# Simultaneous Removal of $Pb^{2+}$ and $Cu^{2+}$ by SBA-15/di-Urea as a Nano Adsorbent

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**ABSTRACT:** *In this study, the potential of SBA-15/di-urea nanoporous silica compound for the removal of $Pb^{2+}$ and $Cu^{2+}$ ions was investigated. The presence of organic groups in the silica framework of SBA-15/di-urea was demonstrated by the FT-IR spectrum. The functionalized product showed the BET surface area 518 $m^2/g$ and pore diameter 6.5 nm, based on adsorption-desorption of $N_2$ at 77 K. SEM revealed a rod-shaped morphology, and the TEM image showed an ordered array of 2D hexagonal mesoporous SBA-15. The ions in the samples were identified by flame atomic absorption spectrometry. The effect of adsorbent amount, contact time, metal concentration, pH, and presence of other metals on removal efficiency has been studied. Simultaneous removal of $Pb^{2+}$ and $Cu^{2+}$ ions from 20 mL of the sample solution containing 60 μg of each ion were completely done at pH greater than 5.0 after stirring for 15 minutes. Langmuir, Freundlich, and Temkin adsorption isotherms were evaluated for both adsorbates and it was determined that the data fitted well with the Langmuir model ($R^2 > 0.98$). The maximum capacity of the adsorbent was found to be 147.0 ± 0.6 mg and 77.0 ± 0.5 mg of $Pb^{2+}$ and $Cu^{2+}$ ions/g SBA-15/di-urea, respectively. The lowest amount of 3M nitric acid for stripping the target species from adsorbent was determined as 20 mL. The application of this methodology for the real sample was tested by an Industrial wastewater sample.*

**KEYWORDS:** *SBA-15/di-urea; Simultaneous removal; $Pb^{2+}$; $Cu^{2+}$; Wastewater.*

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## INTRODUCTION

Heavy metal pollution as a result of rapid technological development is a serious concern for ecology. Toxic metals have been discharged into the environment because of global industrialization and have caused great anxiety worldwide by affecting human health [1, 2]. $Pb^{2+}$ is extremely averse to health [3]. It can affect the hematopoietic function and the nervous, digestive, skeletal, and reproductive systems after accumulating in the food chain and entering the body [4, 5]. Therefore, the removal of lead from water resources is extremely necessary [6, 2]. Lead in the environment arises from both anthropogenic and natural sources. It enters in food, drinking water, air, soil, and dust from old paint containing lead. Lead exposure can result in an extensive range of biological effects depending on the level and duration of exposure [7].

Copper is an essential element for human health, despite the fact that it can be dangerous for the environment and public health in cases of excessive discharge [8]. A high concentration of $Cu^{2+}$ endangers the growth of the plants and aquatic animals prevents the self-purification of the water bodies and also exerts a deleterious effect on human health.

One of the potential remedies for the removal of toxic heavy metal ions from wastewater is the use of adsorption technology [9-14]. One of the mature wastewater treatment technologies is adsorption which it's process and required equipment are simple. Therefore, the development of new, low-cost, and high-yield adsorbent materials has become increasingly important. Especially, inclined attention is seen for metal ions separation by nanomaterials, for the reason of their specific functionality and high surface area [15-27]. For example, *Mahmoud et al.* [15] prepared magnetic graphene oxide functionalized tryptophan nanocomposite for efficient removal of $Pb^{2+}$, $Cd^{2+,}$ and Cr(VI) from natural water samples. In another study, iron oxide was converted into nanoparticulate and crosslinked with starch and was used for $Pb^{2+}$, $Cd^{2+}$ and $Hg^{2+}$ removal from marine water, tap water, and industrial wastewater with percentage recovery 70–94%, 93–97%, and 76–93%, respectively [16]. In other research, nano-chitosan coating nano-iron oxide was prepared and modified with crotonaldehyde and succinic anhydride. These sorbents were applied for the removal of $Pb^{2+}$, $Cd^{2+,}$ and $Cu^{2+}$ [17]. *Soylak et al.* [18] prepared multi-walled carbon nanotubes impregnated with 4-(2-thiazolylazo)resorcinol and used them to separate $Pb^{2+}$, $Cd^{2+}$, $Zn^{2+}$ and $Ni^{2+}$ ions from food samples.

Among nanomaterials, functionalized mesoporous materials have generated considerable interest for adsorption applications including the determination and removal of metal ions [28-33]. Mesoporous silica materials, such as MCM-48, MCM-41, and SBA-15 [34-36] have been synthesized and used for metal ion removal because of their high surface area, ease of surface modification, rapid mass transport inside the nanostructures, good accessibility to active sites and hydrothermal stability [8]. A variety of functional groups can be incorporated or grafted to the surface of mesopore channels and highly effective adsorbents can be prepared [37- 39].

