-second-order rate equation. The pseudo-first-order and pseudo-second-order rate have been employed extensively in this study of adsorption kinetics. Available studies have shown that the pseudo-second-order rate equation is a reasonably good fit of data over the entire fractional approach to equilibrium [29,30]. Plotting of t/q<sub>t</sub> versus t and ln(q<sub>e</sub> - q<sub>t</sub>) versus t for the Nickel ions adsorption onto poly(styrene-co-divinylbenzene) is determined and the fitted correlation parameters are summarized in Table 1. The results reveal that between the two considered models, the pseudo-second order kinetic equation gives higher R<sup>2</sup> values, so it better explains the mechanism of Ni(II) adsorption.

Fig. 5(a) shows the curve of the pseudo-first-order kinetics and Fig. 5(b) pseudo-second-order kinetics. According to the results of the matching equation in Table 1, the pseudo-second-order kinetics are more matches in this adsorption process.

### 1-7. Adsorption Isotherms

Langmuir and Freundlich models listed in Table 2 are adopted to explain the relationship between the amount of adsorbed Ni(II) (q<sub>e</sub>) and concentration (C<sub>e</sub>) at equilibrium at temperature 20 °C, and the corresponding parameters are listed in Table 3.

Where q<sub>e</sub> is the amount adsorbed per gram of adsorbent (mg·g<sup>-1</sup>) and C<sub>e</sub> is the concentration of Ni(II) (mg·l<sup>-1</sup>) in the aqueous solution in equilibrium. Q<sub>m</sub> and b are both constants related to the maximum adsorption capacity (mg·g<sup>-1</sup>) and the adsorption energy (l·mg<sup>-1</sup>), respectively, which are calculated from the isotherm curves (Fig. 6) of Q<sub>m</sub> versus C<sub>e</sub> given in Table 3 along with correlation coefficients (R<sup>2</sup>).

The Freundlich model is more suitable for the adsorption since R<sup>2</sup> > 0.99. So under the assumptions of Freundlich, adsorbent surface is heterogeneous.

### 1-8. Adsorption Thermodynamics

As can be seen from Fig. 7 the adsorption capacity of Nickel onto

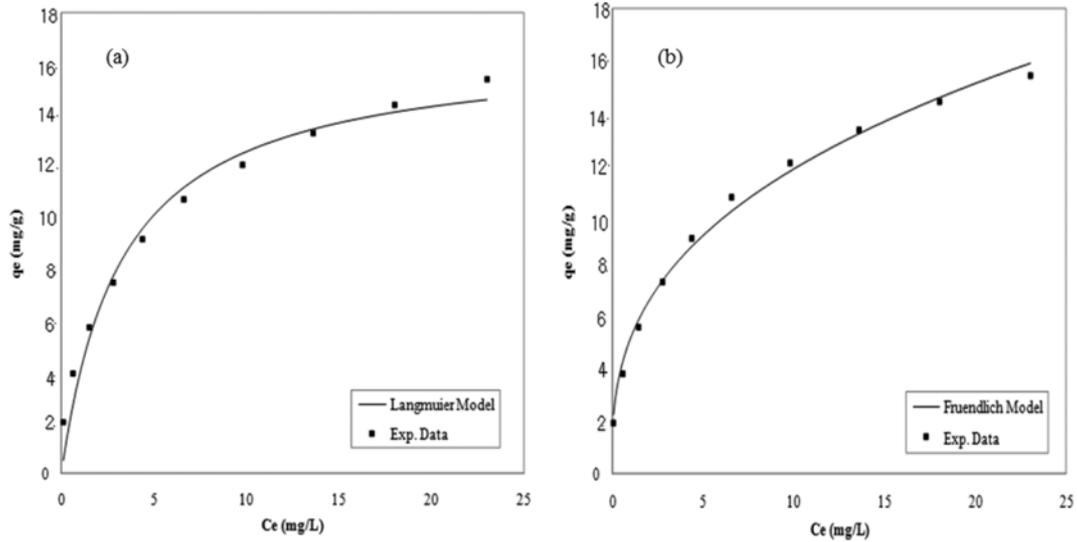


Fig. 6. Adsorption isotherms of nickel ions onto poly(styrene-co-divinylbenzene) from aqueous solution: (a) Freundlich model and (b) Langmuir model.

