Adsorptive and kinetic studies of toxic metal ions from contaminated water by functionalized silica

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Abstract. The objective of the study, to develop adsorbent based purifier for removal of radiological and nuclear contaminants from contaminated water. In this regard, 3-aminopropyl silica functionalized with ethylenediamine tetraacetic acid (APS-EDTA) adsorbent prepared and characterized by Fourier Transform Infrared Spectroscopy (FT-IR), Scanning Electron Microscopy (SEM) and X-ray Diffraction (XRD). Prepared APS-EDTA used for adsorptive studies of Cs(I), Co(II), Sr(II), Ni(II) and Cd(II) from contaminated water. The effect on adsorption of various parameters viz. contact time, initial concentration of metal ions and pH were also analyzed. The batch method has been employed using metal ions in solution from 1000-10000 µg/L, contact time 5-60 min., pH 4-10 and material quantities 50-200 mg at room temperature. The obtained adsorption data were used for drawing Freundlich and Langmuir isotherms model and both models were found suitable for explaining the metal ions adsorption on APS-EDTA. The adsorption data were followed pseudo second order reaction kinetics. The maximum adsorption capacity obtained 1.3037-1.4974 mg/g for above said metal ions. The results show that APS-EDTA have great potential to remove Cd(II), Co(II), Cs(I), Ni(II) and Sr(II) from aqueous solutions through chemisorption and physio-sorption.

Keywords: adsorption; aminopropyl silica; cesium and strontium; removal; toxic metal ions

1. Introduction

Water pollution is one of the biggest environmental issues causing serious problems to living beings. The presence of toxic metal ions in the environment is a distressing issue due to their acute toxicity and long-term exposure to environment (Demirbas 2009, Mohan and Sreelakshmi 2008). Modern day industries like nuclear power operations, metallurgical engineering, mining, printing, electroplating, pigments, textile dyeing, battery, and semiconductor generate various type of pollutants including toxic metal ions to environment which contaminate water (Ghani *et al*. 2009).

Besides water may get contaminate with long lived radionuclides such as Cesium, Strontium and others. The sources of these radionuclides are operation of nuclear power plants, research facilities and the use of radioisotopes in numerous pharmaceutical industries (Kemp *et al*. 2006a, b, Bennett and White 2006, Zuloaga *et al*. 2006a, b, Plecas and Dimovic 2006, Melville *et al*. 2006a, b). Nuclear accidents also possess threat to drinking water. Such events had already occurred at Japan & Chernobyl due to the earthquake and industrial accident respectively. Most of the toxic metal ions are carcinogenic and non-degradable. Toxic metal ions are not metabolized by the body and accumulated in the soft tissues. Co (II), Ni (II) and Cd (II) are especially common metals that tend to accumulate in organisms, causing numerous diseases and disorders (Inglezakis *et al*. 2003a, b). They can cause hypertension,

nephritis, abdominal pain, nausea, vomiting, behavioral changes and development defects (Tunal *et al*. 2006a, b). Prolonged consumption of contaminated water may produce adverse affect on the health of military as well as civilian population. Therefore, the removal of toxic metal ions from water is a necessary requirement.

Various technologies have been implemented to remove heavy metal ions & radionuclides from waste water. Such as ion exchange (Dizge *et al*. 2009, Rafati *et al*. 2010a, b), precipitation, reverse osmosis (Jung *et al*. 2019a, b), membrane separation (Muthusaravanan *et al*. 2021a, b). But most of the technologies are time-consuming, cost-intensive, and produce secondary pollutants in the form of sludges which create additional problems of disposal (Supriya Prasad *et al*. 2022a, b). Out of numerous specified technologies, adsorption process is a unique technique for removal of toxicants like heavy metals or radionuclides present at trace levels (Rambabu *et al*. 2021a, b) in contaminated water. Features like low cost, ease of scalability, easy availability & processability, high removal efficiency, good regeneration potential and environment friendly make this technology superior in compare to other technologies (Muthusaravanan *et al*. 2021a, b) (Nandhini Suresh kumar *et al*. 2020a, b). A number of adsorbents have been reported for removal of these metal ions from wastewater like inorganic material (Ibrahim *et al*. 2003a, b) and organic adsorbent alumina (Wang *et al*. 2006a, b), bentonite (Klika *et al*. 2007a, b) and ion exchanger poly-acrylamide cerium titanate polymer (Chen *et al*. 2008a, b) and titanium tungstate Ibrahim (2010) and carbon materials (Shao *et al*. 2009a, b). The efficiency of these materials depends on many factors, including the surface area, pore

