

## Adsorption isotherms, kinetic, and desorption studies on removal of toxic metal ions from aqueous solutions by polymeric adsorbent

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**ABSTRACT:** Adsorption of Cd(II), Co(II), and Ni(II) on aminopyridine modified poly(styrene-*alt*-maleic anhydride) crosslinked by 1,2-diaminoethane as an ion exchange resin has been investigated in aqueous solution. Adsorption behavior of these metal ions on the resin was studied by varying the parameters such as pH (2–6), adsorbent dose (0–4.0 g/L), contact time (0–240 min), and metal ions concentration (20–300 mg/L). Adsorption percentage was increased by increasing each of these parameters. The isotherm models such as: Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich were used to describe adsorption equilibrium. The results showed that the best fit was achieved with the Langmuir isotherm equation, yielding maximum adsorption capacities of 81.30, 49.02, and 76.92 mg/g for Cd(II), Co(II), and Ni(II), respectively. The pseudo-first-order, pseudo-second-order, and intra-particle diffusion kinetics equations were used for modeling of adsorption data and it was shown that pseudo-second-order kinetic equation could best describe the adsorption kinetics. The intra-particle diffusion study revealed that external diffusion might be involved in this case.  
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**KEYWORDS:** adsorption; desorption; ion exchange resin; isotherms; kinetics; metal ions

Received 17 June 2014; accepted 17 October 2014

DOI: 10.1002/app.41642

### INTRODUCTION

Aquatic environments pollution by toxic metal ions, particularly as a result of industrialization, is increasingly being associated with public health in an urban setting, as toxic metals not only lead to contamination of aquatic life but also cause harm to people's health, even at low concentrations.<sup>1</sup> In recent years, there has been a growing concern with environmental protection. This can be achieved either by decreasing of pollutants invasion to the environment or by their removal from contaminated media. It is necessary to bring up methods to lower their attendance in contaminated media to harmless quantities, as cobalt, chromium, and nickel are among the most toxic of elements.<sup>2</sup> Among these toxic metals, cadmium is of considerable environmental and health significance because of its increasing mobilization and human toxicity. The major sources for the introduction of cadmium in water are nonferrous metals smelting and refining, manufacturing processes related to chemicals and metals, and domestic wastewater.<sup>3</sup> Cadmium also exposes human health to severe risks, as it can provoke cancer, kidney damage, mucous membrane destruction, vomiting, bone damage as well as affect the production of progesterone and testosterone.<sup>4</sup> Major anthropogenic sources of cobalt as a pollutant in the environment include nuclear power plants and many indus-

tries such as mining, metallurgical, electroplating, paints, pigments as well as the electronic industries.<sup>5</sup> In workers exposed to pure cobalt metal powder, cobalt salts, and cobalt-containing dusts, the two main target organs are the respiratory tract and the skin. When plants grow on contaminated soils they will accumulate very small particles of cobalt, especially in the parts of the plant we eat, such as fruits and seeds. So, this contamination which uptake by humans through eating plants can be cause of health effects. Health effects that are a result of the uptake of high concentrations of cobalt are: vomiting and nausea, vision problems, heart problems, and thyroid damage.<sup>6</sup>

Nickel, another pollutant, is the major part of municipal wastewater followed by waste of nonferrous metals smelting and refining causes respiratory cancer of workers that work in nickel refinery factory. Moreover, the presence of nickel exceeding its critical level might bring about serious lung and kidney problems.<sup>7</sup>

Several methods have been widely applied for the removal of toxic metal ions such as precipitation, ion exchange, reduction, electrochemical treatment, reverse osmosis, solvent extraction, membrane filtration, and so forth.<sup>8</sup> Most often, these methods have a high cost, generate secondary pollutants, or are simply incompetent, especially in removing toxic metal ions in trace

**Table I.** Comparison of Adsorption Capacity of Various Adsorbents for Cd(II), Co(II), and Ni(II) Ion Adsorptions

Adsorbent	Adsorption capacity (mg/g)			References
	Cd (II)	Co (II)	Ni (II)	
IRN-77	–	74.63	62.11	18
C3-ATAH	–	126.93	55.20	19
Modified carrot residues (MCR)	–	5.746	6.031	20
Succinylated mercerized cellulose (DIPCI)	68.0			21
Mango peel waste	68.92	–	–	22
CT-8HQbeads	–	–	9	23
Amberlite IRC-748	–	–	62.20	24
Purolite S950 chelating resin	–	9.0	–	25
CSMA-AP	81.30	76.92	49.02	This work

quantities from aqueous solutions.<sup>9</sup> Of all the various methods, adsorption using low-cost adsorbents is considered to be an economical and effective method for removal of toxic metal ions from aqueous solutions.<sup>10</sup> There are many types of adsorbents, including activated carbon fibers,<sup>11</sup> resins, and biosorbents.<sup>12–14</sup> Chelating materials are critically effective and opportune adsorbents.<sup>15,16</sup> Therefore, the most promising technique for removal of toxic metal ions is their adsorption on organic sorbents containing chelating functional groups.<sup>17,18</sup> The adsorption capacities for Cd(II), Co(II), and Ni(II) uptake by different adsorbents were presented in Table I.<sup>19–26</sup>

Synthetic chelating ion exchange resins are receiving considerable attention because of their application in different areas such as the removal of toxic metals, heterogeneous catalysis, solid electrolytes, ion exchange membrane, ion selective electrode, and purification of drinking water and industrial wastewaters.<sup>27,28</sup> In recent years, the development of high performance adsorbents in nanoscale for removal of toxic metal ions from aqueous solutions and other applications is considered a research priority in the wide fields.<sup>29,30</sup> Nanotechnology has been able to deliver a wide range of new materials. Nanomaterials can be made from a range of solid materials such as polymers, organic materials, metals, ceramics, and composites. These new nanomaterials are increasingly becoming the subject of many investigations in several fields, particularly those of engineering, biotechnology, and biomedical sciences. The use of nanomaterials of biodegradable polymers is being extensively studied as they provide an attractive alternative for a number of environmental applications by providing a method for extraction of trace metal and removal of toxic metal ions from water and wastewater.<sup>31–33</sup>

Around the synthetic polymers (styrene-*alt*-maleic anhydride) copolymer (SMA) is the commercial industrial copolymer which is cheaper than any other polymers possessing reactive group in the main chain or side chain for further functionalization.<sup>34</sup> The SMA copolymer is biocompatible compound which has been used in drug delivery and controlled release systems. It can be used in numerous applications but their use in bio-applications is proportional to their purity.<sup>35,36</sup> The SMA copolymer can be a suitable compound for environmental applications. In recent years, various studies have been undertaken

about metal ions adsorption with the SMA copolymer derivatives.<sup>37–40</sup> So, any kind of the crosslinked copolymers (SMA derivatives) can be used in the clean technology methods for the removal of toxic metal ions.

The fundamental concept in adsorption science is that named as the adsorption isotherm. It is the equilibrium relation between the quantity of the adsorbate and the concentration in the bulk fluid phase at constant temperature.<sup>41</sup> The adsorption isotherm forms an important tool for describing adsorption phenomena that occur at various types of interfaces. Among the different isotherm models some kind of commonly models were investigated in this study. Langmuir model has been widely applied to many process of metal ions sorption.<sup>42</sup> This model describes quantitatively the formation of a monolayer adsorbate on the outer surface of the adsorbent, and after that no further adsorption takes place. Thereby, the Langmuir represents the equilibrium distribution of metal ions between the solid and liquid phases. The model assumes uniform energies of adsorption onto the surface and no transmigration of adsorbate in the plane of the surface.<sup>43</sup>

The model of Freundlich adsorption isotherm commonly used to describe the adsorption characteristics for the adsorbents heterogeneous surface. The Freundlich isotherm theory said that the ratio of the amount of solute adsorbed onto a given mass of sorbent to the concentration of the solute is not constant at different concentrations in the solution.<sup>43</sup> The heat of adsorption decreases in magnitude with increasing the extent of adsorption.<sup>44</sup>

The model of Temkin adsorption isotherm contains a factor that explicitly takes into account of adsorbent–adsorbate interactions.<sup>45</sup> This model assumes the following: (i) the adsorption heat of all molecules in the layer decreases linearly with coverage due to adsorbent–adsorbate interactions, and that (ii) the adsorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy.

