



Adsorptive Performance of Iminodiacetic Acid Functionalized Nanoporous Carbon for Removal of Pb(II), Cu(II) and Cd(II) Ions in Aqueous System

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Received: 25/05/2018

Accepted: 26/06/2018

Published: 30/09/2018

Abstract

In recent years, the exploration of nontoxic and inexpensive methods for the removal of heavy metals from wastewaters has been needed with respect to the impact of these toxic metal ions in the environment. Efficient and common adsorption techniques have been widely used for the removal of heavy metals from wastewater due to the economically feasible properties. In this study, Nanoporous carbon (CMK-3) has been prepared and modified with Iminodiacetic Acid (IDA) and used as adsorbent for removal of Pb (II), Cu (II) and Cd (II) from aqueous solution. Prepared samples were characterized by X-ray diffraction (XRD), nitrogen adsorption-desorption isotherms, Fourier transform infrared spectroscopy (FT-IR) and scanning electron microscopy (SEM). The essential factors such as pH of solution and concentration of the eluent solution have been evaluated. The optimum conditions were pH 4 and 0.5M HNO₃. The adsorption isotherms (Langmuir and Freundlich), were investigated. The adsorption capacities were 147.4, 145.1 and 142.3 for Pb(II), Cu(II) and Cd(II) respectively which is higher than of previously reported.

Keywords: CMK-3, IDA, Pb (II), Cu (II), Cd (II), Adsorption

1 Introduction

Nowadays, heavy metal ions have aroused worldwide attention. Heavy metal ions such as Pb (II), Cu (II) and Cd (II) and their compounds are major pollutants in the coastal environment. These metal ions are high toxic and cannot be biodegradable in nature, which would cause damage to human and environment. [1]. There are many methods for removal of heavy metal ions pollution. From the methods used to remove heavy metal ions such as chemical precipitation, ion exchange, membrane and electrochemical technologies, adsorption method shows to be the most effective than the others [2, 3]. Existence of an adsorbent for adsorption method is necessary. Solid adsorbents bind with molecules by physical attractive forces, ion exchange, and chemical binding [4]. Different type of adsorbents have been studied for removal of heavy metal ions [5-16]. The materials such as zeolites, Organic and carbon adsorbents, chitosan, carbon nanotube, metal oxides and graphene oxide are used as adsorbent for removal of heavy metal ions. However, high production costs, slow adsorption rate and low adsorption capacity are disadvantages of these adsorbents. Recently, ordered mesoporous carbons (CMK_x)

such as CMK-1, CMK-3 and CMK-5 are adequate materials for adsorption of several compounds. These materials have attracted much attention due to the high pore structure of ordered mesoporous, high thermal stability, narrow pore size distribution, large specific surface area and excellent chemical and physical stability. Nevertheless, these adsorbents do not disperse well in aqueous systems owing to the hydrophobic property of CMK_x [17-19]. These disadvantages can be solved by the possibility of functionalization with desired functionalities such as basic and acid groups. The functional groups such as carboxylic acid can serve as adsorption centers for heavy metal ions and can increase the hydrophilicity, wettability, of carbonaceous materials [20].

The objective of this work was to preparation of CMK-3 ordered mesoporous carbons modified with Imino diacetic Acid (IDA) and its application of as an adsorbent for removal of Pb(II), Cu(II) and Cd(II) metal ions from aqueous solution. Batch experiments were performed to measure metal ion adsorption capacities. Inductively coupled plasma optical emission spectroscopy (ICP-OES) was used to monitor the remainder of metal ions in aqueous samples.

2. Material and Methods

2.1 Materials

Reagents used in this study were Tetraethylorthosilicate (TEOS, 98%), PluronicP123, HCl (32%), Sucrose,

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Ammonium persulfate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$ and H_2SO_4 (98%), Diethyl Iminodiacetate, $\text{Pb}(\text{NO}_3)_2$, $\text{Cu}(\text{NO}_3)_2$ and $\text{Cd}(\text{NO}_3)_2$. All chemicals were of analytical grade and were prepared from E. Merck (Darmstadt, Germany) except PluronicP123.