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size distribution, polarity, and presence of functional groups (Ewecharoen *et al.* 2009). Defence laboratory is working on development of adsorbents for water purification systems (Misra *et al.* 2011a, b Kumar and Jain 2011, 2013, 2012).

Over the years functionalized silica has been used as effective adsorbents for removal of toxic metal ions from contaminate water. Many research papers were published in which silica was functionalized with different functional roups viz. thiosemicarbazide, carboxyhydrazide (Jal *et al.* 2001a, b), 2-mercaptobenzimidazole (Bagheri *et al.* 2000a, b), polyethyleneimine (Ghoul *et al.* 2003a, b), phosphonic acid (Garcia-Valls *et al.* 2001a, b) and 3-(mercapto)propyl were used for removal of toxic metal ions. In the present study, APS-EDTA prepared and characterized by FT-IR, SEM and XRD. APS-EDTA used for the removal of Cs (II), Sr(II), Co(II), Cd(II) and Ni(II) from contaminated water. All standard solutions of heavy metal were prepared from their respective salts which are radiologically inactive. The removal studies were carried out through batch method at different initial concentration of metal ions 1000-10000 μg/l, at different contact time 10-60 minutes, at different doses of material 50-200 mg and at different pH. The obtained data were applied for Langmuir and Frendulich isotherms to determine adsorption process.

According to the results of this study, the maximum adsorption capacity obtained for Cd, Co, Cs, Ni, Sr are 1.3037 mg/g, 1.3458 mg/g, 1.4974 mg/g, 1.4388 mg/g and 1.3192 mg/g respectively through Langmuir isotherm. In view of results, APS-EDTA material can be used as an adsorbent for removal of toxicants.

2. Materials and methods

2.1 Instrumentation

All atomic absorption spectrometer (AAS) (Analytik-Jena-Nova-400) measurements were carried out on flame mode with single beam. AAS equipped with 100 mm and 50 mm burner, a cross flow nebulizer 5.0 mL/min and 1.2 mm slit were used throughout the experiments. Each experiment was duplicated under identical conditions using this instrument for concentration determination.

IR spectra were recorded on JASCO FT-IR spectrometer model Jasco-610 by using KBr pellets. X-ray diffraction pattern were recorded on a Panalytical X'pert PRO Diffractometer with a Cu Kα source. Scanning electronic microscope (SEM) images & energy dispersion spectroscopy (EDS) spectra were performed on Carl-Zeiss EVO-MA-50. The pH measurements were made on a digital pH meter (HACH, sension 1, model 51935-00) equipped with a gel-filled pH electrode. The meter was calibrated with the buffers of 4, 7 and 10.

2.2 Chemicals and solutions

Analytical-grade reagents were used. All laboratory wares used for analytical determination were cleaned first by trace metal grade nitric acid and hydrochloric acid, followed by repeated rinsing with de-ionized water. All the solutions were prepared with ultrapure water (resistivity:
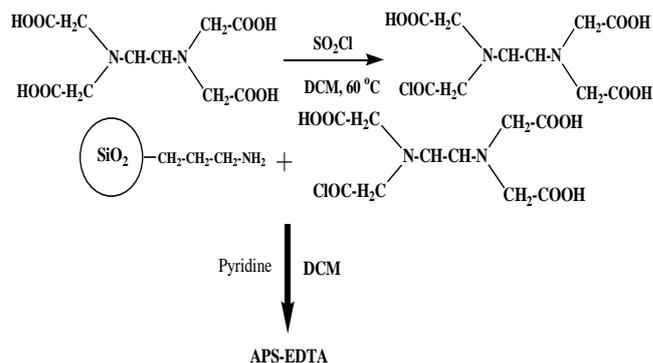
Scheme: Preparation Steps of APS-EDTA