Dubin and Radushkevich<sup>46</sup> have proposed another isotherm which is not based on the assumption of homogeneous surface or constant adsorption potential, but is applied to estimate the mean free energy of adsorption. This model is generally applied to express the adsorption mechanism with a Gaussian energy

distribution onto a heterogeneous surface.<sup>47</sup> To evaluate the nature of interaction between metal ions and the binding sites, mean free energy of adsorption per mole of the adsorbate, which is the energy required to transfer 1 mole of an adsorbate to the surface from infinity in solution, given by Hobson.<sup>48</sup>

In this study, the usage of CSMA-AP resin was demonstrated as an adsorbent for the removal of Co (II), Ni (II), and Cd (II) ions from aqueous solutions to investigate the equilibrium and kinetic parameters of the resin using the batch equilibration technique. To determine the performance of the CSMA-AP, it is important to get an accurate equilibrium relationship between the solid- and liquid-phase concentrations of toxic metal ions.<sup>49</sup> In this study, it is essentially required to test the equilibrium data obtained for removal of some toxic metal ions such as Cd(II), Co(II), and Ni(II) using CSMA-AP resin with different isotherm models. For the adsorption studies, the kinetics investigations is important too, because it can predict the rate at which a toxic metal ion is removed from aqueous solutions and provides valuable data for understanding the mechanism of adsorption reactions. The various parameters such as pH, contact time, concentrations of metal ion, mass of resin, and agitation speed were investigated on adsorption effect.

## EXPERIMENTAL

### Measurements and Chemicals

Atomic absorption spectrophotometer (AAS) (analytic jenanov AA 400) fitted with cobalt, cadmium, and nickel hollow cathode lamps was used for determination of the metal ions concentration. The wavelengths used for the analysis of cobalt, cadmium, and nickel were 240.7, 228.8, and 232.0 nm, respectively. For the pH measurements, a digital pH meter (Metrohm 827 pH lab) was used. The pH value of each metal ion solution was adjusted with 0.1N HCl or NaOH solution purchased from Merck (Germany). The systems were shaken by horizontal bench shaker (Heidolph PROMAX 2020). FTIR spectra were measured with a Fourier transform infrared spectrophotometer (Nexus-670, Thermo Nicolet). The CSMA-AP resin was prepared in polymer Lab of our department.<sup>37</sup> The XRD spectra were recorded on an X'pert Philips X-ray photoelectron spectrometer using nonmonochromated Mg K $\alpha$  radiation as the excitation source (The Netherlands). Stock solutions of Ni(II), Co(II), and Cd(II) were prepared by dissolution of reagent-grade CoCl<sub>2</sub>·6H<sub>2</sub>O, CdCl<sub>2</sub>·H<sub>2</sub>O, and NiCl<sub>2</sub>·6H<sub>2</sub>O (Merck) in deionized water, respectively.

### Preparation of CSMA-AP

The Crosslinked 2-aminopyridine functionalized SMA copolymer (CSMA-AP) was prepared by simultaneous reaction of the SMA copolymer with 2-aminopyridine and 1,2-diaminoethane as crosslinking agent. The reaction mixture was refluxed for 3 h under inert gas in presence of ultrasonic irradiation along with vigorous stirring bar in THF. It can be said that the preparation of crosslinked resin in presence of ultrasonic irradiations along with vigorous magnetic stirring give rise polymeric particles in nanoscale.<sup>33,50</sup> The obtained product was filtered, washed thoroughly with THF, and dried by vacuum oven at 60°C for 24 h.

### Adsorption Studies

Batch adsorption experiments were performed by mixing the CSMA-AP (0.05 g) and 20 mL of toxic metal ions solution (50

mg/L) in a 100 mL beaker. Desired amount of toxic metal ions test solutions was prepared using appropriate subsequent dilutions of the stock solution. The system was shaken (200 rpm) in determined time and after completing the adsorption the mixture was filtered and the metal ion concentration was determined in filtrate by AAS. In this study, all the experiments were performed at room temperature (25 ± 1)°C. The obtained data were used to calculate the removal percentage of toxic metal ions using the following mass balance relationship:

$$\% \text{ toxic metal ions removal} = \left( \frac{C_o - C_e}{C_o} \right) \times 100 \quad (1)$$

where  $C_o$  and  $C_e$  are the initial and equilibrium concentration (mg/L) of the toxic metal ion solution, respectively.

**Effect of pH on Adsorption.** The effect of pH was investigated on the adsorption of toxic metal ions by the CSMA-AP resin. For this propose, several metal ion solutions (20 mL, 50 mg/L) was adjusted using 0.1N HCl or NaOH solutions at various pH between 2 and 6. Then determined amount of CSMA-AP resin was introduced to each sample and agitated in a horizontal bench shaker for 60 min. The mixture was filtered through Whatman 42 filter paper and the filtrate was analyzed using AAS. Each measurement was repeated four times and the obtained result was their average values.

**Effect of Contact Time.** Effect of contact time was investigated with batch adsorption experiments from 10 to 240 min for toxic metal ions concentration of 50 mg/L in 20 mL solution with the CSMA-AP resin (0.05 g) at pH = 5. The samples were taken at time intervals for the analysis of residual metal ion concentration in the aqueous solutions.

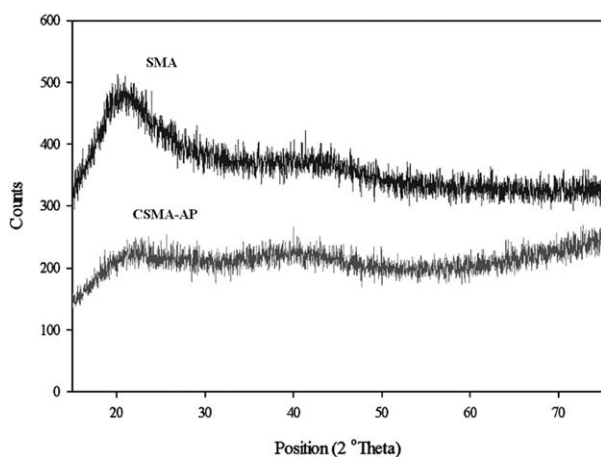
**Effect of Adsorbent Dosage.** Batch adsorption experiments were performed at a different weight of CSMA-AP resin (0.01–0.08 g) for uptake of toxic metal ions from aqueous solutions (20 mL, 50 mg/L) at pH = 5, for 60 min. The samples were filtered and the filtrates were analyzed by AAS.

**Effect of Metal Ion Concentration.** The effect of metal ion concentration was investigated on adsorption behavior of CSMA-AP resin. For this propose, the resin (0.05 g) was poured in metal ion solution with various concentration (20 mL, 20–300 mg/L) at pH = 5. The contents of the beakers were equilibrated on the shaker for 60 min. After adsorption, the samples were filtered and the metal ions were measured in filtrate by AAS.

**Effect of Agitation Speed.** To study the effect of agitation speed on adsorption of metal ions, agitation speed was varied from 50 to 300 rpm. Suitable amount of the adsorbent (0.05 g) was added to different bakers containing 20 mL of heavy metal ions (50 mg/L, pH = 5) and agitated in a shaker for 1 h at room temperature of 28°C. The content of each solution was then filtered and analyzed by AAS after the agitation time.

### Desorption and Repeated Use

Desorption of metal ions was performed by 0.5M HCl solution. The CSMA-AP–metal ion complexes were immersed in 0.5M HCl solution and the mixture was shaken until equilibrium was reached (30 min). Then the mixture was filtrated and the final



**Figure 1.** X-ray diffraction patterns of the copolymer and polymeric adsorbent.

concentrations of metal ion in the aqueous solution were determined by AAs. The desorption ratio ( $D\%$ ) of toxic metal ions from the CSMA-AP resin was calculated with following equation:

$$D\% = \frac{C_d V_d}{(C_o - C_e) V} \times 100 \quad (2)$$

where  $V$  is the volume of the solution (L);  $C_d$  is the concentration of the toxic metal ions in the desorption solutions (mg/L); and  $V_d$  is the volume of the desorption solution (L).

The collected CSMA-AP resin from the desorption process was washed thoroughly with deionized water and dried by vacuum pump at  $60^\circ\text{C}$  for repeated use.

