

# Using Silica Nanocomposite Modified with Amino Groups for Effective Wastewater Treatment

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## Abstract

Nanosilica modified with aminogroup is created for Cu (II) and Pb(II) adsorption. The microspheres were characterized by scanning electron microscope (SEM) and Fourier transform infrared spectroscopy (FTIR). Batch adsorption tests indicated that NH<sub>2</sub>-Si exhibited higher adsorption affinity toward Cu (II) and Pb(II). The Langmuir model could fit the adsorption isotherm very well with maximum adsorption capacity of 163.16 and 147.79 mg/g, respectively, implying that adsorption processes involved monolayer adsorption. Pb(II) and Cu(II) adsorption could be well described by the pseudo second-order kinetics model, and was found to be strongly dependent on pH. The Pb(II)- and Cu(II)-loaded microspheres were effectively desorbed using 0.01 mol/L HCl. NH<sub>2</sub>-Si have promise for use as adsorbents in the removal of Pb(II) and Cu(II) in wastewater treatment processes. Any how this study indicated that modified silica nanoparticles can be used in different conditions as an effective, usable and inexpensive adsorbent for the heavy metals removal in aqueous solutions which values are higher than the standard level

**Keywords:** heavy metals; adsorption; treatment; silica-functionalization

## Introduction

To Water contamination caused by heavy-metal ions generated from alloys, pigments, electroplating, mining, metallurgical activities, nuclear power plant operations, aerospace industries, electrical contacts, printing, and the manufacture of paper, rubber, plastics, and batteries is a global problem receiving worldwide attention. The extended persistence of water contamination in biological systems and the tendency to bioaccumulate while moving up the food chain is a serious threat to human health, living resources, and ecological systems [1]. The increased use of heavy substances metals in industry has resulted in increased availability of metallic in natural water sources [2]. The toxicity of such metal ions arise due to their non- biodegradable nature thereby accumulating in the living cells and impairing the normal functions of various organs of living beings. Technologies like chemical precipitation, electrochemical separation, membrane separation, reverse osmosis, ion exchange and adsorption resins though effective for metal remediation, yet are not competitive in industrial application [3-16].

For the heavy metals removal process are used various conventional methods such as redox reactions, solvent extraction, chemical precipitation and filtration, reverse osmosis, electrochemical treatment methods, ion exchange and lime coagulation which are characterized by low removal yields and high cost of operation. In the past years the adsorption process using nanomaterials was studied as an alternative solution, materials such as magnetic oxides, polymers, ceramic, silica and derivatives of carbon have been developed for wastewater treatment [17]. Adsorption treatments have been extensively developed to remove heavy metals in aqueous environments due to their simplicity and high efficiency. Nanoparticles have shown remarkable potential as adsorbents because these materials have large surface areas for the adsorption of heavy metals [18-20]. Modified nanosilica particles is an ideal support for functional groups because it is an inorganic material, stable under acidic conditions and non-swelling, and has high mass exchange characteristics and very high thermal resistance [21]. The chemical modification of nanosilica has shown great promise in improving the efficiency of adsorption due to the increase of functional groups [22].

## Experimental

All chemicals were utilized without further purification.

For all experiments, Milli-Q water was utilized. Cetyltrimethylammonium bromide (CTAB) and tetraethyl orthosilicate (TEOS) were from Sigma-Aldrich.

### Synthesis of mesoporous silica nanospheres

The synthesis of mesoporous silica products was achieved by the ammonia-catalyzed hydrolysis of TEOS in a mixed solvent of water, diethyl ether and acetone using CTAB as a template at room temperature as described before [23]. Typically, 0.5 g of CTAB was dissolved in 100 ml of Milli-Q water and stirred for 30 min, followed by adding 40 g of acetone and stirred for 30 min, then, we added 20 g diethyl ether. After vigorous stirring for 30 min, 2.5 gm of TEOS was added and stirred for more 30 min, followed by adding 1.5 g NH<sub>3</sub> (25 wt.%). The resulting gel was vigorously stirred in a closed vessel at room temperature for 24 h. The particles were collected by filtration, cleaned with deionized water and dried at 80 °C for 24 h. Then they were calcined from room temperature to 550 °C for 4 h. followed by heating at 550 °C for 8 h more.

### Preparation of NH<sub>2</sub>-MS

silica microspheres were dispersed in a mixture of ethanol/DI water, followed by addition of ammonium hydroxide. 3-Aminopropyltrimethoxysilane was added under mild stirring and ultrasonication. After 24 hr reaction and being washed with ethanol and DI water three times each, NH<sub>2</sub>- MS were obtained.