2.2 preparation of Adsorbent

In the our previous study, CMK-3 was synthesized and modified with with 2-amino-5-mercapto-1,3,4-thiadiazole for Hg(II) removal from aqueous media[21]. In this study, O-CMK-3 modified with IDA. For this purpose, O-CMK-3 dispersed in a solution of SOCl_2 , and stirred at 70°C for 24 h. The excess SOCl_2 was removed at 50°C and then adsorbent was dried under vacuum. After that, the obtained CMK-3-COCl was mixed with Diethyl Iminodiacetate under argon atmosphere at 70°C for 48 h. the product was separated, succulated with DMF and washed with deionized water, and reacted with 2.0mol/L HCl (75 mL) under argon atmosphere at 50°C for 12 h. The IDA-CMK-3 was washed with deionized water and dried under vacuum.

2.3 Characterization

X-ray powder diffraction (XRD) patterns were recorded by XRD diffractometer (Philips 1830) equipped with a liquid nitrogen-cooled germanium solid-state detector using Cu-K α radiation over a range of $1^\circ < 2\theta < 4^\circ$. The specific surface area was evaluated by Nitrogen adsorption-desorption using the Brunauer-Emmett Teller (BET) method in order to determine the textural properties of adsorbents. Scanning electron microscopy (SEM) images of adsorbents were observed using a Philips XL30 instrument after gold metallization in order to increase their conductivity before scanning Fourier transform infrared spectra (FTIR) were recorded on a DIGILABFTS 7000 instrument under attenuated total reflection (ATR) mode using a diamond module in the range of $400\text{--}4000\text{cm}^{-1}$. Preparation of aqueous solution of metal ions: Batch adsorption experiments were performed in bottles of multi-ions solution of Pb(II), Cu(II) and Cd(II) (pH = 2-6) containing various concentrations of 10, 100, 200, 300 and 400 mg/L, stirring at 150 rpm at ambient temperature for 70 min contact time and dose of 1 g/L IDA-OCMK-3. After equilibrium adsorption, the concentration of the remaining metal ions in sample solutions was measured with ICP-OES. Then, the adsorbed heavy metal ions were eluted with

0.1-0.7M HNO_3 . The desorbed solutions were analyzed using ICP-OES. The amounts of analyte adsorbed by adsorbents (q_e : mg/g) were calculated using Eqs. (1).

$$q_e = \frac{(C_0 - C_e)}{m}V \quad (1)$$

where C_e (mg/L) is equilibrium concentrations of metal ions, V is the volume in L of metal ions solution, m is the weight in g of the adsorbent and C_0 is the initial concentrations of metal ions. The Langmuir and Freundlich models, which correspond to homogeneous and heterogeneous adsorbent surfaces, are used to describe the equilibrium isotherm data. The Langmuir model is given by Eq. (2):

$$q_e = \frac{q_m \times b \times c_e}{1 + b \times c_e} \quad (2)$$

where q_m (mg/g) and b (L/mg) are maximum adsorption capacity of adsorbent and the Langmuir constant related to the adsorption energy coefficient, respectively.

The Freundlich model is given by Eq. (3):

$$q_e = k_f \times c_e^{\frac{1}{n}} \quad (3)$$

where k_f (mg/g) and n (L/mg) are the Freundlich constants related to adsorption capacity and intensity, respectively[22, 23].

3. Results and Discussion

3.1 Characterization

The XRD patterns of ordered structure of CMK-3, O-CMK-3 and IDA-OCMK-3 are shown in Figure 1a. As seen in this figure, three diffraction peaks that can be indexed to (100), (110), and (200) in the 2θ range from 1 to 4° , representing well-ordered hexagonal mesopores[24]. The XRD patterns showed well-resolved reflections indicating that CMK-3 nicely maintains its original structure even after the modification with $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and functionalization with IDA.

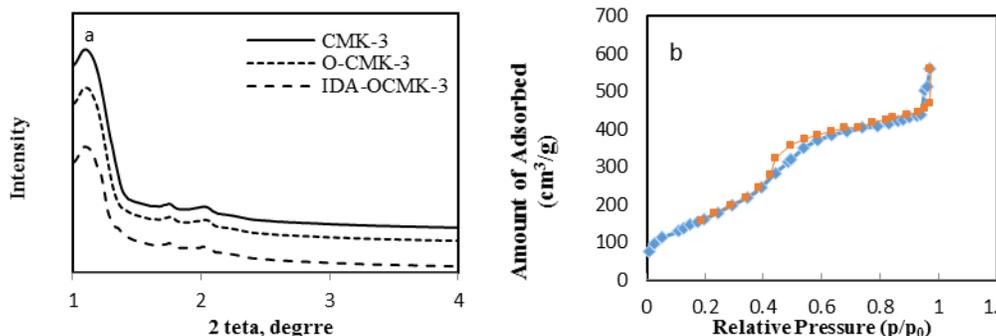


Figure 1: a) XRD patterns of CMK-3, OCMK-3 and IDA-OCMK-3 and b) The adsorption-desorption isotherm of IDA-OCMK-3