#### Equilibrium Isotherm

The study of equilibrium isotherms was performed by agitating of 0.05 g CSMA-AP resin in a solution containing various concentrations of metal ion for 60 min at  $\text{pH} = 5$ . After filtration, the AAS was used to determine the metal ion concentration in the filtrate. The amount of metal adsorbed  $q_e$  (mg/g) was determined using the following mass balance relationship:

$$q_e = \frac{(C_o - C_e) V}{m} \quad (3)$$

where  $V$  is the volume of the solution (L); and  $m$  is the mass (g) of the adsorbent.

#### Kinetic Study

For the kinetic studies, the resin (0.05 g) with 20 mL samples at the initial concentration of metal ion ( $C_o$ ) of 50 mg/L was agitated in a 100 mL beaker. The removal rate of metal ions was investigated by measurement of metal ions concentrations after predetermined time intervals by the AAS method. The amount of adsorbed metal ion at time  $t$ ,  $q_t$  (mg/g), was calculated by following equation:

$$q_t = \frac{(C_o - C_t) V}{m} \quad (4)$$

where the  $C_t$  is the concentration of metal ions in solution at specified time (mg/L).

## RESULTS AND DISCUSSION

### Preparation and Morphology of CSMA-AP

The SMA copolymer was functionalized by 2-aminopyridine and crosslinked by 1,2-diaminoethane. The morphology and average diameter of copolymer network were shown at previous work by SEM image in two scales  $1\ \mu\text{m}$  and  $500\ \text{nm}$ .<sup>37</sup> It was found that the SEM micrographs of crosslinked copolymer in which particles possess almost uniform distribution of size. Average diameter of the observed particles in SEM images can be estimated under  $100\ \text{nm}$  with reasonable uniformity and grainy shape. This result indicates that there might be different particle size in these copolymer powders, although more of the grain size could be in nanometer-scale resolution of the SEM.

XRD measurements (Figure 1) indicate the predominantly amorphous nature of the SMA and CSMA-AP.

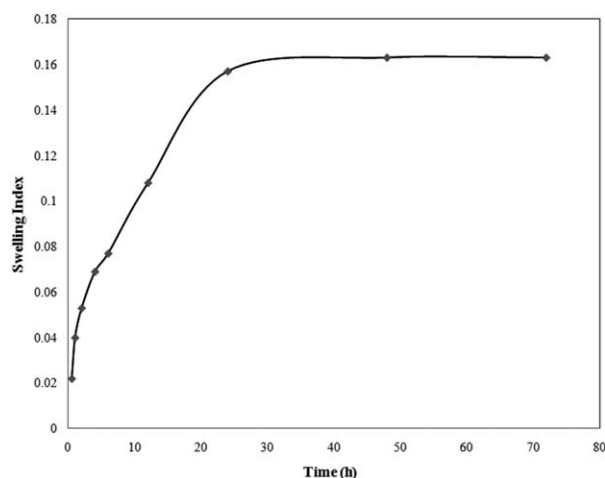
### The Swelling Index

By stirring the resin in water, it was swelled without any dissolving. The swelling index of the copolymer is shown in Figure 2. The results clearly indicated that the uptake of water related to the structure characterization such as holes and the functional groups which can be increase or decrease the hydrophilicity of the resin.<sup>51</sup> The swelling index was determined with the following equation:

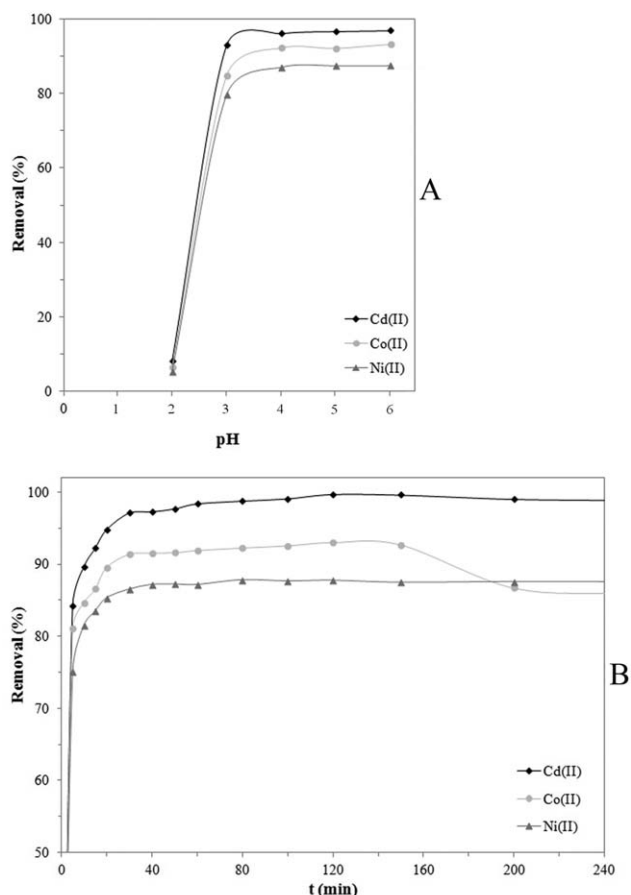
$$x = \frac{\text{Wt of the wet resin} - \text{Wt of dry resin}}{\text{Wt of dry resin}} \quad (5)$$

### Effect of pH Value on Metal Ions Adsorption

The pH of aqueous solutions is one of the most important controlling parameter that affects the removal percentage of toxic metal ions on adsorbent. The effect of pH on the adsorption of Cd(II), Co(II), and Ni(II) ions was investigated in various pH of metal ion solution in the range of 2–6 because these metal ions could be precipitated by  $\text{OH}^-$  to form metal(II) hydroxide above pH 6. The results were depicted in Figure 3(A). The extractability of the metal ions from the solution phase depends on the pH, because its effect on the solubility of the metal ions, concentration of the counter ions on the functional groups of adsorbent, and the degree of ionization of the adsorbate during



**Figure 2.** Swelling index of CSMA-AP resin.



**Figure 3.** Effect of pH value on metal ions adsorption by CSMA-AP resin A and effect of contact time on metal ions adsorption by resin B (concentration of metal ions = 50 mg/L, adsorbent dose = 2.5 g/L, contact time = 90 min, and pH = 5).

reaction. The results showed that there is approximately no adsorption at pH = 2, and the removal percentage of CSMA-AP for metal ions increases significantly with the increase of the pH values. The maximum removal efficiencies of Cd(II), Co(II), and Ni(II) ions were 97.92%, 93.67%, and 87.95%, respectively. In fact in acidic pH, the adsorbent surface will be completely covered with hydronium ions which compete strongly with toxic metal ions for adsorption sites at acidic pH, with an increase in pH, the concentration of  $H_3O^+$  ions decreases facilitating the adsorption of metal ions by the adsorbent.<sup>52</sup>

#### Effect of Contact Time on Metal Ions Adsorption

Contact time plays an important role in the adsorption of metal ions on solid surface. Removal percentage of toxic metal ions is found to be commensurate to contact time up to equilibrium achieved, after which it is independent of time due to the fact that at equilibrium the rate of adsorption and desorption will be same. Effect of contact time for the removal of Cd(II), Co(II), and Ni(II) by the CSMA-AP resin showed rapid adsorption of these metal ions in the first 10 min and, thereafter, the adsorption rate decreased inchmeal and the adsorption reached equilibrium in about 30–40 min as shown in Figure 3(B). The relatively fast sorption of Cd(II), Co(II), and Ni(II) ions on the

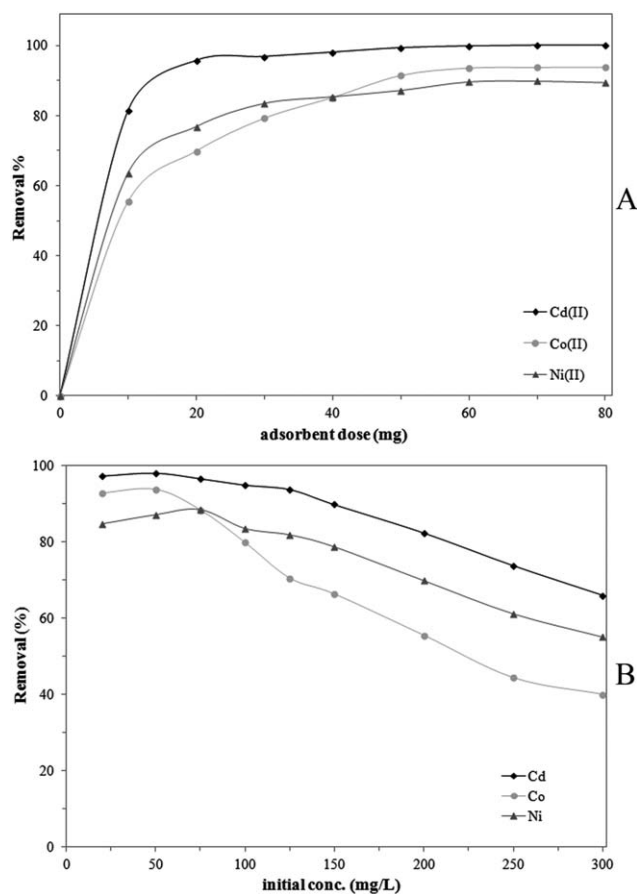
CSMA-AP resin probably reflects high accessibility of the these metal ions to the ion exchange sites in the CSMA-AP.