## Instruments

Small angle X-ray diffraction (SAXRD) patterns were obtained by using XPERT – PRO – PANalytical with monochromated CuK $\alpha$  ( $\lambda = 1.54060 \text{ \AA}$ ), wide angle X-ray diffraction (WAXRD) patterns were measured by using Bruker D8 Discover diffractometer with monochromated CuK $\alpha$  ( $\lambda = 1.54178 \text{ \AA}$ ) at 40 kV, and 45 mA. The adsorption/desorption isotherms were collected using Quantachrom Autosorb system at 77 K. Prior to analysis, the samples were outgassed at 80 °C for 24 h. The BET surface areas pore volume and pore size distribution were calculated from N<sub>2</sub> adsorption data. The pore size distributions were obtained using the adsorption branch of the nitrogen isotherms by applying the Barrett–Joyner–Halenda (BJH) method. Field emission scanning electron microscopy (FESEM) images were obtained with a Zeiss Leo Supra55 microscope. The samples for FESEM observations were observed without any metal coating. A high-resolution transmission electron microscope (HR-TEM, Tecnai G20,

FEI, and Netherland) was used for imaging, crystal structure revelation, and elemental analysis.

## Result and Discussion

### The morphology and structure of mesoporous silica nanospheres (MSNs)

Mesoporous silica nanospheres were prepared in a basic solution at room temperature utilizing acetone, ethyl ether, and water as cosolvents and cetyltrimethylammonium bromide (CTAB) as a surfactant. The small angle X-ray diffraction (SAXRD) patterns of the calcined MSNs (Fig. 1A) demonstrate a strong diffraction with a  $2\theta$  value of  $2.2^\circ$ . As a result, this sample was MCM-41 analogs, however, with a worm-like structure [24]. The absence of the peak at  $2\theta = 4.0\text{--}5.0^\circ$  in MSNs showed that the mesopores were less ordered. This was confirmed visually by the TEM pictures showed in Fig. 4. Wide edge X-ray diffraction (WAXRD) demonstrate a strong diffraction peak in the range of  $17$  to  $30^\circ 2\theta$  (Fig. 1B), which revealed normal occasional varieties of the electronic density because of the long-range ordering of the pores in the material [25].

As indicated by nitrogen adsorption–desorption analysis, mesoporous silica nanospheres showed type IV, with a precarious adsorption step at relative pressure of  $p/p_0 = 0.35$  and a wide hysteresis loop at  $p/p_0 = 0.5\text{--}1.0$  (Figure 2A), comparing to a bimodal pore structure (Figure 2B). The little pores with diameter of 3 nm are identical in the typical mesoporous silica templated by CTAB and, in this manner, doled out to the main channel of the composite, while, a large distribution of mesopores with diameters around 25 nm likewise appeared for the mesoporous silica nanosphere, inferring the dissolution of

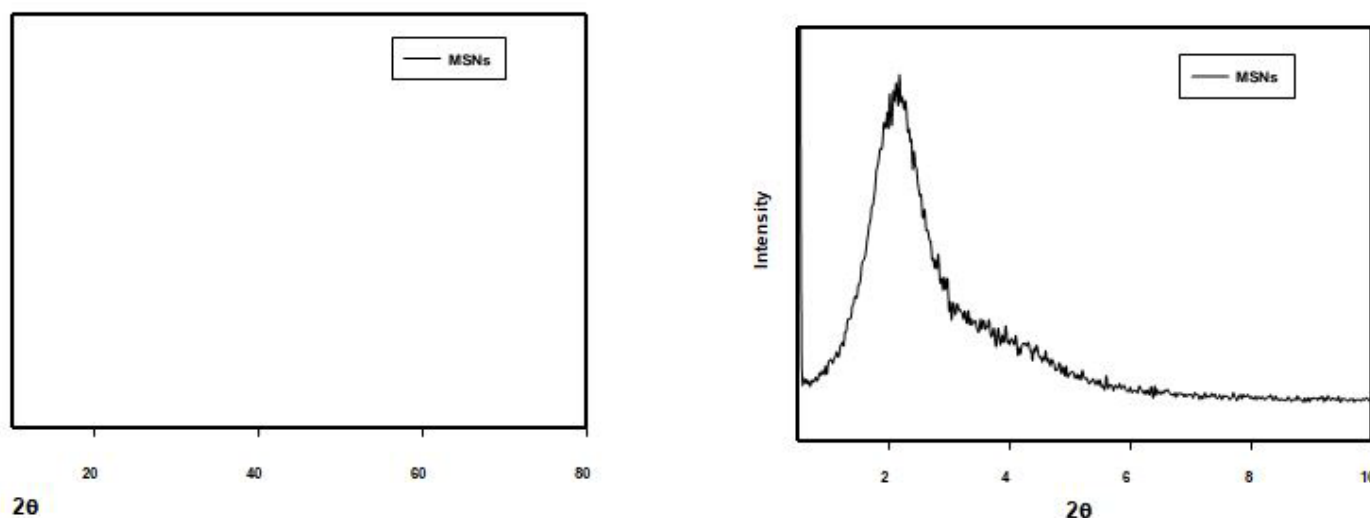
unnecessary ethyl ether into the micelle of CTAB to expand the pore of resulting sample, and lead to the decline of mesostructure simultaneously [24].