18.2 MΩ.cm,) from an Elix analytical reagent-grade water purification system.

Calibration standard solutions and internal standards were prepared from commercial metal standard solutions. Analytic grade nitric acid (Fisher) was used as acid for the preparation of all the calibration standard solutions and analytical solutions. Standard working solutions 1000 mg/L of metal ions were prepared from their salts and solutions of varying initial concentrations were prepared from a 1000 mg/L by serial dilution using distilled deionized water. 3-Aminopropyl silica (APS), SO_2Cl and EDTA were purchased from Sigma-Aldrich.

2.3 Preparation of ethylenediamine tetraacetic acetic acid functionalized silica (APS-EDTA)

APS-EDTA prepared in two steps. In the first step, acyl chlorinated EDTA prepared by reaction of EDTA and Thionyl chloride (Molar ratio 1:1) in dichloromethane (DCM) at 60ºC for 3 'h' with continuous stirring. Excess thionyl chloride and DCM filter and obtained acylchlorinated EDTA. In second step, acylchlorinated EDTA treated with equimolar 3-aminopropyl silica in dichloromethane (DCM) in presence of pyridine at 60⁰C for 4 'h' with continuous stirring. The obtained product washed with distilled water and dried. The obtained product characterized with various techniques.

2.4 Adsorption studies with batch method

Two standard metal ions concentration i.e. 1000 μg/L (1 ppm) & 10000 μg/L (10 ppm) were prepared separately each for Cd (II), Co(II), Cs(I), Ni(II) and Sr(II). For Batch adsorption experiments were carried out at 30±1 ⁰C in 100 mL beakers (containing 100 mg APS_EDTA). To it 10 mL standard solutions of two selected concentrations were added for each metal ions. The beakers were kept for 5-60 min and solutions containing above said metal ions were filtered using Whatman quantitative filter paper (No. 42). After each experiment, the residual concentration of metal ions was determined by AAS. As per publicly available literature mathematically, adsorption capacity can be defined as amount of adsorbate taken up by the adsorbent per unit mass of the adsorbent. The amount of metal ion adsorbed by APS-EDTA was calculated according to the following equation (Rambabu *et al.* 2020a, b).
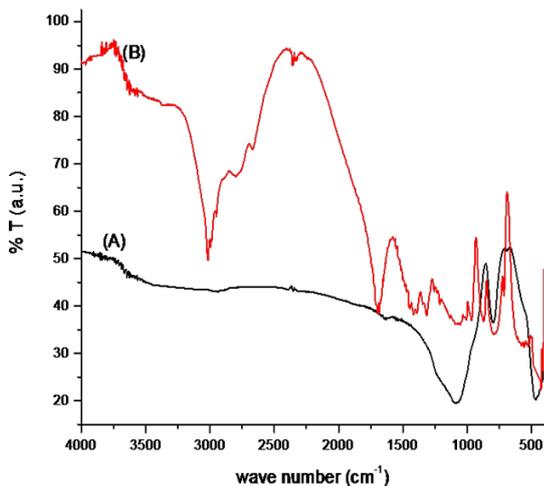
Fig. 1 Comparative FT-IR spectra of (A) 3-aminopropyl silica (B) APS-EDTA
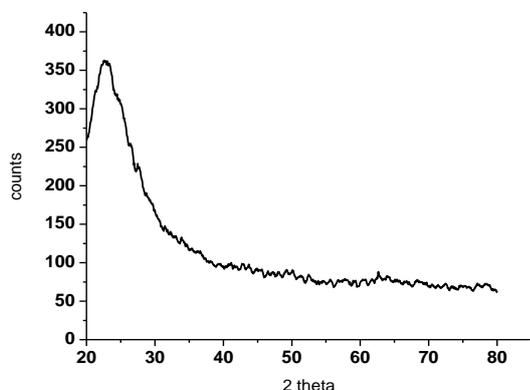
Fig. 2 XRD of APS-EDTA
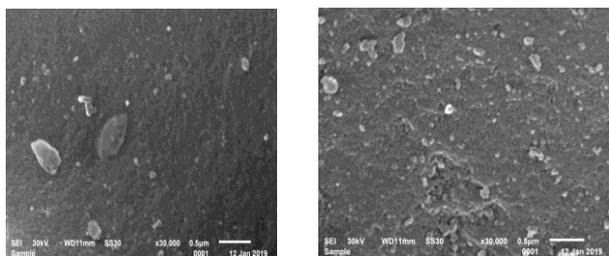
Fig. 3 SEM image of (A) 3-aminopropyl silica (APS) (B) APS-EDTA
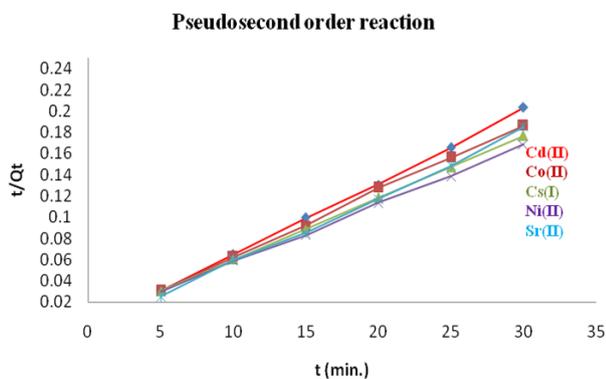
Fig. 4 Second order kinetic plot for the adsorption of different metal ions