#### Effect of Adsorbent Dose on Metal Ions Adsorption

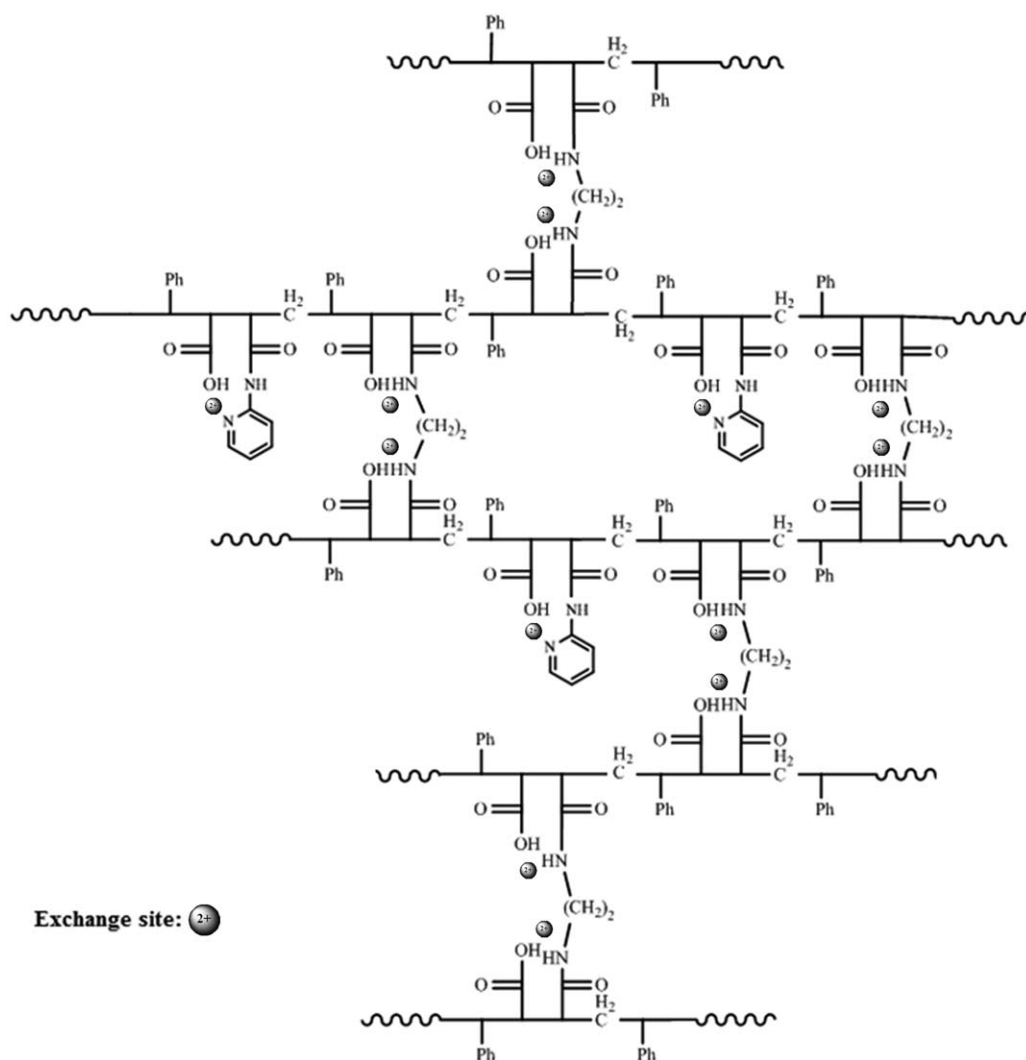
The effect of adsorbent dosage is an important parameter on the removal percentage of toxic metal ions from aqueous solutions, because it determines the capacity of an adsorbent for a given concentration.<sup>53</sup> The adsorption efficiency for Co(II), Cd(II), and Ni(II) ions as a function of adsorbent dosage was investigated and the results can be observed in Figure 4(A). The experimental data revealed that the removal efficiencies of metal ions increased inchmeal with increasing amounts of CSMA-AP. This may be attributed to the fact that increasing the adsorbent dose provides more adsorption sites for the metal ions. By increasing the adsorbent dose for Cd(II), Co(II), and Ni(II) ions from 0.5 to 4.0 g/L, the adsorption of above-mentioned ions was increased from 81.36% to 99.97%, 55.40% to 91.80%, and 71.60% to 89.39%, respectively.

#### Effect of Concentration of Metal Ion on the Adsorption

The rate of adsorption is a function of the concentration of metal ion, which makes it an important factor to be considered for efficient adsorption.<sup>54</sup> The effect of metal ions concentration was investigated on the adsorption behavior of CSMA-AP resin



**Figure 4.** Effect of adsorbent dose on metal ions adsorption by CSMA-AP (A) and effect of concentration of metal ion on metal ions adsorption by CSMA-AP(B) (contact time = 60 min, concentration of metal ions = 50 mg/L, pH = 5, and adsorbent dose = 2.5 g/L).



**Scheme 1.** The structure of crosslinked copolymer (Ph = Phenyl).

at different concentration (20–300 mg/L), and the results are demonstrated in Figure 4(B). Generally, Figure 4(B) indicates that by increasing the metal ions concentration with constant amount of the adsorbent, the metal ions adsorption was increased up to 50 mg/L for Cd(II) and Co(II) and 75 mg/L for Ni(II). Further increases in the metal ion concentration were accompanied by reduction in the removal percentage. This phenomenon might be due to saturation of the active sites of the CSMA-AP with the toxic metal ions at higher concentrations. The structure of copolymer network was shown in Scheme 1. We can observe that this resin has so many active ion exchange sites for removal of heavy metal ions from aqueous solution.

#### FTIR Investigation

FTIR spectroscopy has been used for the characterization of copolymer–metal complexes because of the frequency at which a characteristic group of the polymer absorbents is modified by metal ions complexation.<sup>55</sup> As shown in Figure 5, after CSMA-AP adsorbing metal ions, the band at  $1570\text{ cm}^{-1}$  sharpened and shifted to lower frequency (at about  $1555\text{ cm}^{-1}$ ), indicating a stronger copolymer–metal bond has formed between metal ions and carboxyl oxygen in carboxylate salts.<sup>56</sup> Additionally, a

prominent peak was observed at  $3280\text{ cm}^{-1}$  expressing the N–H stretching vibrations of metal salts of amid.<sup>57</sup>

#### Effect of Agitation Speed on Adsorption of Heavy Metal Ions

The effect of agitation speed was studied under the specified conditions (at optimum contact time of 1 h, 0.05 g resin, 20 mL solution 50 mg/L, pH = 5, and at a room temperature of  $28^\circ\text{C}$ ) with CSMA-AP as adsorbent; it was observed that increase in agitation speed from 50 to 300 rpm, the removal percentage of toxic metal ions (Cd, Co, and Ni) increased up to 300 rpm as shown in Figure 6. Hence, at a agitation speed of 200 rpm, maximum recoveries were obtained for all the three metal ions, with 97.23% removal of Cd(II), 93.60% of Co(II), and 87.88% removal of Ni(II). Also Cd(II) attained maximum removal of 96.51% at a lower agitation speed of 150 rpm. The increase in agitation speed resulting to increase in metal ions removal percentage was due to the fact that increase in stirring rate enhanced the metal ions diffusion to the surface of the adsorbent; and also caused reduction in the film boundary layer around the adsorbent.