The  $N_2$  isotherms portrayed in Fig. 2A, ( $N_2$  uptake) demonstrating the surface area of MSNs. The obvious Brunauer–Emmett–Teller (BET) surface area value of the parent MSNs ( $873.55\text{ m}^2\text{g}^{-1}$ ). The pore volume of the MSNs ( $1.135\text{ cm}^3/\text{g}$ ). The pore size distribution of the MSNs demonstrates a novel peak focused at around 3.83 nm diameters (Figure 2B).

FESEM of the MSNs (A) and MSNs-NH<sub>2</sub>(B) samples is shown in Figure 3: Based on the FESEM observations, the material occurs as nanospheres. The TEM images representative nanospheres of 700 nm in size (Figure 4), and large slitlike mesopores with the length of 20–50 nm are homogeneously distributed on the nanosphere surface. The contrast and distribution of dark and pale parts around the edge of nanosphere also indicate the existence of large radially oriented mesopores (Figure 4).

The SEM images representative nanospheres of MSNs and NH<sub>2</sub>-MSNs show the particles of MSNs was stick together as shown in Figure 5(A). On the other hand, the SEM image of NH<sub>2</sub>-MSNs particles embedded was depicted in Figure 5(B) the distribution of highly porous characteristic of NH<sub>2</sub>-MSNs particles on the surface is clearly shown. Thus surface pores increased the effective surface area of the nanocomposite as compared to the MSNs

The functional groups present in silica and NH<sub>2</sub>-silica hybrid materials were monitored by FT-IR spectroscopy. In Fig. 6 (B) shows that The Si-O bond exhibits peaks at  $485\text{ cm}^{-1}$  and  $3693\text{ cm}^{-1}$  is the NH stretching vibration peak of the amines. The



**Figure 1:** (A) Small-angle X-ray diffraction (SAXRD) patterns and (B) wide-angle XRD (WAXRD) patterns of the calcined MSNs.