The intensities of the XRD peaks for O-CMK-3 and IDA-O CMK-3 are substantially lower than those measured for CMK-3, which is probably caused by the pore filling effect of the CMK-3 channels and the anchoring ligands on the outer surface of CMK-3. As shown in Fig. 1b, the adsorption-desorption isotherm of IDA-OCMK-3 exhibit a type IV profile according to the BET classification. The determined BET specific surface area was $751 \text{ m}^2/\text{g}$, pore volume was $0.83 \text{ cm}^3/\text{g}$ and d spacing was 3.9 nm .

The surface morphology of the obtained CMK-3 and IDA-OCMK-3 were observed by SEM. As shown in Figure. 2 it is clear that the IDA-OCMK-3 almost maintain a rod-like shape with only a few deformations.

Figure. 3 shows the FT-IR spectra of CMK-3, O-CMK-3 and IDA-OCMK-3. A broad band at around 3450 cm^{-1} was observed in all samples. It is mainly due to the O–H stretching vibration of the adsorbed water molecule. The broad band that appeared at 1150 cm^{-1} is caused by the stretching vibrations of C–O bonds. The characteristic peaks at 1744 cm^{-1} is due to the stretching and bending vibration modes of –COOH on CMK-3. The new bands at 1620 cm^{-1} (IDA-OCMK-3 spectrum) are evidence of formation of amide bond that confirms the successful functionalisation of O-CMK-3 with Iminodiacetic acid groups.

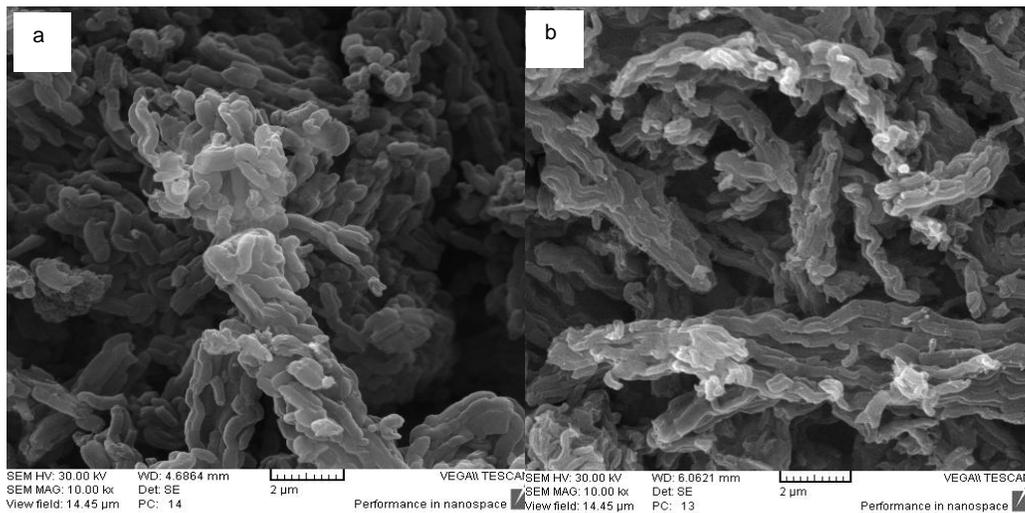


Figure 2. SEM photographs of a) CMK-3 and b) IDA-OCMK

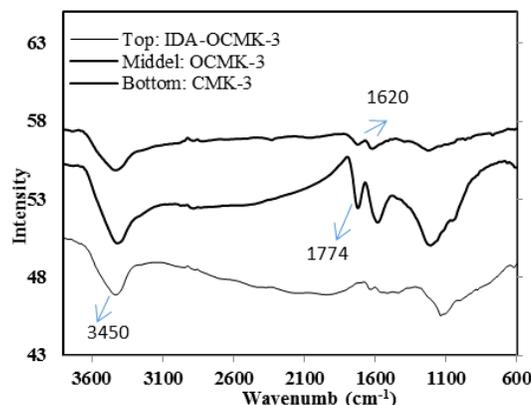


Figure 3. IR spectra of CMK-3, OCMK-3 and IDA-OCMK-3.