#### Desorption and Repeated Use

For advanced adsorbents recycling, regeneration and repeated availability are important factors. Such adsorbents not only

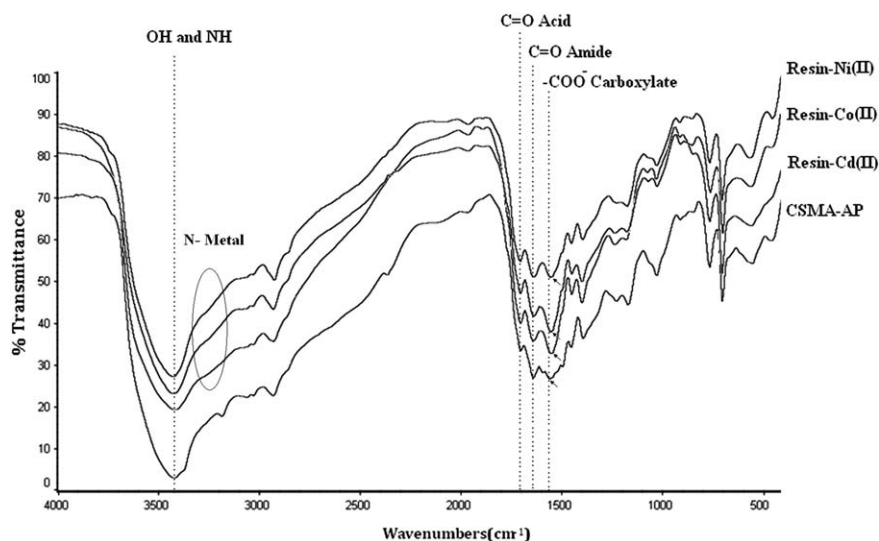


Figure 5. FTIR spectra of CSMA-AP resin before and after complexation with Cd(II), Co(II), and Ni(II).

possess higher adsorption capabilities but also display better desorption properties. Better desorption significantly reduces the overall costs associated with adsorbate removal, especially when high costs currently limit their potential use. Conversely, after desorption, the metal ions can be recovered. Desorption of Cd(II), Co(II), and Ni(II) ions from CSMA-AP-metal ion complexes was performed using 0.5M HCl solution at room temperature. As stated previously, when the adsorption of the metal ions was tended to 0 at pH = 2, demonstrates that, 0.1M H<sup>+</sup> (pH = 1) could complete prevent the adsorptions of the Co(II), Cd(II), and Ni(II) ions. Thus, in this work, the concentration of H<sup>+</sup> was raised to 0.5M to improve the desorption efficiency. Figure 7(A) shows the effect of time on the desorption of Cd(II), Co(II), and Ni(II) ions from CSMA-AP metal complex. The desorption process reached equilibrium at 30 min and the desorption ratios were 90% for Cd(II), 95% for Co(II), and 92% for Ni(II). To examine the reusability of CSMA-AP, consecutive adsorption-desorption cycles were repeated 15 times using the same resins and the data are shown in Figure

7(B). The absorption capacity of the adsorbent did not significantly change during the repeated adsorption-desorption operations for all metal ions. The results were shown that the CSMA-AP resin is a good reusable adsorbent in removal of Cd(II), Co(II), and Ni(II) from their single-metal ion solutions.

#### Determination of the Equilibrium Distribution Coefficient ( $k_d$ )

The distribution coefficient can be determined according to eq. (6)<sup>38</sup>:

$$k_d = \frac{\text{amount of metal ion in adsorbent}}{\text{amount of metal ion in solution}} \times \frac{V}{m} \quad (6)$$

where  $V$  is the volume of the solution (mL) and  $m$  is the weight of adsorbent (g).

The  $k_d$  value can be used as a valuable tool to study the metal cation mobility. High values of  $k_d$  indicated that the metal ion has been uptake by the solid phase, while low values of  $k_d$  indicated that a large fraction of the metal ion remains in solution.

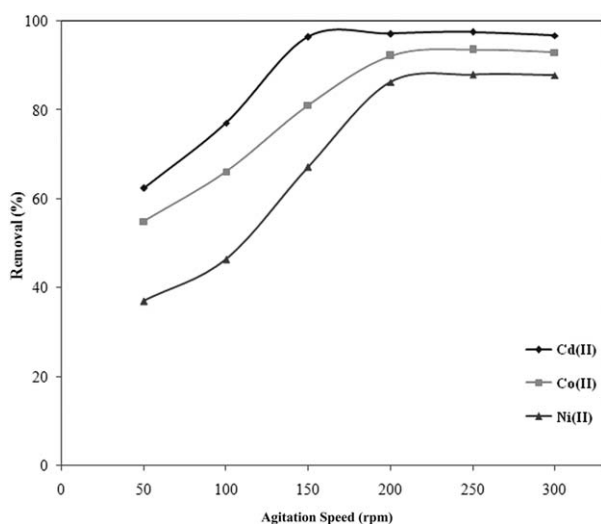


Figure 6. Effect of agitating speed on adsorption of heavy metal ions.

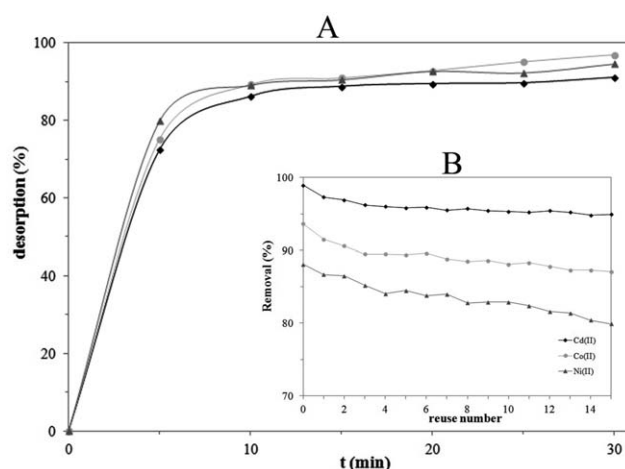


Figure 7. Desorption of metal ions from CSMA-AP-metal ions complex by 0.5M HCl solution (A) and removal of metal ions after repeated adsorption-desorption operations at 25°C (B) (concentration of metal ions = 50 mg/L, adsorption time = 60 min, pH = 5, adsorbent dose = 2.5 g/L).

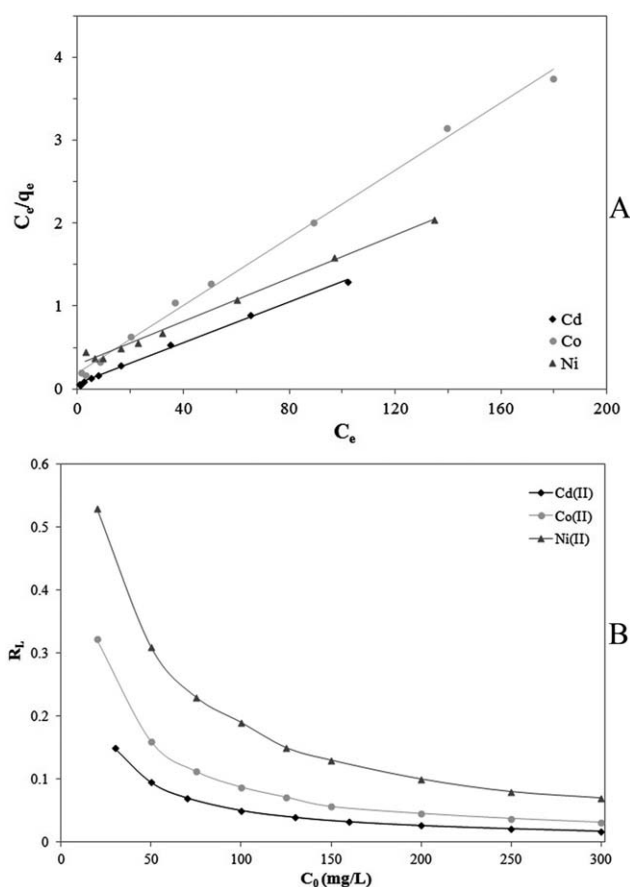
**Table II.** Distribution Coefficient,  $k_d$ , of Toxic Metal Ions Adsorption by CSMA-AP Resin at pH = 5 (Concentration of Metal Ions = 50 mg/L, Resin Dose = 2.5 g/L, Time = 60 min)

Resin	$k_d$ (mL/g) $\times 10^3$		
	Cd(II)	Co(II)	Ni(II)
CSMA-AP	21.34	6.03	1.04

Table II shows the  $k_d$  value for adsorption of toxic metal ions. These findings prove that the  $k_d$  value is approximately high in the case of Cd(II), Co(II), and Ni(II) ions, so the CSMA-AP resin had a good capability in the removal of Cd(II), Co(II), and Ni(II).