$$Q_e = (C_i - C_e) \times \frac{V}{m} \qquad (1)$$

where

C_i = Initial concentration (µg/L) of metal ions
C_e = Equilibrium concentration (µg/L) of metal ions
V (L) = Volume of the sample solution
m (g) = Mass of the APS-EDTA

The observed adsorption data were used for Langmuir and Freundlich isotherms measurements

2.5 Kinetic adsorption experiment

To understand the effect of time on the extent of adsorption, equilibrium data were used for kinetic study. The equilibrium concentration of Cd(II), Co(II), Cs(I), Ni(II) and Sr(II) were determined at different time interval (5-30 min) with initial concentration of metal ions 1000 µg/L, APS-EDTA 100 mg and pH 7. The series of samples are quenched at time interval by filtration. The concentrations of the filtrate were analysed by AAS. These results were used to obtain the adsorption kinetic.

2.6 pH effect

The effect of pH on adsorption of metal ions on APS-EDTA was evaluated at constant initial metal ion concentration (i.e., 1000 µg/L of 10 mL volume (10mL), at constant adsorbent amount (100 mg) and at constant contact time (i.e., 30 minute) with different pH (4, 7, and 10). Then residual concentration of metal ions was determined by AAS.

3. Results and discussion

3.1 Characterization of EDTA functionalized silica (APS-EDTA)

The FT-IR spectrum of APS-EDTA was performed in Fig. 1. FT-IR of 3-aminopropyl silica (Fig. 1(A) shows absorption band at 1,150 cm^{-1} for Si-O-Si group and O-H stretching of silanol group at 3450 cm^{-1}. After functionalization with EDTA new absorption bands (Fig. 1(B) appear at 3436, 3000, 1750 cm^{-1} which may assigned to NH stretching, O-H stretching and C=O stretching. The presence of absorption bands of these group confirmed that 3-aminopropyl silica functionalized with EDTA (APS-EDTA).

XRD spectra of EDTA functionalized silica shown in Fig. 2. The XRD pattern for functionalized silica three peaks at 100, 110 & 200 that are characteristics of hexagonal packing. XRD spectra of EDTA functionalized silica shown in figure revealed that silica is crystalline state. There is no reportable difference between 3-aminopropyl silica and EDTA functionalized silica. The particle size of silica is obtained 67 µm.

SEM images of silica and functionalized silica provide visual evidence of hexagonal pores. No difference in pore was obtained before and after functionalization of silica.