3.2 Effect of pH

To assess the pH dependence of the adsorption, solutions in the range of pH 2–6 were chosen. Figure. 4 shows the effect of the pH on the removal efficiency of Pb(II), Cu(II) and Cd(II) (the initial metal concentration of 100 mg/L and dose of adsorbent was 1 g/L). As can be

seen, adsorption efficiency increases with increasing the pH from 2 to 4, and then decreases at the pH value higher than 4. The increase in the metal removal as the pH increases ($2 < \text{pH} < 4$) could be due to the decrease in competition between proton and metal species for the surface sites and decrease in positive surface charge, which results in a lower

coulombic repulsion of the adsorbing metal. The maximum adsorption was observed at pH 4 for all ions. However, Low adsorption of the analytes at high pH (>4.0), is because of the competition between the formation of hydroxylated complexes of the metal ions on the active sites of the IDA-OCMK-3.

3.3 Effect of concentration of eluent on desorption

The selection of suitable eluent is important for desorption of the heavy metal ions. Eluent selected should be capable of extracting the analyte and should not affect the adsorbent. As shown in Figure. 4; adsorption of heavy metal ions was decreased at low pH. Therefore, the acidic eluent is the best solution for desorption of the analytes. In this regard HNO₃ with different concentration in the range of 0.1-0.7 were investigated in Figure. 5. Finally, 0.5mol/L HNO₃ was specified for desorption of Pb (II), Cu (II) and Cd (II).

3.4 Regeneration of adsorbent

One of the most important characterizations of the adsorption systems is the multiple reuse of the adsorbent, which significantly decreases the process cost. Regeneration of the IDA-OCMK-3 was evaluated by 0.5 mol/L HNO₃. The results shown in Figure. 6 indicates that

the adsorbent is stable in operation process, enabling more than 10 adsorptions–desorption cycles with only minor decrease in the desorption of Pb (II), Cu (II) and Cd(II)ions. Figure. 6. The effect of adsorbent reuse on desorption of Pb(II),Cu(II) and Cd(II)by IDA-OCMK-3 [initial concentration = 100mg/L, solution pH was 4, dose of adsorbent was 1 g/L, HNO₃ (0.5M)].

3.5 Isotherm study in Batch study

The experimental data on the effect of an initial concentration of Pb (II), Cu (II) and Cd (II) ions on the IDA-OCMK-3 was fitted to Langmuir and Freundlich isotherm models. The graphical representation of these models is presented in Figure.7, and all of the constants are presented in Table.1. The value of correlation coefficient (R²) shows that the data conform well to the Langmuir equation. The maximum adsorption capacity (q_{max}) for the adsorption of these ions on IDA-OCMK-3 were compared with those of adsorbents used. This result is listed in Table 2. This revealed that q_m of IDA-OCMK-3 obtained in this study was higher than the previously reported values.

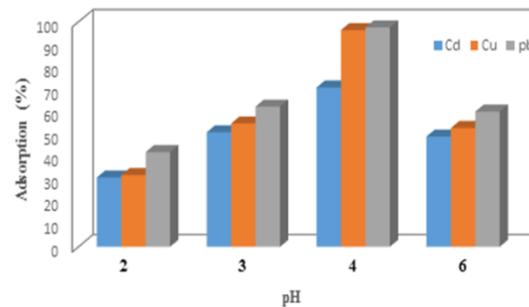
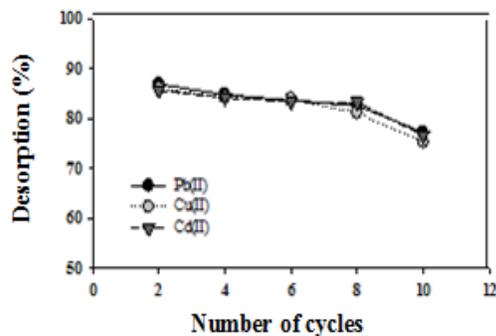


Figure 4. Effect of pH adsorption of Pb(II), Cu(II) and Cd(II) over IDA-OCMK-3 [Initial concentration = 100 mg/L and dose of adsorbent was 1 g/L].