### Adsorption Isotherm

The adsorption equilibrium is usually described by an isotherm equation whose parameter expresses the affinity of the adsorbent. To determine the performance of the resin, it is important to get an accurate equilibrium relationship between the solid- and liquid-phase concentrations of toxic metal ions.<sup>58</sup> In this study, it is essentially required to test the equilibrium data obtained for removal of some toxic metal ions such as Cd(II), Co(II), and Ni(II) using CSMA-AP resin with different isotherm models.



**Figure 8.** Langmuir isotherms for Cd(II), Co(II), and Ni(II) adsorption onto CSMA-AP (A) and separation factor ( $R_L$ ) profile for biosorption of Cd(II), Co(II), and Ni(II) as function of concentration of metal ion by CSMA-AP (B) (pH = 5, time = 60 min, resin dose = 2.5 g/L).

**Langmuir Isotherm.** Langmuir model<sup>42</sup> has been widely applied to some process of metal ions sorption. The basic assumption of the Langmuir theory is that uptake of metal ions occurs on a homogenous surface by monolayer adsorption without any interaction between adsorbed metal ions that is all the adsorption sites have equal adsorbate affinity and that the adsorption at one site does not affect the adsorption at an adjoining site. So, the Langmuir isotherm is valid for monolayer adsorption onto a surface containing a finite number of identical sites.

The Langmuir adsorption isotherm model is given by<sup>59</sup>

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (7)$$

where  $C_e$  is the equilibrium concentration (mg/L),  $q_e$  is the amount adsorbed at equilibrium (mg/g),  $q_m$  is the maximum adsorption capacity corresponding to the complete monolayer coverage (mg/g), and  $K_L$  is the Langmuir constant related to the adsorption energy. The model of Langmuir adsorption isotherm can be rearranged as follows:

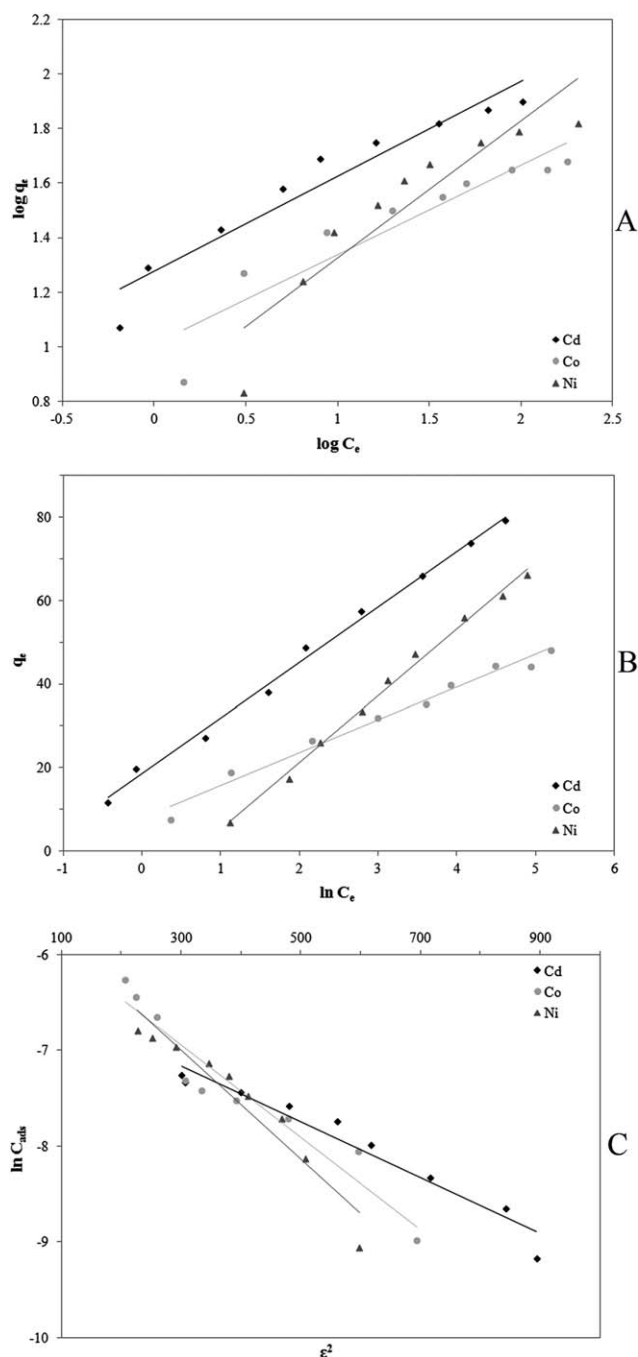
$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \quad (8)$$

The linear plot of Langmuir adsorption isotherm ( $C_e/q_e$  vs.  $C_e$ ) demonstrated the applicability of Langmuir adsorption isotherm for this work that was shown in Figure 8(A). The values of  $q_m$  and  $K_L$  for Cd(II), Co(II), and Ni(II) ions were calculated from the slope and the intercept of the linear plots  $C_e/q_e$  versus  $C_e$ . The results are listed in Table III. The results showed that good fit was achieved with the Langmuir isotherm equation.

**Table III.** Isotherm Parameters and Regression Data for Cd(II), Co(II), and Ni(II) Ions Using CSMA-AP as Adsorbent (pH = 5, Time = 60 min, Resin Dose = 2.5 g/L, Concentration of Metal Ions = 50 mg/L)

Isotherms	Parameters	Metal ions		
		Cd(II)	Co(II)	Ni(II)
Langmuir	$q_m$ (mg/g)	81.30	49.02	76.92
	$K_L$ (L/mg)	0.1907	0.1052	0.0440
	$R_L$	0.05	0.09	0.19
	$R^2$	0.9973	0.9963	0.9933
Freundlich	$K_F$	18.95	10.19	6.63
	$N$	2.87	3.04	1.99
	$R^2$	0.9306	0.8666	0.8474
Temkin	$b_T = RT/B_T$	0.187	0.316	0.155
	$A_T$	4.17	2.70	0.51
	$R^2$	0.9958	0.9807	0.9943
Dubinin-Radushkevich	$X_m$ (mol/g)	$1.87 \times 10^{-3}$	$4.06 \times 10^{-3}$	$5.07 \times 10^{-3}$
	$\beta$ ( $\text{kJ}^2/\text{mol}^2$ )	0.0029	0.0048	0.0057
	$E$ (kJ/mol)	13.16	10.20	9.35
	$R^2$	0.9497	0.9244	0.9213





**Figure 9.** Freundlich isotherms (A), Temkin isotherms (B), and Dubinin–Radushkevich isotherms (C) for Cd(II), Co(II), and Ni(II) adsorption onto CSMA-AP (pH = 5, time = 60 min, resin dose = 2.5 g/L).

The Langmuir parameters can also be used to predict affinity between the adsorbate and the adsorbent using the dimensionless separation factor ( $R_L$ ), which has been defined as below<sup>43</sup>:

$$R_L = \frac{1}{1 + K_L C_o} \quad (9)$$

where  $K_L$  is the Langmuir constant (L/mg) and  $C_o$  is the concentration of toxic metal ions, in mg/L. The value of  $R_L$  indicates the type of the isotherm to be either unfavorable ( $R_L > 1$ ), linear ( $R_L = 1$ ), favorable ( $0 < R_L < 1$ ), or irreversible ( $R_L$

$= 0$ ). Figure 8(B) showed that adsorption of Cd(II), Co(II), and Ni(II) increased concomitantly with concentration of metal ion. The calculated  $R_L$  values for this toxic metal ions adsorption indicate that adsorption is favorable even for higher concentrations of metal.