Table 1 Langmuir and Freundlich parameters of different metal ions adsorption

Metal	Langmuir Model			Freundlich Model		
	Q_m (mg/g)	b (L/mg)	R^2	K (mg g^{-1}) ((Lmg^{-1})$^{1/n}$)	1/n	R^2
Cd(II)	1.3037	1.1854	0.99	5.754	1.00	0.97
Co(II)	1.3458	1.0445	0.99	6.698	1.02	0.96
Cs(I)	1.4974	0.7434	0.99	5.140	1.00	0.97
Ni(II)	1.4388	0.5275	0.99	7.585	1.00	0.97
Sr(II)	1.3192	1.1682	0.99	6.531	1.00	0.96

Table 2 Kinetic parameters for different metal ions adsorption onto APS-EDTA

Metals	Pseudo second order			
	C_0 (µg/L)	k_2 [g/(min µg)]	Q_e (mg/g)	R^2
Cd(II)	1000	1.105×10^{-2}	203	0.98
Co(II)	1000	1.392×10^{-2}	215	0.99
Cs(I)	1000	1.296×10^{-2}	186	0.97
Ni(II)	1000	1.172×10^{-2}	193	0.98
Sr(II)	1000	1.586×10^{-2}	210	0.99

Table 3 Effect of pH on adsorption of metal ions on APS-EDTA

pH	Removal (%)
4	90-98
7	90-93
10	50-65

3.2 Adsorption isotherm

The adsorption isotherms of metal ions onto APS-EDTA from aqueous solution is shown that the adsorption capacity of metal ions onto EDTA- functionalized silica increases with increasing the initial concentration of metal ions and continued up to 1000 µg/L and level off thereafter. The initial concentrations of metal ions (1000-10000 µg/L) were used for investigation of adsorption isotherm. The equilibrium concentrations of above said metal ions are obtained after 30 min. of contact time. Langmuir (1916) and Freundlich (1906) isotherms are employed to describe the adsorption process. Langmuir isotherms signifies chemisorption process where as Freundlich signifies physio-adsorption process.

The Langmuir isotherm model is expressed as

$$\frac{C_e}{Q_e} = \frac{1}{bQ_m} + \frac{C_e}{Q_m} \qquad (2)$$

where,

C_e = Eequilibrium concentration obtained from the initial concentration upon a certain period of contact time with the APS-EDTA,

Q_e = Amount of metal ions adsorbed per gram of APS-EDTA (mg/g) at equilibrium; it is derived from the Eq. (1).

Q_m = Maximum adsorption capacity (mg/g).

b = Langmuir parameter related to energy of adsorption.

The linear plot of C_e/Q_e vs. C_e gives the intercept and slope corresponding to $1/(Q_m b)$ and $1/Q_m$, respectively, from which both Q_m and b are derived. A plot of C_e/Q_e vs C_e obtained straight line if the Langmuir equation is obeyed by the adsorption equilibrium ([Gupta and Babu 2009) . The adsorption data were used for plot C_e/Q_e vs. C_e and obtain straight line. The values of Q_m and b were calculated from plot and presented in Table 1.

Freundlich isotherm is expressed as

$$\text{Log } Q_e = \frac{1}{n} \log C_e + \log K \qquad (3)$$

where,

$K ==$ Freundlich constants, indicating the sorption capacity, $1/n=$ Freundlich constants, indicating the sorption intensity, C_e = Equilibrium concentration of metal ions in aqueous solution and Q_e =Sorption capacity.

The plot of log Q_e against log C_e gives the intercept and slope corresponding to log K and $1/n$, respectively, from which both K and n are obtained.

The regression equations parameters Q_m, K, 1/n and the correlation coefficient are summarized in Table 1. It is seen that Langmuir as well as Freundlich model are suitable to fit the adsorption data since the correlation coefficients are higher than 0.97.

3.3 Adsorption kinetics

The kinetic property of metal ions adsorbed on APS-EDTA was assessed in Fig. 4. The adsorption rates were determined at pH 7, metal ions concentrations 1000 µg/L and contact time 5-30 minutes in aqueous solution.

The adsorption kinetic mechanism was evaluated using one conventional model, namely the pseudo-second-order equations (Ho and McKay 2000). In the case of pseudo-first-order, very low correlation coefficient values were obtained, so that this model was not suitable for absorption of metal ions on APS-EDTA.