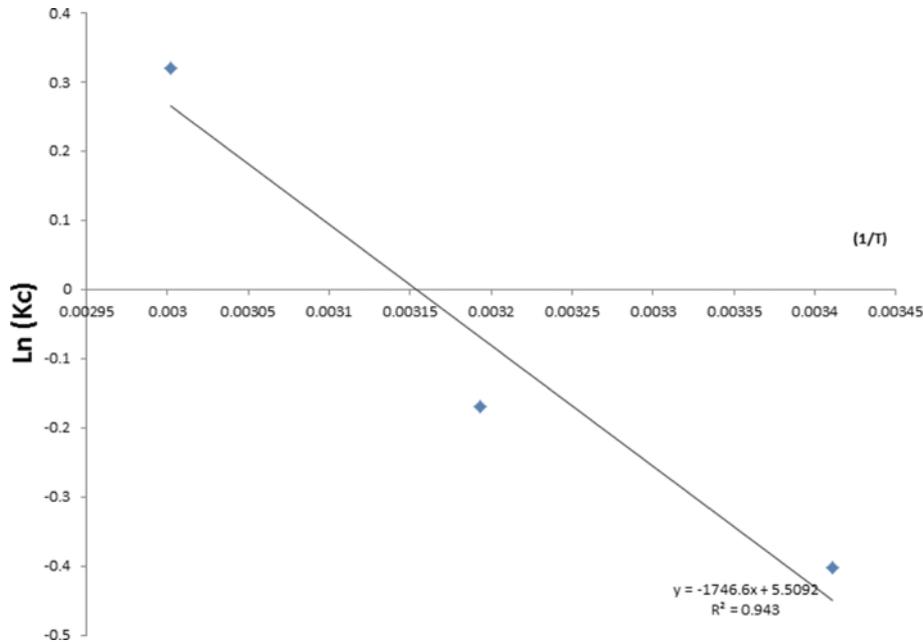


Fig. 7. Adsorption thermodynamic curves for the Nickel ions adsorption onto poly(styrene-co-divinylbenzene).

poly(styrene-co-divinylbenzene) increases with increasing the temperature, suggesting an endothermic process [31].

The thermodynamic parameters such as Gibbs free energy, enthalpy and entropy change for adsorption on poly(styrene-co-divinylbenzene) nanoparticles are calculated and represented in Table 4.

The standard thermodynamic equilibrium constant  $K_c$ , is calcu-

Table 4. Thermodynamic parameters of nickel ions adsorption on poly(styrene-co-divinylbenzene)

Delta H	Delta S	Delta G
14.49962	59.12917	-17319.2

lated by using the following equation:

$$\ln K_c = -\left(\frac{\Delta H^\circ}{RT}\right) + \left(\frac{\Delta S^\circ}{R}\right) \tag{7}$$

where  $R=8.314 \text{ J}\cdot\text{mol}^{-1} \text{ K}^{-1}$  is the universal gas constant,  $T$  (K) is the absolute temperature and  $K_c=q_e/c_e$  ( $\text{L}\cdot\text{mg}^{-1}$ ).

In addition, the Gibbs free energy change is calculated by the following relation:

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

As seen in Table 4 the value of enthalpy change is positive ( $\Delta H^\circ > 0$ ) so the process of adsorption is endothermic; also the positive