SBA-15 is a highly ordered material. It has a regular two-dimensional hexagonal array of channels with a pore diameter of 7–10 nm. In this study, the potential of SBA-15/di-urea was examined as a new adsorbent for the simple and fast removal of $Pb^{2+}$ and $Cu^{2+}$ ions from water and wastewater samples. To the best of our knowledge, this is the first application of SBA-15/di-urea for simultaneous removal of $Pb^{+2}$ and $Cu^{+2}$ ions.

## EXPERIMENTAL SECTION

### *Reagents*

All of the organic solvents and tetraethylorthosilicate (TEOS) were procured from Merck Co. (Darmstadt, Germany). pluronic P123 triblock copolymer, *o*-phenylenediamine, 3-(triethoxysilyl) propyl isocyanate were purchased from Sigma-Aldrich (MO, USA). The nitrate salts of Cu, Ag, Ni, Zn, Cd, Pb, Mn, Co, Cr, K, Ca. Mg and Na were of analytical grade purity and were not further treated before use. All solution making and washing procedures were performed using double-distilled water (DDW). The metal ion solutions were prepared by diluting 1000 mg/L stock solutions of the corresponding ions in DDW.

### *Apparatus*

Flame atomic absorption spectrometry analyses were on a PG-990 spectrometer, with hollow cathode lamps, using air-acetylene mixtures in the burner. The spectrometer had a slit width of 0.4 nm, a lamp current of 5.0 mA, and the wavelengths used for $Pb^{2+}$ and $Cu^{2+}$ were 217.0 nm and 324.7 nm. The background corrections were made using a deuterium lamp. Fourier Transform

InfraRed (FT-IR) analyses were performed over the range of 400-4000 $cm^{-1}$ using a RAYLEIGH WQF-510A instrument and KBr pellets. $N_2$ adsorption-desorption isotherm measurements at 77 K with a BELSORP-mini, BEL Japan, Inc. Scanning Electron Microscopy (SEM) was taken by LEO 1455VP and Transmission Electron Microscopy (TEM) was performed on Zeiss EM900 instrument at an accelerating voltage of 80 kV. pH readings were conducted using a Jenway 3520 pH-meter using a combined glass-calomel electrode.

***Synthesis of SBA-15/di-urea***

Mesoporous silica SBA-15 and SBA-15/di-urea sample was prepared according to our previously published procedure [40, 41]. Briefly, 1mmol of *o*-phenylenediamine was reacted with 2 mmol of 3-(triethoxysilyl) propyl isocyanate (2 mmol) in 30 mL of dry toluene under refluxed in $N_2$ atmosphere (6h). After that, 0.4 g of SBA-15 was added to the as-prepared solution under reflux conditions and stirred overnight. Finally, the obtained solid was centrifuged, washed with ethanol and THF, and dried at 80 °C for 24h.

***Batch adsorption experiments***

The stock solutions were prepared from corresponding salts of metal ions in ultrapure water. Then the solutions for use in the experiments were obtained by dilution from them. The general ion removal procedure by the SBA-15/di-urea was as follows: To 20 mL of the sample solution containing 60 µg $Pb^{2+}$ and 60 µg $Cu^{2+}$, 15 mg of SBA-15/di-urea was added and stirred for at least 15 minutes. Then, the resulting mixture was filtrated by passing through a 0.45 µm paper. After that, the extracted ions by the SBA-15/di-urea which remained on the paper were stripped using 20 mL of 3.0 mol/L solution of nitric acid into 25 mL volumetric flask. The $Pb^{2+}$ and $Cu^{2+}$ ion content in extracted and stripping solution were measured by FAAS. The adsorption capacity of the adsorbent at equilibrium was calculated by the equation:

$$q_e = (C_0 - C_e / m) \times V \quad (1)$$

Where $C_o$ and $C_e$ represent the initial and equilibrium ions concentrations (mg/L), *m* is the mass of functionalized SBA-15 (g), and *V* is the solution volume (L).

***Equilibrium study***

The major idea behind studying adsorption isotherms is discovering the relationship between the concentration of the target species at equilibrium (*Ce*) and the ratio of the mass of the target species to that of the adsorbent (*qe*; mg/g). The studies in this work involved using the Freundlich, Langmuir, and Temkin isotherm models to evaluate the equilibrium isotherms. The former model is based on the assumption of a heterogeneous surface over which the heat of adsorption is non-uniformly distributed, while the latter assumes that the sorption phenomena occur at homogeneous sites.