A pseudo-second-order reaction (Allen and Brown 1995) is guided by the expression

$$\frac{t}{Q_t} = \frac{1}{(k_2 Q_e)^2} + \frac{t}{Q_e} \qquad (4)$$

where Q_e (µg/g) is the amount of metal ion adsorbed at equilibrium, Q_t (µg/g) is the amount of metal ion on the surface of the sorbent at time t and k_2 [g/(µg min)] is the rate constant of pseudo-second-order adsorption.

The plot of t/Q_t versus t is shown in Fig. 4 and values of k_2 and Q_e were derived from the intercept and slope of the linear plot as. The obtained values were summarized in Table 2. High correlation coefficient (R^2) values were obtained for pseudo-second-order reaction of different metal ions. Therefore, it is suitable and applicable for adsorption of metal ions on APS-EDTA. The kinetic data for second-order assessment are listed in Table 2.

3.4 Effect of contact time

The impact of contact time on adsorption of Cd(II), Co(II), Cs(I), Ni(II) and Sr(II) metal ions onto functionalized

APS-EDTA was analyzed at constant concentration of metal ion from 0 to 60 min at an interval of 5 min. It is observed that adsorption increases till 30 min., and then equilibrium point reached. As a consequence of it, very little change in adsorption was observed which was not highly significant.

3.5 Effect of pH

The activity of the adsorbents functional groups is strongly affected by the solution of pH. The point of zero charge pH (pHpzc) is the pH of the solution at which the overall observed charge on the surface of adsorbent is zero. This is due to hydrogen ions are strongly competing with metals. At this pH, protonation of chelating group also takes place. Therefore complexation with available ligands is reduced and hence the percentage removal decreases. At pH > pHpzc deprotonating of functional group occur and salt formation is take place. Therefore percentage uptake of metal ions decreases. The removal percentage is shown in range due to different pHpzc value for different metal ions. EDTA-functionalized silica form complex with divalent metal ions in acidic medium or neutral. The pHpzc depends on APS-EDTA and metal ions as shown in Table 3.

3.6 Effect of adsorbent dosage

As increase in adsorption dosage, adsorption increases at constant initial concentration & constant contact time.

4. Conclusions

APS-EDTA was prepared by condensation the reaction of acyl chlorinated EDTA and 3-aminopropyl silica and characterized by FT-IR, SEM and XRD. Prepared APS-EDTA was used for adsorption of toxic ions viz. Cd(II), Co(II), Cs(I), Ni(II) and Sr(II). The results of the experiments indicated that concentration of toxic ions, contact time and pH have very significant effects on adsorption of above mentioned ions on APS-EDTA. The isotherm experimental data fits well to Langmuir model as well as Freundlich model and found high correlation coefficient (R^2 = 0.97-0.99). The adsorption capacities of APS-EDTA for different metal ions are listed in Table 1. The value of adsorption capacity is higher than mentioned other reference study. EDTA-functionalized silica can be used an effective and inexpensive adsorbent for radiological and nuclear contaminants from water.