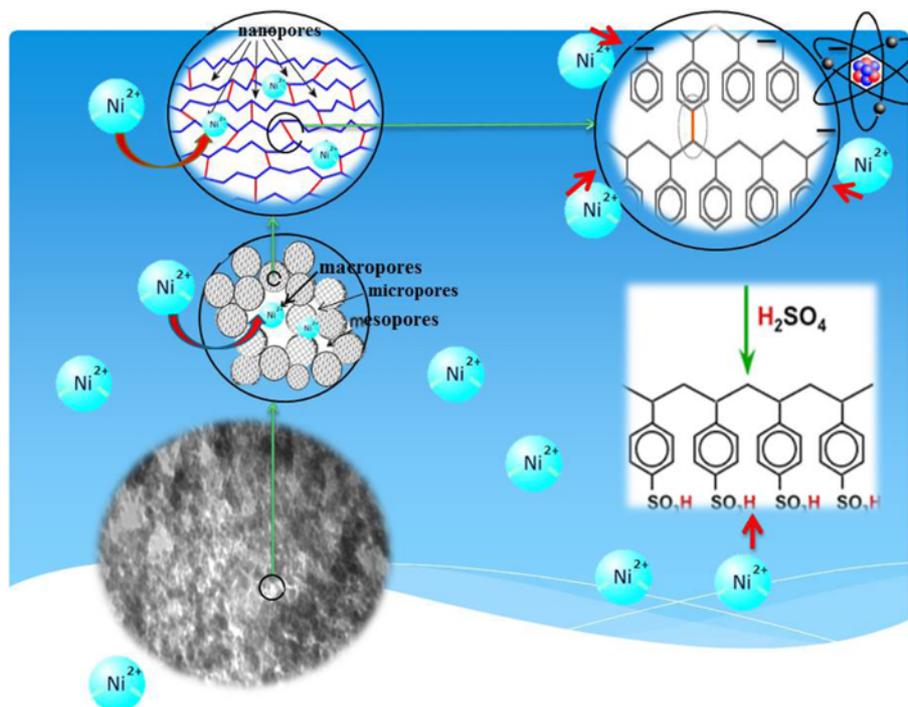


Fig. 8. Mechanisms of nickel ions adsorption onto poly(styrene-co-divinylbenzene).

value of entropy change ( $\Delta S^\circ > 0$ ) illustrates that Ni(II) adsorption causes disorderliness in the system.

#### 1-9. Adsorption Mechanism

As can be seen in SEM and TEM images, the structure of synthesized copolymer has many nano and also macro pores that are much firm and fixed because of high cross link grafts. We can say that most of the removal is because of this porous structure and specific surface area. Nickel ions that have the atomic radius of 200 pm are attracted into the surface pores by physical force and polarity and trapped in there. In general, specific surface area, pore structure and polarity are thought to be the main factors influencing the adsorption [32]. Therefore, although the adsorption capacity is high, it will take a long time. Beside this main mechanism, perhaps it can probably be that resonance in polymeric network is stable because of extent of network, and so negative charge causes the adsorption of nickel ions that have orbital of 3d8-4s0 and demanding an electron. Due to high capacity of this copolymer because of high porosity can with put the sulfone group on benzene ring and create the ion exchange process, increasing the adsorption capacity significantly. In this case, we sulfonated the copolymer by sulfuric acid, and after performing an adsorption test, we observed that adsorption time was reduced from 180 to 5 min. Therefore, the sulfone group in the copolymer structure and performing ion exchange improved the adsorption characteristics. These mechanisms are shown in Fig. 8.

#### CONCLUSIONS

Poly(styrene-co-divinylbenzene) nanospheres having a diameter range of 15-90 nm were synthesized by precipitation polymerization under various conditions, and the effects of the polymeriza-

tion parameters on the polymerization and the final particles were studied and compared with dispersion polymerization. It was demonstrated the possibility to increase the adsorption of Nickel ions and by the appropriate tailoring of the surface functionality of the polymeric adsorbent. The kinetic studies indicated that the adsorption of nickel ions onto Poly(styrene-co-divinylbenzene) adsorbents followed the pseudo-second order model. The experimental data for Ni(II) adsorption onto poly(styrene-co-divinylbenzene) were correlated by the Freundlich isotherm model. In terms of adsorption thermodynamics, negative value of  $\Delta G^\circ$  in the adsorption of Ni(II) on Poly(styrene-co-divinylbenzene) indicates the spontaneity of the adsorption process, while positive value of  $\Delta S^\circ$  showed that Ni(II) adsorption caused disorderliness in the system. Generally, poly(styrene-co-divinylbenzene), besides the morphology and porous resistant structure and ability to synthesize and deposition potential of functional groups, is suitable for the adsorption of metal cations, so the adsorption behavior was evaluated here.