The linearized description for the Langmuir is [42]:

$$C_e / q_e = 1 / b q_m + C_e / q_m \quad (2)$$

Where *b* is the equilibrium constant (L/mg), and $q_m$ represents the highest adsorption capacity that can be achieved if a monolayer of the target species completely covers the surface.

The linearized form of the Freundlich model, on the other hand, is given by [43]:

$$Log\ q_e = log\ K_f + \frac{1}{nf} log\ C_e \quad (3)$$

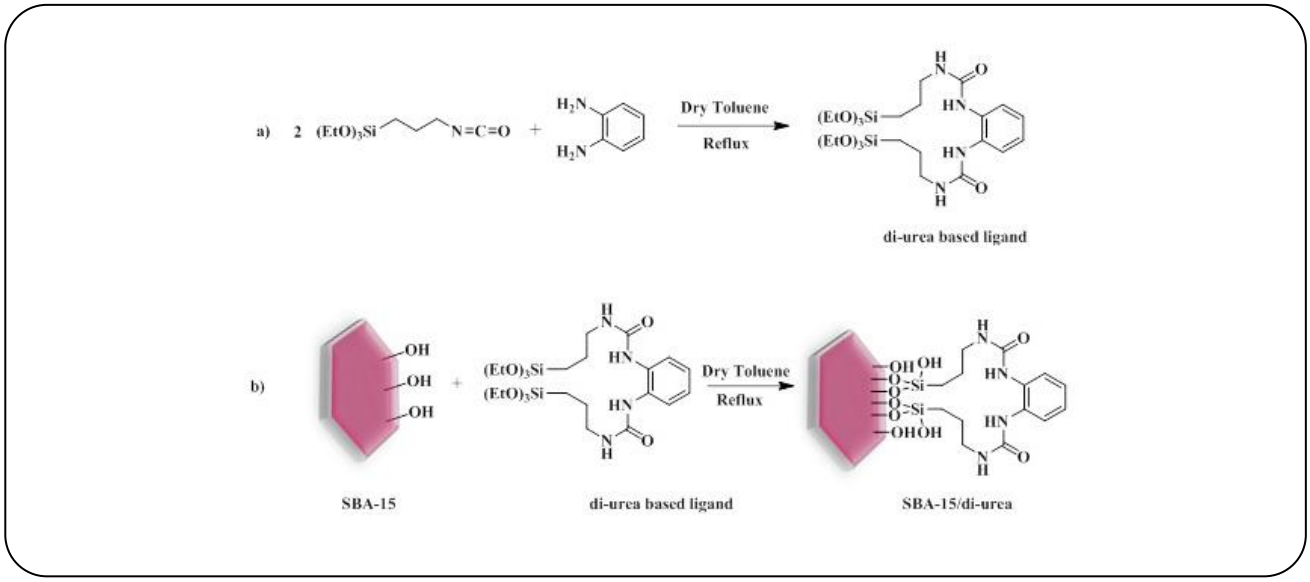
Where $K_f$ is a rough index of the adsorption capacity, and $1/n_f$ expresses the adsorption intensity or surface homogeneity and becomes more heterogeneous as its value gets closer to zero.

An isotherm model commonly used in the case of systems with heterogeneous surface energy (i.e., uniform sorption heat) is the Temkin model [44], which has the following linearized form:

$$q_e = B\ Ln\ k_t + B\ Ln\ C_e \quad (4)$$

in which B = RT/b is a constant which is dependent on the heat of sorption (J/mol); b is the isotherm constant, *R* represents the universal gas constant (8.314 J/mol.K ), *T* is the temperature in Kelvin; and $K_t$ expresses the equilibrium binding constant (L/g) of the Temkin model.

For determination of the best isotherms, some solution with the initial metal ions concentrations between 50 mg/L and 700 mg/L were prepared and the batch experiments were done. The remaining metal ions in solutions were measured by AAS in order to calculate *Ce* and *qe*.




***Scheme 1: Schematic diagram of SBA-15/di-urea fabrications.***

## RESULTS AND DISCUSSION

### *Mesoporous adsorbent*

The SBA-15/di-urea structure was prepared according to Scheme 1. Firstly, orthophenylenediamine (1mmol) and 3-isocyanatopropyltriethoxysilane (2 mmol) were reacted together to produce C-N bond between amine and isocyanate parts in substrates to give 1,1′-(1,2-phenylene) bis (3-(3-(triethoxysilyl)propyl) urea (donated as a di-urea ligand). Afterward, SBA-15 was reacted with the prepared di-urea ligand to gain the SBA-15/ di-urea mesoporous structure.