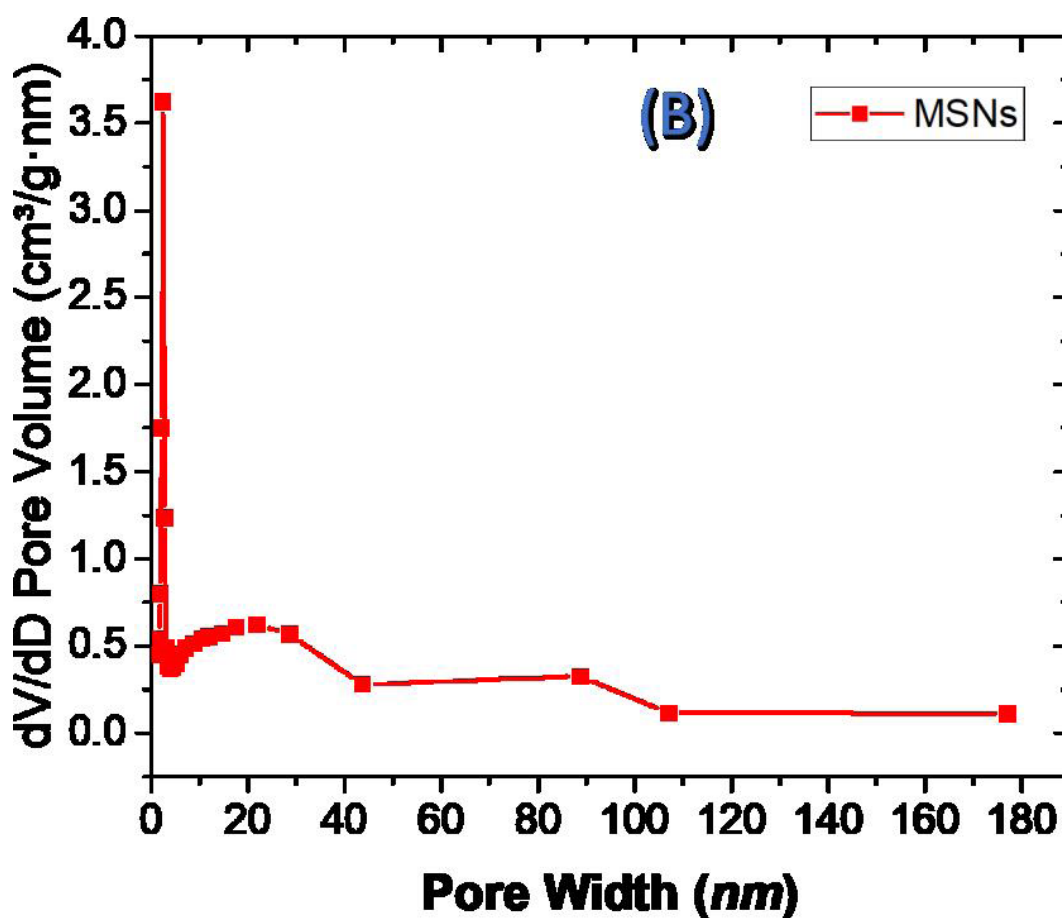
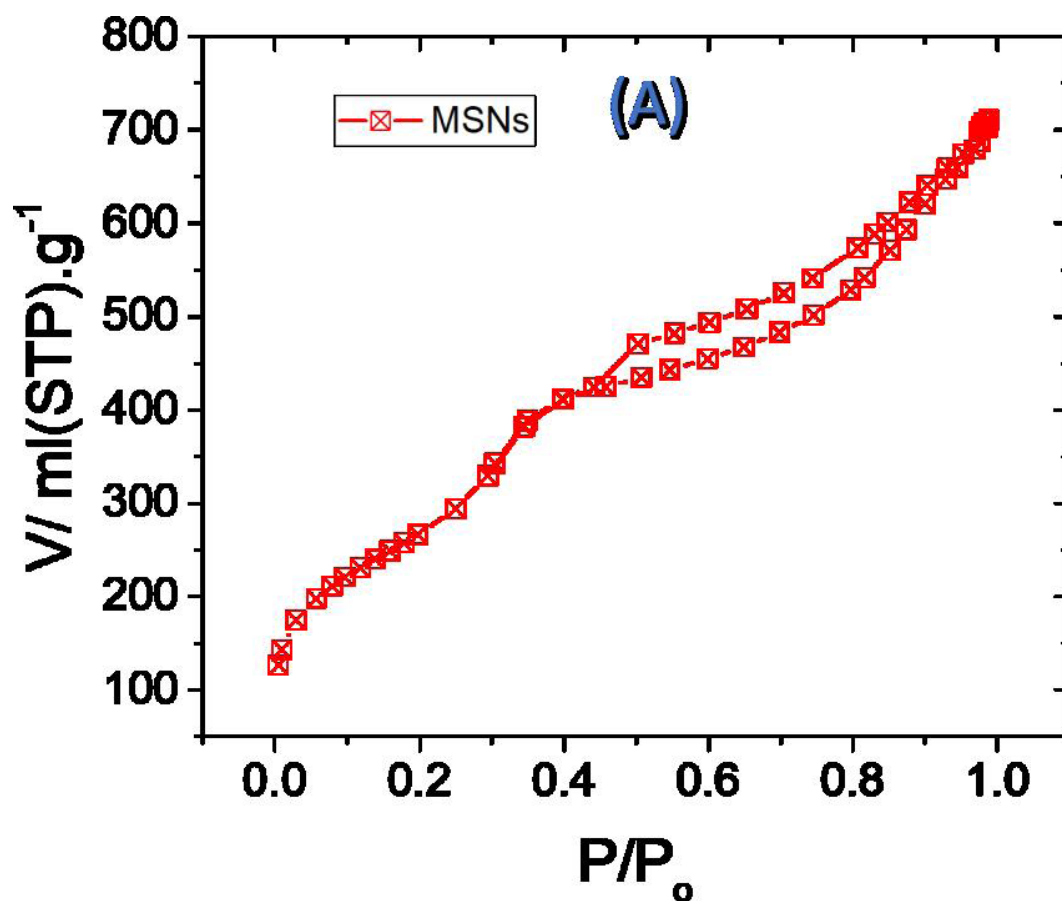


Figure 2: Nitrogen adsorption isotherms (A) and pore size distribution (B) of MSNs and the TMK sensor.