#### REFERENCES

1. D. Urban and K. Takamura (eds.), *Polymer dispersions and their industrial applications*, Wiley-VCH, Weinheim (2002).
2. H. Fudouz and Y. Xia, *Adv. Mater.*, **15**, 892 (2003).
3. J. Ugelstad, P. Stenstad, L. Kilaas, W.S. Prestvik, A. Rian, K. Nustad, R. Herje and A. Berge, *Macromol. Symp.*, **101**, 491 (1996).
4. J. C. Moore, *J. Polym. Sci.*, **A-2**, 835 (1964).
5. J.-G. Park, J.-W. Kim, S.-G. Oh and K.-D. Suh, *J. Appl. Polym. Sci.*, **87**, 420 (2003).
6. B. Likozar and M. Krajnc, *J. Appl. Polym. Sci.*, **110**, 183 (2008).
7. S. Kaang, W. Jin, M. Abdul Kader and C. Nah, *Polym.-Plast. Technol. Eng.*, **43**, 1517 (2004).

8. Y. Lu, L. Liu, M. Tian, H. Geng and L. Zhang, *Eur. Polym. J.*, **41**, 589 (2005).
9. A. B. Samui, V. G. Dalvi, L. Chandrasekhar, M. Patri and B. C. Chakraborty, *J. Appl. Polym. Sci.*, **99**, 2542 (2006).
10. Y. Lu, L. Liu and C. Yang, *Eur. Polym. J.*, **41**, 577 (2005).
11. C. Garcia-Diego and J. Cuellar, *Ind. Eng. Chem. Res.*, **44**, 8237 (2005).
12. C. Garcia-Diego and J. Cuellar, *Ind. Eng. Chem. Res.*, **45**, 3624 (2006).
13. L. A. Cantarero, J. E. Butler and J. W. Osborne, *Anal. Biochem.*, **105**, 375 (1980).
14. L. L. Lloyd, *J. Chromatogr.*, **544**, 201 (1991).
15. O. Okay, *Prog. Polym. Sci.*, **25**, 711 (2000).
16. H. G. Yuan, G. Kalfas and W. H. Ray, *J. Macromol. Sci., Rev. Macromol. Chem. Phys.*, **C-31**, 215 (1991).
17. E. Vivaldo-Lima, P. E. Wood, A. E. Hamielec and A. Penlidis, *Ind. Eng. Chem. Res.*, **36**, 939 (1997).
18. A. E. Hamielec and H. Tobita, *Polymerization Process-In Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH, Weinheim, Germany (2002).
19. P. A. Lovell and M. S. El-Aasser, *Emulsion polymerization and emulsion polymers*, Wiley, New York (1999).
20. D. H. Napper, *Polymeric stabilization of colloidal dispersions*, Academic, London (1983).
21. I. M. Abrams and J. R. Millar, *React. Funct. Polym.*, **35**, 7 (1997).
22. D. B. Gazda, J. S. Fritz and M. D. Porter, *Anal. Chim. Acta*, **508**, 53 (2004).
23. K. Allmer, A. Hult and B. Raanby, *J. Polym. Sci.*, **A 27**, 3405 (1989).
24. L. M. Landoll and D. S. Breslow, *J. Polym. Sci.*, **A 27**, 2189 (1989).
25. H. Hasar, *J. Hazard. Mater.*, **B-97**, 49 (2003).
26. P. Panneerselvam, V. SathyaSelvaBala, N. Thinakaran, P. Baskaralingam, M. Palanichamy and S. Sivanesan, *E-J. Chem.*, **6**, 729 (2009).
27. X. Y. Yang and B. Al-Duri, *J. Colloid Interf. Sci.*, **287**, 25 (2005).
28. L. J. You, Z. J. Wu, T. Kim and K. Lee, *J. Colloid Interface Sci.*, **300**, 526 (2006).
29. J. H. Yoon, J. I. Baek, Y. Yamamoto, T. Komai and T. Kawamura, *Chem. Eng. Sci.*, **58**, 5229 (2003).
30. S. Paul, A. K. Ghoshal and B. Mandal, *Chem. Eng. Sci.*, **64**, 313 (2009).
31. B. L. He and W. Q. Huang, *Ion exchange and adsorption resin*, Shanghai Science and Education Press, Shanghai (1995).
32. J. Huang, G. Wang and K. Huang, *Chem. Eng. J.*, **168**, 715 (2011).