To investigate the SBA-15/di-urea structure, FT-IR spectroscopy was applied for the SBA-15, SBA-15/di-urea, and free di-urea ligand. As indicated in Fig. 1, the N-H and C=O stretching vibrations referred to di-urea ligand are clear at 3342 and 1741 $cm^{-1}$, respectively. The absence of characteristic absorption bonds for isocyanate group (2300 $cm^{-1}$), as well as the absence of two sharp peaks of $–NH_2$ groups for the *o*-phenylenediamine at 3400 $cm^{-1}$, indicates that 3-isocyanatopropyltriethoxysilane substrate successfully reacted with *o*-phenylenediamine to produce di-urea ligand. In the SBA-15 spectrum, the symmetric and asymmetric stretching vibration of Si–O–Si bonds at 800 and 1085 $cm^{-1}$ as well as a band at 1634 $cm^{-1}$ due to O-H bending vibration are clear [45]. Interestingly, in the SBA-15/di-urea spectrum, all the characteristics of absorption bonds referred to both the di-urea ligand and SBA-15 are preserved indicating successfully grafting of di-urea ligand on the SBA-15 channels in SBA-15/di-urea structure.

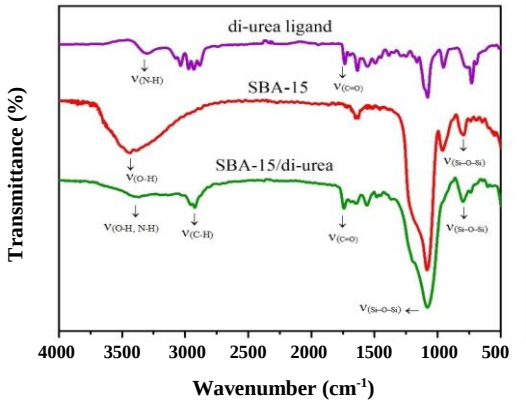



***Fig. 1: FT-IR spectra of SBA-15, SBA-15/di-urea, and free di-urea ligand.***

The $N_2$ adsorption/desorption analysis was carried out for SBA-15 and SBA-15/di-urea samples (Fig. 2). Moreover, the results of surface area ($S_{BET}$), total pore volumes ($V_{total}$), and the pore diameters ($D_{BJH}$) of these samples are demonstrated in Table 1.

As indicated in Fig. 2, both samples demonstrated the type IV in nature with a $H_1$ hysteresis loop, characteristic of mesoporous solids with uniform cylindrical pores according to the IUPAC classification. As clear in the results of Table 1, after the incorporation of di-urea ligand to mesoporous silica SBA-15 pores, the pore size of SBA-15 shifted to a smaller diameter (from 8.1 nm to 6.5 nm)

***Table 1: Textural properties of SBA-15, SBA-15/di-urea***

| Entry | Sample | $S_{BET}$ ($m^2/g$) | $D_{BJH}$ (nm) | $V_{total}$ ($cm^3/g$) |
|---|---|---|---|---|
| 1 | SBA-15 | 824 | 8.1 | 1.45 |
| 2 | SBA-15/di-urea | 518 | 6.5 | 0.81 |

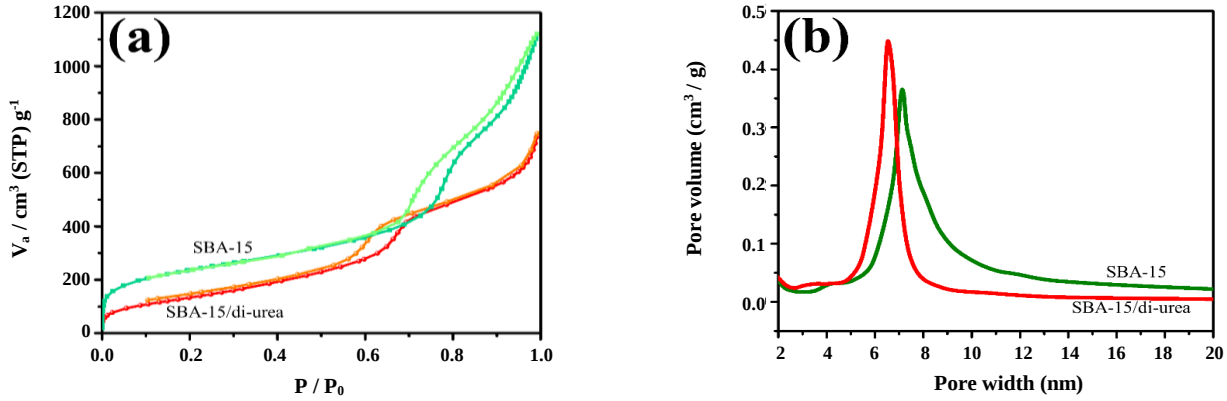



***Fig. 2: $N_2$ adsorption/desorption isotherms and BJH pore size distribution curves of SBA-15 and SBA-di-urea samples.***