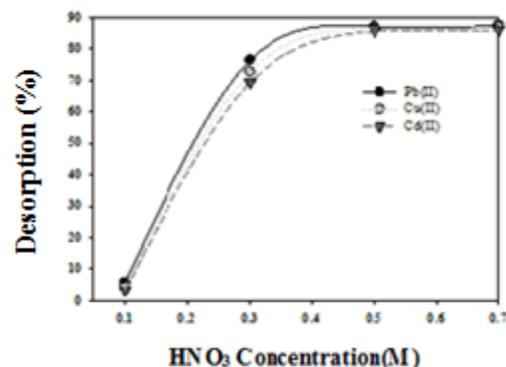
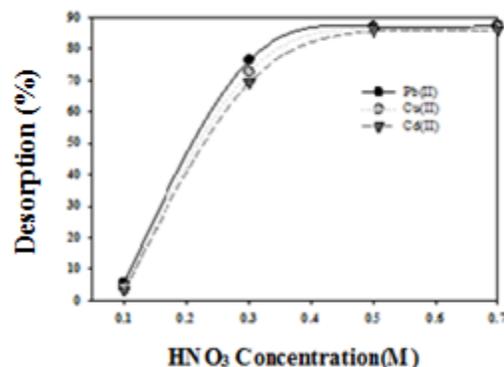


Figure 5. Effect of eluent concentration on desorption of Pb(II), Cu(II) and Cd(II). [initial concentration = 100mg/L, solution pH was 4, dose of adsorbent was 1 g/L].