Acknowledgments

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Appendix
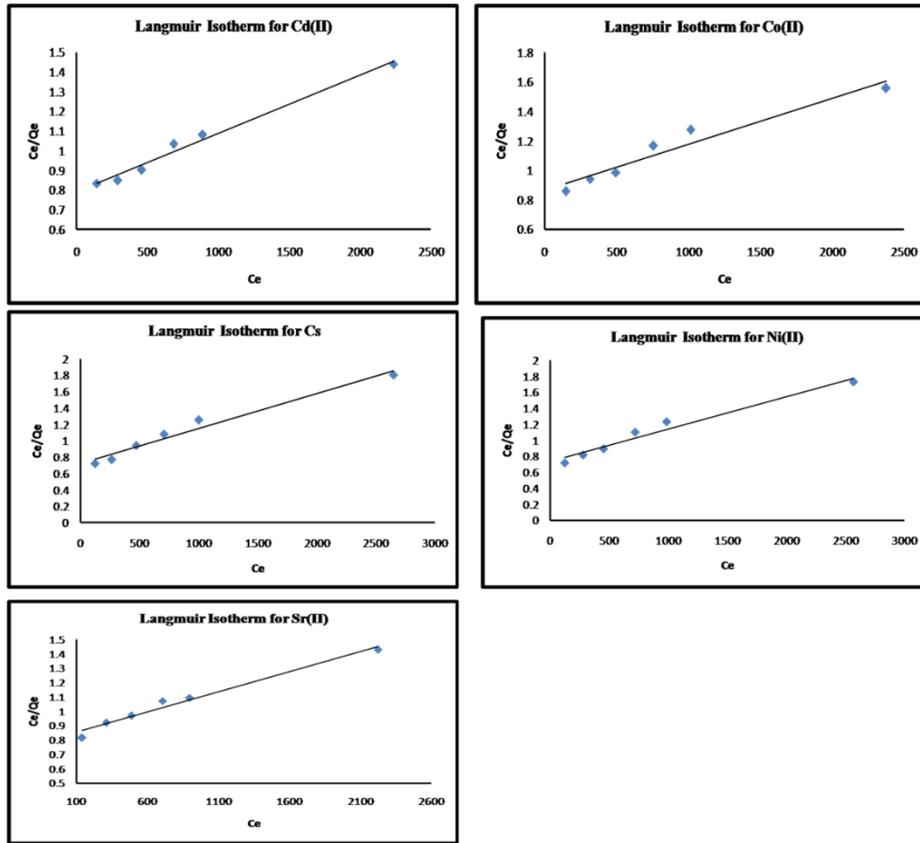
Fig. A1 Langmuir isotherm of adsorption metal ions on APS-EDTA
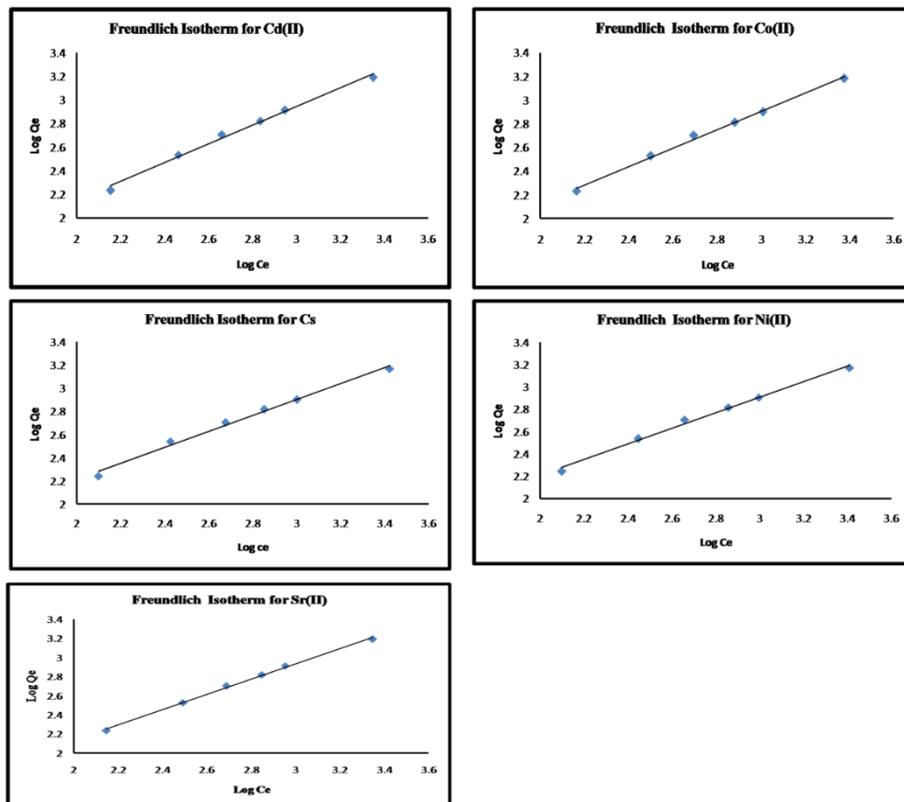
Fig. A2 Freundlich isotherm of adsorption metal ions on APS-EDTA