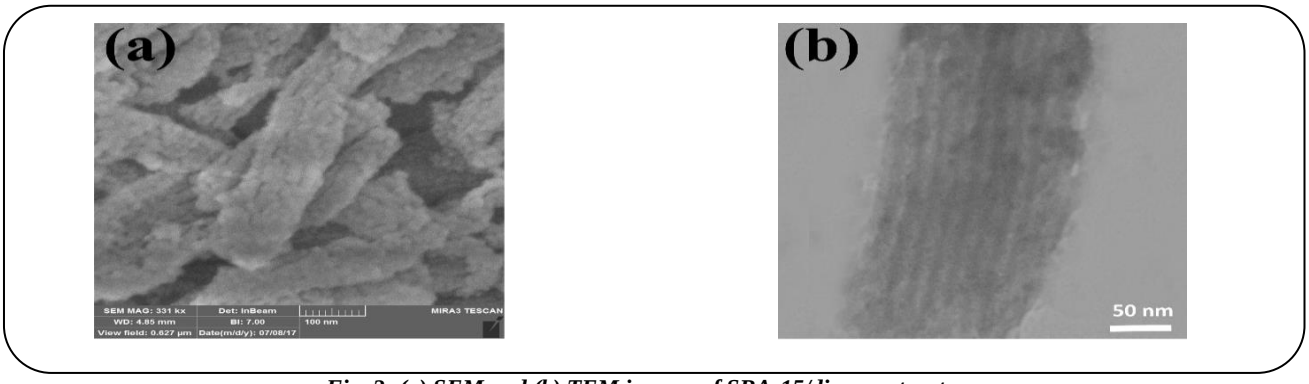



***Fig. 3: (a) SEM and (b) TEM images of SBA-15/di-urea structure.***

and pore volume and surface area reduced considerably. These results clearly confirm that the di-urea functionalization that occurred in the SBA-15 and SBA-15/di-urea structure is produced successfully.

Fig. 3 indicates SEM and TEM images of SBA-15/di-urea samples. As shown in Fig 3a, this structure reveals a rod-shaped morphology that is in accordance with expectations for SBA-15-based structures. Fig 3b demonstrates the TEM image of the SBA-15/di-urea sample. As clear in this image, the structure is organized in ordered arrays of 2D hexagonal mesoporous SBA-15 and the attachment of the di-urea ligand has no distinct influence on the morphology of pore channels.

***The influence of the pH on the $Pb^{2+}$ and $Cu^{2+}$ ions removal***

One of the most important parameters that affect heavy metal adsorption is the pH of the solution. The pH changes of the medium change both metal ions' speciation and the surface charge of the adsorbent [35]. The effect of the pH on the removal of 60 µg $Pb^{2+}$ and $Cu^{2+}$ ions from 20 mL solution was investigated in the pH range 2.0-9.0 (pH adjustment was done using 1 mol/L of either sodium hydroxide or nitric acid solution). Higher pH has not been investigated because of the possibility of damaging the adsorbent structure. Nitrogen donor atoms of SBA-15/di-urea form charged complex with metal ions which are neutralized with its counter ions, so the pH remains constant during the extraction.

The results of extraction are shown in Fig. 4. As can be seen, $Pb^{2+}$ and $Cu^{2+}$ ions can be removed quantitatively (more than 99%) by the adsorbent in the pH ≥ 4.0 and pH ≥ 5.0 respectively. Therefore, simultaneous removal of $Pb^{2+}$ and $Cu^{2+}$ ions can be done at pH greater than 5.0. At higher acidic media, the nitrogen atoms of the SBA-15/di-urea could be protonated so fewer $–NH_2$ sites available on the surface. On the other hand, the electrostatic repulsion between the protonated amino groups of the surface of SBA-15/di-urea and $Pb^{2+}$ and $Cu^{2+}$ ions increases, and the stability of the complex formation between them decrease. The pH profiles indicate that by reducing the pH values, $Pb^{2+}$ and $Cu^{2+}$ ions can be recovered and SBA-15/di-urea regenerated.

***The effect of contact time on removal efficiency***

The effect of contact time on the removal efficiency was investigated in a time interval between 5 and 30 min for a series of solutions containing 60 µg of $Pb^{2+}$ and $Cu^{2+}$ ions. As Figure 5 shows, within the first 5 min, $Pb^{2+}$ ions can be removed more than 99% by the SBA-15/di-urea while for $Cu^{2+}$ ions it took more than 15 minutes. Based on this, 15 min was chosen and used in the rest of the experiments for simultaneous removal of $Pb^{2+}$ and $Cu^{2+}$ ions.