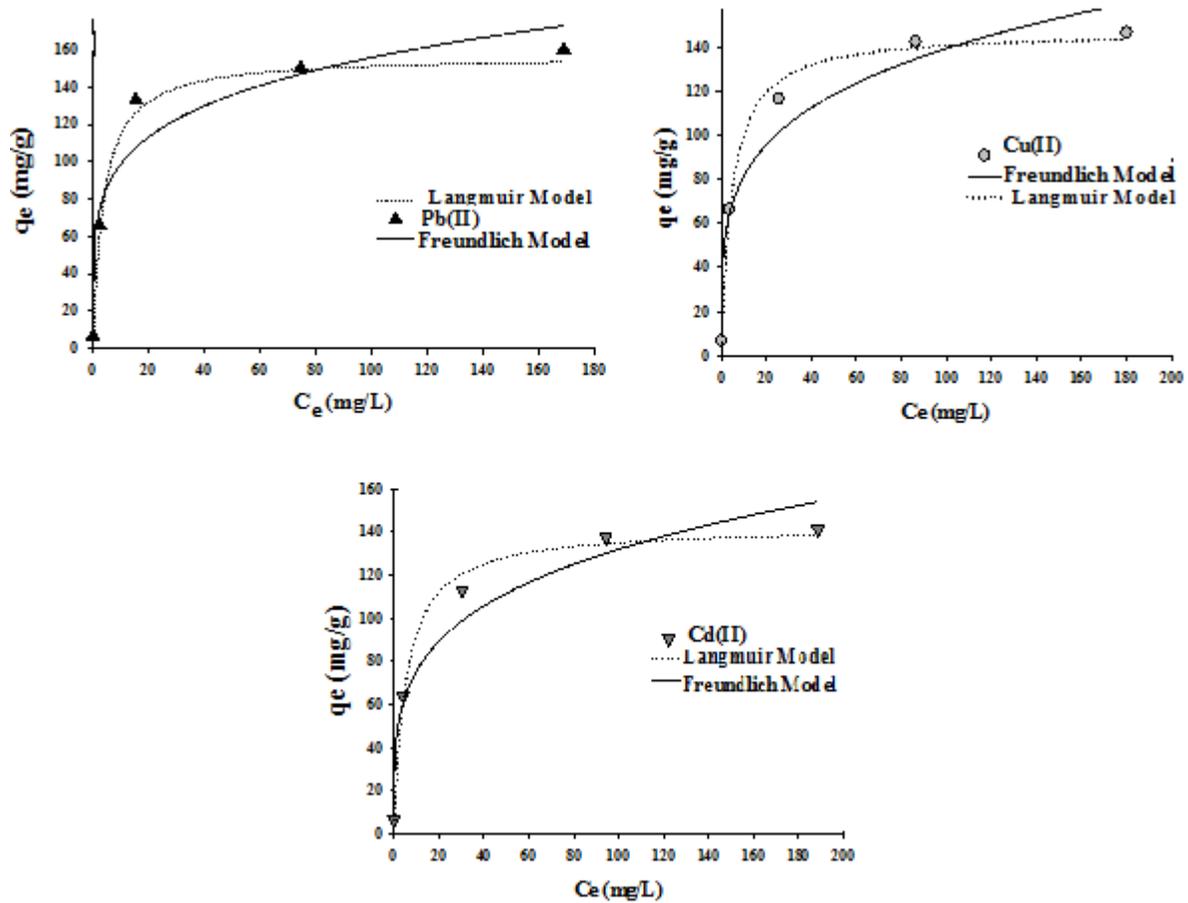


Figure 7. Adsorption isotherm of \blacktriangle) Pb(II), \blacksquare) Cu(II) and \bullet) Cd(II) on IDA-OCMK-3 at the adsorbent dose of 1 g/L, pH 4.0 and ambient temperature.

Table 1: Langmuir and Freundlich parameters for adsorption of Pb(II), Cu(II) and Cd(II) on IDA-OCMK-3

| Metals | Langmuir | | | Freundlich | | |
|--------|------------------|------------|--------|------------|------------|--------|
| | q_{max} (mg/g) | b (L/mg) | R^2 | KF(mg/m) | n (L/mg) | R^2 |
| Pb(II) | 160.55 | 0.31 | 0.9967 | 62.66 | 5.06 | 0.9226 |
| Cu(II) | 147.20 | 0.21 | 0.9920 | 47.56 | 4.28 | 0.9339 |
| Cd(II) | 142.38 | 0.18 | 0.9934 | 43.05 | 4.11 | 0.9336 |

Table 2: Comparative data of the adsorption capacity of IDA-OCMK-3 with those of adsorbents used

| Adsorbent | Modifying agent | Adsorbent dose (g/L) | Metal conc. (mg/L) | Adsorption capacity(mg/g) | | | Reference |
|-----------------------|--------------------------------|----------------------|--------------------|---------------------------|--------|--------|------------|
| | | | | Pb(II) | Cu(II) | Cd(II) | |
| SBA-15 | AEAPTMS | 1.1 | 113 | - | 9.4 | - | [25] |
| SBA-15 | DETA | 10 | 11 | 1.1 | 1.0 | 1.1 | [26] |
| SBA-15 | N-propylsalicylaldimine | 1 | 318 | 57.2 | 57.2 | - | [27] |
| SBA-16 | MPTS | 5 | 127 | 36.4 | 36.4 | - | [28] |
| MCM-41 | APTS | 5 | 50 | - | - | 18.2 | [29] |
| SBA-15 | Melamine-based NH ₂ | 1 | 100 | 94.8 | 90.3 | 71.1 | [30] |
| SNHS | dendrimer | 3 | 100 | 26.86 | - | 20.82 | [31] |
| NH ₂ -SG | Non | 3 | 100 | 31.89 | - | 31.89 | [31] |
| NH ₂ -SNHS | APTS | 3 | 100 | 40.73 | - | 40.73 | [31] |
| CMK-3 | APTS | 1.5 | 300 | 147.4 | 145.1 | 142.3 | This study |
| | IDA | | | | | | |

AEAPTMS: N-3-(trimethoxysilyl) propyl ethylene] diamine; Mercaptopropyltriethoxysilane; APTS: 3-Aminopropyltriethoxysilane.

DETA: Trimethoxysilyl propyl diethylenetriamine; MPTS: 3-

4 Conclusions

In this study, the IDA-OCMK-3 has been successfully synthesized and modified by Iminodiacetic acid and used for removal of Pb(II), Cu(II) and Cd(II) in batch system. The optimum conditions were pH 4 and HNO₃ 0.5M. This adsorbent exhibited good adsorption-desorption properties. The adsorption isotherm of these ions using IDA-OCMK-3 is carried out in batch experimental system. The Langmuir isotherm was fitted the equilibrium data better than the Freundlich isotherm. The adsorption capacity was 147.4, 145.1 and 142.3 mg/g for Pb(II), Cu(II) and Cd(II), respectively.

Acknowledgment

The authors are highly thankful to Iran National Science Foundation for the financial support to this project.

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