**Freundlich Isotherm.** The Freundlich isotherm theory<sup>43</sup> said that the ratio of the amount of solute adsorbed onto a given mass of sorbent to the concentration of the solute in the solution is not constant at different concentrations. The heat of adsorption decreases in magnitude with increasing the extent of adsorption.<sup>44</sup>

The model of Freundlich adsorption isotherm, which is an indicative of surface heterogeneity of the sorbent, is given by eq. (10).<sup>43</sup>

$$q_e = K_F C_e^{1/n} \quad (10)$$

Equation (10) can be expressed in a linear form:

$$\log q_e = \frac{1}{n} \log C_e + \log K_F \quad (11)$$

where  $K_F$  and  $1/n$  are Freundlich constants related to adsorption capacity and adsorption intensity, respectively. The values of  $n$  and  $K_L$  for Cd(II), Co(II), and Ni(II) ions were calculated from the slope and the intercept of the linear plots  $\log q_e$  versus  $\log C_e$  [Figure 9(A)] with the correlation coefficients which were presented in Table III. The resin showed better fit for Langmuir isotherm than Freundlich isotherm.

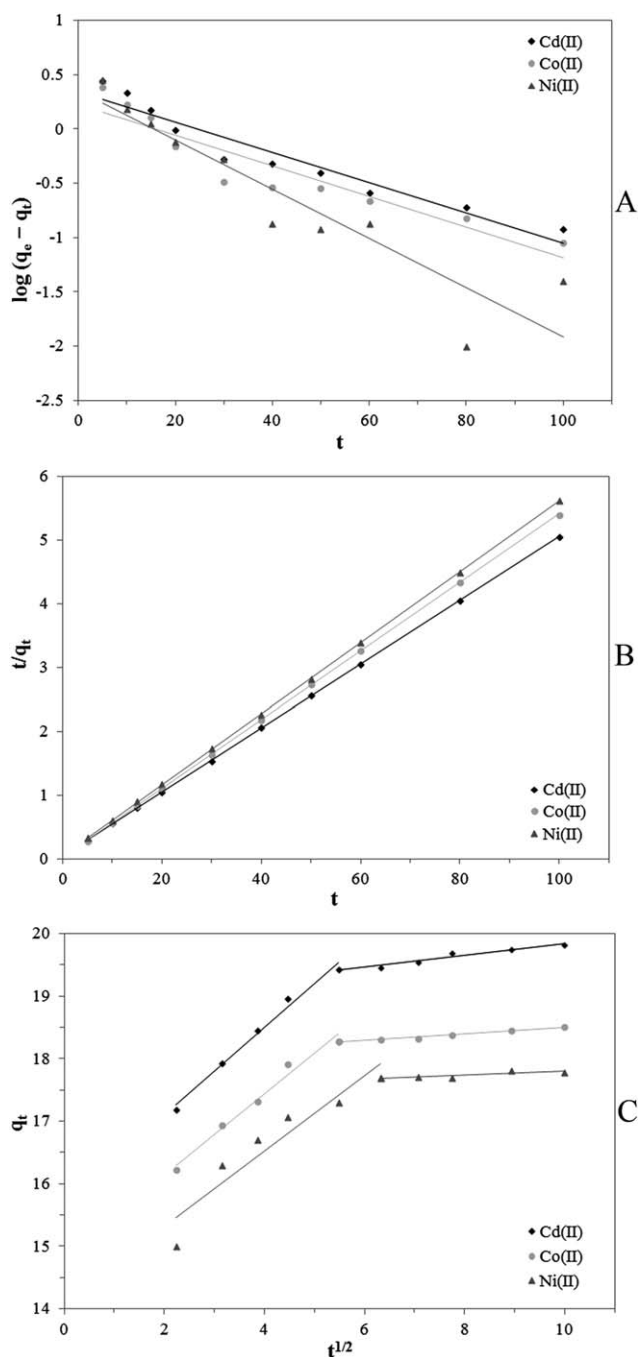
**Temkin Isotherm.** The model of Temkin adsorption isotherm<sup>45</sup> contains a factor that explicitly takes into account adsorbent–adsorbate interactions. This model assumes the following: (i) the adsorption heat of all molecules in the layer decreases linearly with coverage due to adsorbent–adsorbate interactions, and that (ii) the adsorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy. By ignoring the extremely low and large value of concentrations, the model assumes that heat of adsorption (function of temperature) of all molecules in the layer would decrease linearly rather than logarithmic, as implied in the Freundlich equation. The Temkin isotherm is applied in the following form<sup>60</sup>:

$$q_e = \frac{RT}{b_T} \ln(A_T C_e) \quad (12)$$

The linear form of Temkin equation is

$$q_e = B_T \ln A_T + B_T \ln C_e \quad (13)$$

where  $B_T = RT/b_T$ ,  $T$  is the absolute temperature in K, and  $R$  is the universal gas constant ( $8.314 \times 10^{-3}$  kJ/mol K). The constant  $b_T$  is related to the adsorption heat (kJ/mol),  $A_T$  is the constant of equilibrium binding (L/g) corresponding to the maximum binding energy. Thus, the constants can be obtained from the slope and intercept of a straight line plot of  $q_e$  versus  $\ln C_e$  [Figure 9(B)]. Temkin isotherm generates a satisfactory fit to the experimental data as indicated by correlation coefficients. From Table III, it can be seen that value of  $A_T$  is larger for Cd(II) than Co(II) and Ni(II), Cd(II) > Co(II) > Ni(II). This means in cation exchange processes using CSMA-AP resin, adsorbent–adsorbate interactions are more effective for cadmium comparing with cobalt and nickel.



**Figure 10.** Pseudo-first-order plot (A), pseudo-second-order plot (B), and intra-particle diffusion plot (C) for Cd(II), Co(II), and Ni(II) adsorption onto CSMA-AP (pH = 5, concentration of metal ions = 50 mg/L, resin dose = 2.5 g/L).

**Dubinin–Radushkevich (D–R) Isotherm.** Dubinin and Radushkevich<sup>46</sup> have proposed another isotherm model which is not based on the assumption of homogeneous surface or constant adsorption potential, but is applied to estimate the mean free energy of adsorption ( $E$ ). Mean free energy of adsorption per mole of the adsorbate, which is the energy required to transfer one mole of an adsorbate to the surface from infinity in solution, given by Hobson to evaluate the nature of interaction between metal ions and the binding sites.<sup>48</sup> If the value of  $E$  is

between 8 and 16 kJ/mol, the adsorption process can be assumed to involve chemical sorption. Conversely, values lower than 8 kJ/mol indicate that the adsorption process is of a physical nature.<sup>61</sup> This adsorption model is given by<sup>62</sup>:

$$C_{\text{ads}} = X_m e^{-\beta s^2} \quad (14)$$

The linear form of D–R isotherm equation is represented by the following equation:

$$\ln C_{\text{ads}} = \ln X_m - \beta s^2 \quad (15)$$

where  $C_{\text{ads}}$  is the amount of toxic metal ions adsorbed per unit weight of the resin (mol/g),  $X_m$  is the adsorption capacity (mol/g),  $\beta$  is a constant related to adsorption energy (mol<sup>2</sup>/kJ<sup>2</sup>), and  $\varepsilon$  is the Polanyi potential, which can be calculated from eq. (16):

$$s = RT \ln \left( 1 + \frac{1}{C_e} \right) \quad (16)$$

where  $R$  is the universal gas constant (kJ/mol K), and  $T$  is the temperature (K). If  $\ln C_{\text{ads}}$  is plotted against  $\varepsilon^2$ ,  $\beta$ , and  $X_m$  will be obtained from the slope and intercept, respectively. Figure 9(C) indicated the experimental results. The straight lines obtained were useful in calculating the D–R isotherm constants, which are given in Table III.

The adsorption energy can also be worked out using the following relationship:

$$E = \frac{1}{\sqrt{-2K}} \quad (17)$$

In this study, the  $E$  values obtained using the D–R constant were 13.16 kJ/mol for Cd(II), 10.20 kJ/mol for Co(II), and 9.35 kJ/mol for Ni(II), indicating that the adsorption of these ions onto CSMA-AP resin occurs via a chemical process.

### Adsorption Kinetic

The kinetic investigations are important for the adsorption studies because it can predict the rate at which a toxic metal ion is removed from aqueous solutions and provides valuable data for understanding the mechanism of adsorption reactions. Three known kinetic models are used to investigate the adsorption mechanism.