***Optimization of amount of the* SBA-15/di-urea**

Extraction experiments were performed using different quantities of SBA-15/di-urea in the range of 5-20 mg. According to the results (Fig. 6) the adsorption efficiency was initially enhanced by increasing the quantity of the adsorbent and then reached a constant value. Based on the results 15 mg was chosen as the optimal amount of SBA-15/di-urea for the removal of both metal ions.

***Extraction from three-component mixtures***

The tests involved performing the extraction experiments on 20 mL aliquots of $Pb^{2+}$ and $Cu^{2+}$ solutions in water containing 60 µg of the target species and different amounts of various cations. The results (Table 2**)** indicated that in the presence of rather high amounts of the third cation, the $Pb^{2+}$ and $Cu^{2+}$ ions were effectively removed by the SBA-15/di-urea and no serious interference could be observed. The high affinity of adsorbent for $Cu^{2+}$ and $Pb^{2+}$ ions is probably related to complexation reactions of $Cu^{2+}$ and $Pb^{2+}$ as intermediate acids with the ligand's amine groups as intermediate bases. If the third cation

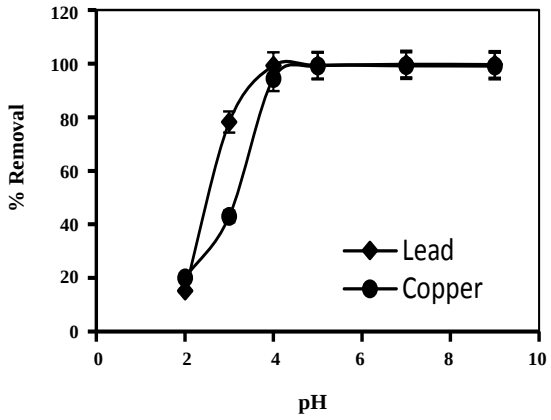



***Fig. 4: The effect of pH on the removal of $Pb^{2+}$ and $Cu^{2+}$ on SBA-15/di-urea.***

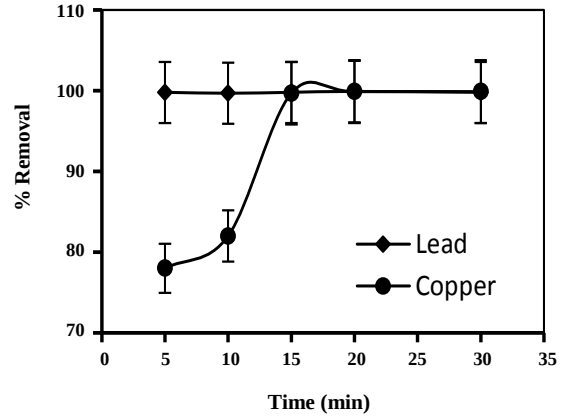



***Fig. 5: The contact time effect on the $Pb^{2+}$ and $Cu^{2+}$ removal by SBA-15/di-urea.***

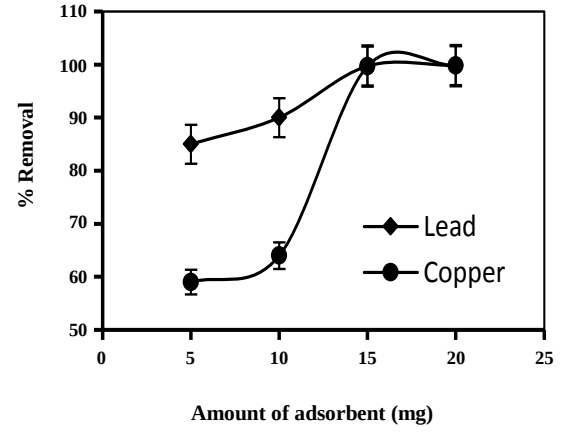



***Fig. 6: The effect of different amounts of adsorption on removal efficiency of $Pb^{2+}$ and $Cu^{2+}$.***

***Table 2: Extraction of $Pb^{2+}$ and $Cu^{2+}$ ions from mixtures [a]***

| Diverse ions | Amount taken (μg) | % Extraction of $Pb^{2+}$ | % Extraction of $Cu^{2+}$ |
|---|---|---|---|
| $Na^{+}$ | 600 | 95.8 (0.8)[b] | 96.5 (0.7) |
| $K^{+}$ | 600 | 97.1 (1.0) | 97.3 (0.8) |
| $Ca^{2+}$ | 600 | 98.0 (0.9) | 96.9 (1.1) |
| $Co^{2+}$ | 400 | 95.0 (0.9) | 96.2 (1.2) |
| $Ni^{2+}$ | 400 | 99.7 (0.8) | 100.0 (1.3) |
| $Ag^{+}$ | 400 | 97.2 (0.7) | 98.6 (0.9) |
| $Cr^{3+}$ | 400 | 99.8 (0.8) | 100.0 (1.0) |
| $Mn^{2+}$ | 600 | 95.0 (1.1) | 96.1 (0.9) |
| $Mg^{2+}$ | 600 | 96.6 (0.9) | 97.4 (0.8) |
| $Cd^{2+}$ | 600 | 95.3 (1.2) | 95.8 (1.4) |
| $Zn^{2+}$ | 400 | 100.0 (0.9) | 99.9 (1.3) |

*a) Initial samples contained 60 μg $Pb^{2+}$ and $Cu^{2+}$ ions in 20 mL water*
*b) Values in parentheses are RSDs based on three replicate analysis*

***Table 3: Values of isotherm constant for sorption of $Pb^{2+}$ and $Cu^{2+}$ ions.***

| Isotherm | Parameters | $Pb^{2+}$ | $Cu^{2+}$ |
|---|---|---|---|