**Pseudo-First-Order Kinetic.** Lagergren showed that the adsorption rate of ions on the adsorbent is based on the adsorption capacity. It followed a pseudo-first-order equation<sup>63</sup> which is often used for estimating  $k_1$  considered as mass transfer coefficient in the design calculations. The non-linear form of the pseudo-first-order equation is described by eq. (18):

$$\frac{dq_t}{dt} = k_1 (q_e - q_t) \quad (18)$$

Equation (18) can be expressed in linear form:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (19)$$

where  $q_e$  and  $q_t$  are the amounts of toxic metal ions adsorbed (mg/g) at equilibrium and at time  $t$  (min), respectively, and  $k_1$  (1/min) is the rate constant of first-order adsorption. Values of  $k_1$  are calculated from the plots of  $\log(q_e - q_t)$  versus  $t$  [see Figure 10(A)] for samples Cd(II), Co(II), and Ni(II) ions. The obtained  $R^2$  values are relatively small and the experimental  $q_e$

**Table IV.** Kinetic Parameters for Cd(II), Co(II), and Ni(II) Ions Using CSMA-AP as Adsorbent (pH = 5, Concentration of Metal Ions = 50 mg/L, Resin Dose = 2.5 g/L)

Kinetic models	Parameters	Metal ions		
		Cd(II)	Co(II)	Ni(II)
Pseudo-first order model	$q_{e,exp}$ (mg/g)	19.94	18.60	17.82
	$q_{e,cal}$ (mg/g)	2.18	1.66	2.23
	$k_1$ (1/min)	0.0320	0.0322	0.0520
	$R^2$	0.9273	0.8773	0.8598
	S.D. (%)	29.69	30.36	29.16
Pseudo-second order model	$q_{e,exp}$ (mg/g)	19.94	18.60	17.82
	$q_{e,cal}$ (mg/g)	20.00	18.69	18.02
	$k_2$ (g/mg min)	0.0480	0.0581	0.0557
	$R^2$	1	1	1
	S.D. (%)	0.03	0.16	0.37
Intra-particle diffusion model	$K_{p1}$ (mg/g min <sup>1/2</sup> )	0.7036	0.6499	0.6000
	$K_{p2}$ (mg/g min <sup>1/2</sup> )	0.0953	0.0528	0.0324
	$C_1$	15.683	14.832	14.119
	$C_2$	18.888	17.974	17.474
	$(R_1)^2$	0.9869	0.9807	0.8929
	$(R_2)^2$	0.9630	0.9722	0.7029

values do not agree with the calculated values obtained from the linear plots. The data are listed in Table IV.

**Pseudo-Second-Order Kinetic.** Ho developed a pseudo-second-order kinetic expression for the adsorption system of divalent metal ions using the sphagnum moss peat.<sup>64</sup> This model has since been widely applied to a number of metal/adsorbent adsorption systems. The adsorption of Cd(II), Co(II), and Ni(II) ions onto the chelating resin at a short time scale may involve a chemical adsorption which implies the strong electrostatic interaction between the negatively charged surface and this metal ions. The second-order kinetics equation is described in the following form:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (20)$$

Equation (20) can be expressed in linear form:

$$\frac{1}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (21)$$

where  $k_2$  (g/mg min) is the rate constant of second-order adsorption. The activation energy of adsorption can be evaluated with the pseudo-second-order rate constants. The linear plot of  $t/q_t$  versus  $t$  is shown in Figure 10(B) and the obtained  $R^2$  values are 1 for Cd(II), Co(II), and Ni(II) ions. It also shows a good agreement between the experimental and the calculated  $q_e$  values (Table IV), indicating the applicability of this model to describe the adsorption process of Cd(II), Co(II), and Ni(II) ions onto the CSMA-AP.

**Intra-Particle Diffusion Kinetic.** As the above two kinetic models were not able to explain the diffusion mechanism, thus the kinetic model of intra-particle diffusion based on the theory

or equation proposed by Weber and Morris is tested.<sup>65</sup> It is an empirically functional relationship, common to the most adsorption processes. The adsorbate uptake varies almost proportionally with  $t^{1/2}$  rather than with the contact time  $t$ . According to the following Weber–Morris's equation:

$$q_t = k_{pi} t^{1/2} + C_i \quad (22)$$

where  $k_{pi}$  is the rate parameter of  $i$  stage (mg/g h<sup>1/2</sup>), calculated from the slope of the straight line of  $q_t$  versus  $t^{1/2}$ .  $C_i$  is the intercept of  $i$  stage, giving an idea about the thickness of boundary layer, that is, the larger the intercept, the greater the boundary layer effect is. For intra-particle diffusion,  $q_t$  versus  $t^{1/2}$  will be linear and if the plot passes through the origin, then the rate-limiting process is only due to the intra-particle diffusion.<sup>66</sup>

Figure 10(C) presents a linear fit of intra-particle diffusion model for adsorption of Cd(II), Co(II), and Ni(II) ions onto CSMA-AP. Such types of plots present multilinearity, indicating that two or more steps take place. It can be observed in Figure 10(C) that the data points are related by two straight lines. The first sharper portion is attributed to the adsorbate diffusion through the solution to the external surface of the adsorbent (external diffusion) and the second portion describes the gradual adsorption stage, corresponding to the adsorbate diffusion inside the pores of the adsorbent (intra-particle diffusion). The rate parameters for CSMA-AP resin (Table IV) show that the  $k_{p1}$  and  $k_{p2}$  values for Cd(II) are larger than that for Co(II) or Ni(II). Further observation demonstrates  $k_{p1} > k_{p2}$ . That is easy to understand because the concentration of toxic metal ions left in the solutions gradually decreases.

**Validity of Kinetic Model.** Normalized-standard deviation, S.D. (%), is used to find the most applicable model that could

describe the kinetic study of adsorption of Cd(II), Co(II), and Ni(II) ions on the CSMA-AP. The normalized standard deviation S.D. (%) was calculated using the following equation<sup>67</sup>:

$$S.D.(\%) = 100 \times \left\{ \sum \frac{[(q_{e,exp} - q_{e,cal}) / q_{e,exp}]^2}{N-1} \right\}^{1/2} \quad (23)$$

where  $N$  is the number of data points,  $q_{e,exp}$  and  $q_{e,cal}$  (mg/g) are the experimental and calculated equilibrium adsorption capacity values, respectively. The results are summarized in Table IV. The values of S.D. obtained for the pseudo-first-order kinetic model, which were relatively high as compared to the S.D. values obtained for the kinetic model of pseudo-second order. Based on the highest  $R^2$  values (for all the metal ions  $R^2 = 1$ ) and the lowest S.D. values, the pseudo-second-order model was the most suitable equation to describe the adsorption kinetics of Cd(II), Co(II), and Ni(II) using CSMA-AP. This suggested that the overall rate of the adsorption process was controlled by chemisorption which involved valence forces through sharing or exchange of electrons between the adsorbent and adsorbate.

## CONCLUSION

Adsorption of Cd(II), Co(II), and Ni(II) is found to be effective in the pH range of 3–6 by CSMA-AP resin. The removal percentage increases by increasing the adsorbent dose from 0.5 to 4.0 g/L. The contact time studies in adsorption of selected metal ions show that the removal percentage increases with time up to 30–40 min and after this time it remains constant. The equilibrium data have been analyzed using Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich isotherms. The characteristic parameters for each isotherm and related correlation coefficients have been determined. The experimental data yielded excellent fits within the following isotherms order: Langmuir > Temkin > Dubinin–Radushkevich > Freundlich, based on its correlation coefficient values. From the Dubinin–Radushkevich isotherm, the adsorption energy was found 13.16, 10.20, and 9.35 kJ/mol for Cd(II), Co(II), and Ni(II), respectively, indicative of the removal of toxic metal ions was done by chemical adsorption phenomena. Three simplified kinetic models, pseudo-first-order, pseudo-second-order, and intra-particle diffusion were tested to investigate the adsorption mechanism. The pseudo-second-order kinetic model fits very well with the dynamical adsorption behavior of Cd(II), Co(II), and Ni(II) ions based on the highest  $R^2$  values. The results have shown that the CSMA-AP is a reusable resin with a good potential for adsorption of metal ions up to 15 cycles by maintaining performance. It can be said that the CSMA-AP resin has a good potential for removal of toxic metal ions such as Cd(II), Co(II), and Ni(II) from aqueous solutions. Using this resin for the removal of toxic metal ions is simple, green, and clean technology method and has approximately high efficiency and maybe can provide a strategic approach to remove heavy metal ions from industrial sewage.

The authors are grateful to Mehrdad Akhgari and Ahmad Rajaeifar in departments of analytical chemistry and physics for AAS and XRD analysis, respectively.

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