| Langmuir | $q_m$(mg/g) | 147.0 | 77.5 |
| | b(L/mg) | 0.003 | 0.02 |
| | $R^2$ | 0.9884 | 0.9856 |
| Freundlich | 1/n | 0.695 | 0.450 |
| | $K_f$(mg/g) | 1.542 | 3.275 |
| | $R^2$ | 0.7832 | 0.9837 |
| Temkin | B | 26.631 | 9.337 |
| | $K_t$(L/g) | 0.047 | 0.496 |
| | $R^2$ | 0.8613 | 0.7301 |

concentration in solution is more than the reported concentration (Amount taken), it can compete with $Cu^{2+}$ and $Pb^{2+}$ ions and decreases the extraction efficiency of $Cu^{2+}$ and $Pb^{2+}$ ions.

### *Adsorption isotherms*

The relationship between an adsorbent and adsorbate is described by the equilibrium adsorption isotherm [2]. The constants presented in Table 3, which were determined through the linear regression analysis, indicate the Langmuir isotherm model, with a higher $R^2$ led to a better fit. The respective $R^2$ values for the model were around 0.9884 and 0.9856 for $Pb^{+2}$ and $Cu^{+2}$. It can be said that a monolayer of $Pb^{2+}$ and $Cu^{2+}$ ions are adsorbed on the sorbent surface. According to the analyses with the Langmuir model, the maximum adsorption capacity values for $Pb^{+2}$ and $Cu^{+2}$ were calculated to be 147.0 ± 0.6 and 77.0 ± 0.5 mg ion/g of SBA-15/di-urea.

### *Desorption and reuse study*

The regeneration property of SBA-15/di-urea is one of the important indexes to evaluate its practicability and economic benefit. Hence some experiments were done in order to choose a proper volume of nitric acids 3.0 mol/L for the recovery of $Pb^{2+}$ and $Cu^{2+}$ ions after extraction of 60 μg $Pb^{2+}$ and $Cu^{2+}$ in 20 mL solution by the SBA-15/di-urea.

***Table 4: Effect of stripping acid volume on the recovery of ions.***

| Eluent | Recovery% | |
|---|---|---|
| | $Pb^{2+}$ | $Cu^{2+}$ |
| $HNO_3$(10 mL) | 90 | 80 |
| $HNO_3$(15 mL) | 100 | 86 |
| $HNO_3$(20 mL) | 100 | 100 |
| $HNO_3$(25 mL) | 98 | 99 |

***Table 5: Removal of $Pb^{2+}$ and $Cu^{2+}$ ions from wastewater.***

| Samples | $Pb^{2+}$ | | | $Cu^{2+}$ | | |
|---|---|---|---|---|---|---|
| | $C_o$[a] (mg/L) | $C_e$[b] (mg/L) | %Removal | $C_o$ (mg/L) | $C_e$ (mg/L) | %Removal |
| wastewater sample | 110 (1.4)[c] | 7.5 (0.8) | 93.0 (1.5) | 6 3 (0.7) | 8.1 (1.1)[a] | 87.0 (1.9) |

*a,b) $C_o$ and $C_e$ represent the initial and equilibrium ions concentrations*
*c) Values in parentheses are RSDs based on three replicate analyses.*

As can be seen in Table 4 among different volumes used, 20 mL of 3.0 mol/L nitric acid solutions can recover whole of $Pb^{2+}$ and $Cu^{2+}$ ions from the SBA-15/di-urea, while fewer acid volumes used were unsuitable for the complete elution of these ions.

After that, the adsorbent was used in some cycles of the adsorption/desorption process. Results showed that after three adsorption-desorption recycling experiments, the removal efficiency of $Pb^{2+}$ and $Cu^{2+}$ still exhibited an acceptable removal efficiency (97.0 % removal efficiency for $Pb^{2+}$, 94.0 % removal efficiency for $Cu^{2+}$). Therefore, the SBA-15/di-urea can be considered an economic nano sorbent in wastewater treatments.

### *Removing of $Pb^{2+}$ and $Cu^{2+}$ ions from industrial wastewater*

The applicability of the developed adsorbent was evaluated using an electroplating wastewater sample. At first, this sample was filtered using a 0.45-mm pore size membrane filter to remove suspended particulate matter.

One aliquot (50 mL) of the wastewater was diluted to 500 mL. Then, 50 mg of SBA-15/di-urea was added to 40 mL wastewater after adjusting the pH to 6. The mixed solution was shacked for 15 min. Because of the matrix effect, the tests were performed through the standard addition method, and the initial and final concentrations of the target species (before and after removal with the recommended procedure) were determined. For this aim, four 100 mL volumetric flasks were each filled with 10 mL of wastewater sample. Then, the different amounts of the standard (0, 1, 2, and 3 mL of 100 mg/L) were added and the solutions in the flasks were diluted to the mark and mixed well. The amounts of ions in the solution were determined by the flame atomic absorption spectrometry method and the absorption versus standard concentration was plotted. A simple Linear Least Squares analysis was conducted using the slope and intercept functions of Microsoft Excel. To find the original concentration of the unknown, the value of X at y=0 from y= mX+b was calculated. As shown in Table 5, the proposed method is suitable for the removal of $Pb^{2+}$ and $Cu^{2+}$ ions in a wastewater sample.

### *Comparison of the previously reported similar methods of $Pb^{2+}$ and $Cu^{2+}$ retention with the proposed method*

The contact time, the maximum capacity, and working pH range of the SBA-15/di-urea and some other previously reported modified adsorbents for the $Pb^{2+}$ and/or $Cu^{2+}$ retention are compared in Table 6.

The results clearly reveal that the maximum capacity of SBA-15/di-urea for $Pb^{2+}$ and $Cu^{2+}$ ions exceeds or is approximately closed to those of most previously reported functionalized SBA-15 adsorbents [21, 22, 46]. It is noteworthy that the adsorbent has fewer adsorption capacities [2, 17] and a narrower working pH range [2, 21] in comparison with some previous reports, but it excels in terms of contact time.

## CONCLUSIONS

$Pb^{2+}$ and $Cu^{2+}$ cause serious environmental and public health problems in cases of excessive discharge. Thus, this study has demonstrated the application of SBA-15/di-urea

***Table 6: Comparison of the proposed method with the previously reported.***

| Adsorbent | Maximum capacity (mg/g) | Contact Time (min) | Working pH range | Removed ions | Ref. |
|---|---|---|---|---|---|
| Amino-functionalized SBA-15/calcium | 1029.58 | 100 | pH> 2.3 | $Pb^{+2}$ | [2] |
| Modified nano-chitosan coating nano-iron oxide | 559.44<br>298.67 | 10-30 | pH=6 and 7 | $Pb^{+2}$<br>$Cu^{+2}$ | [17] |
| Diethylenetriamine functionalized SBA-15 | 183.0<br>156.0 | 15 | pH≥ 3 | $Pb^{+2}$<br>$Cu^{+2}$ | [21] |
| Guanidine functionalized SBA-15 | 89.1<br>57.2 | 10 | pH≥ 5 | $Pb^{+2}$<br>$Cu^{+2}$ | [22] |
| SBA-15/Diphenyl Carbazon/ SDS | 100 | 15 | pH=8 | $Cu^{+2}$ | [46] |
| SBA-15/di-urea | 147.0<br>77.0 | 15 | pH≥ 5 | $Pb^{+2}$<br>$Cu^{+2}$ | (This work) |

for effective removal of $Pb^{2+}$ and $Cu^{2+}$ ions as a reusable and economical adsorbent. The adsorption of ions to SBA-15/di-urea was fast and agreed well to the Langmuir adsorption model with maximum adsorption capacities of 147 and 77 mg $Pb^{2+}$ and $Cu^{2+}$/g respectively. The results reveal that metals can be recovered and the SBA-15/di-urea regenerated for reuse by reducing the pH values. This recovery was done with 20 mL nitric acid 3 mol/L. Hence, this methodology can be suitable for the large-scale removal of pollutants from water and wastewater.

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