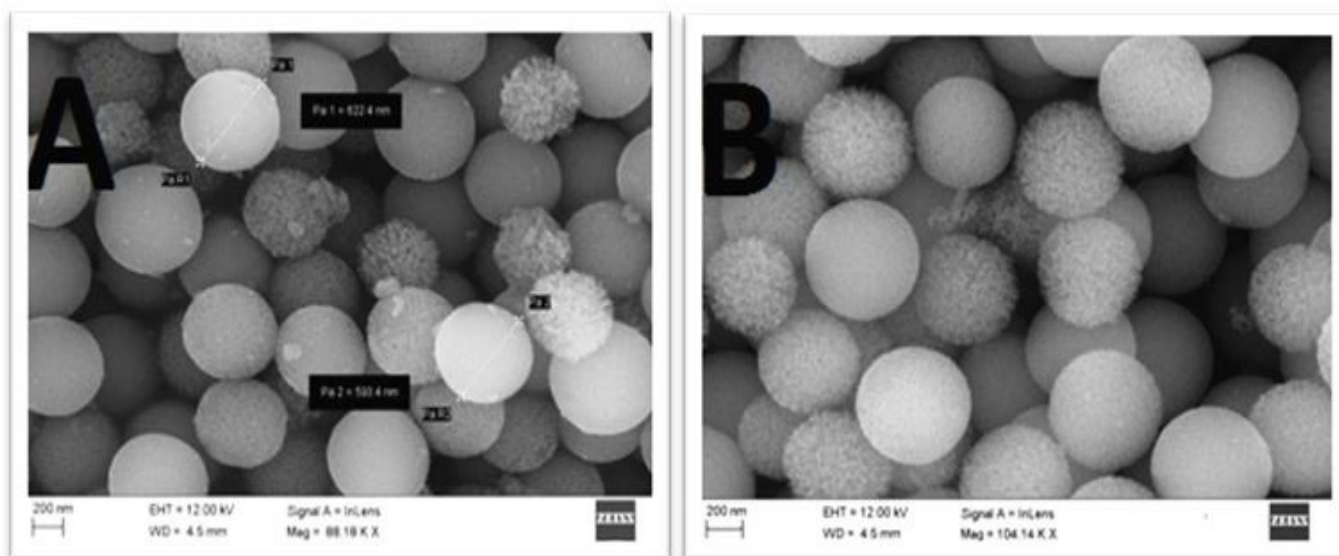


Figure 3: FESEM images of the MSNs(A) and MSNs-NH<sub>2</sub>(B)

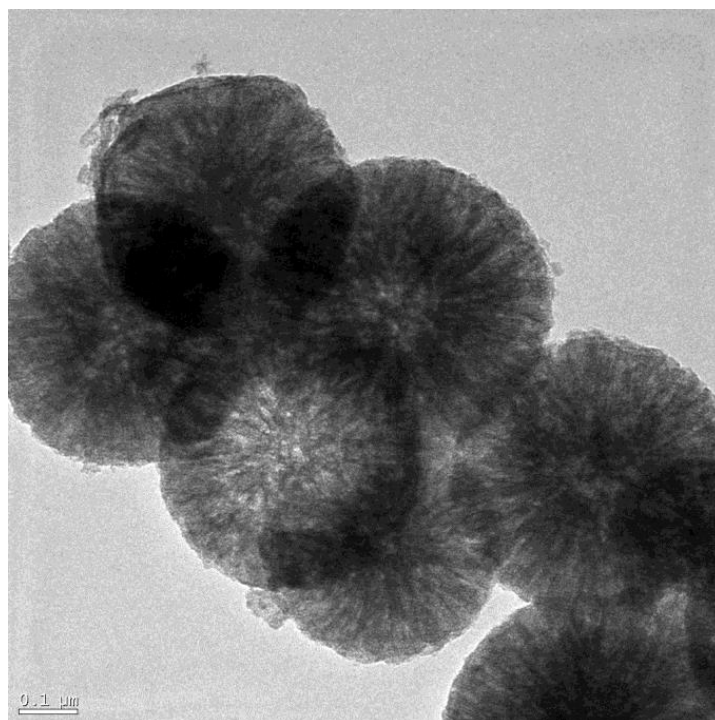


Figure 4: Representative TEM images of the MSNs

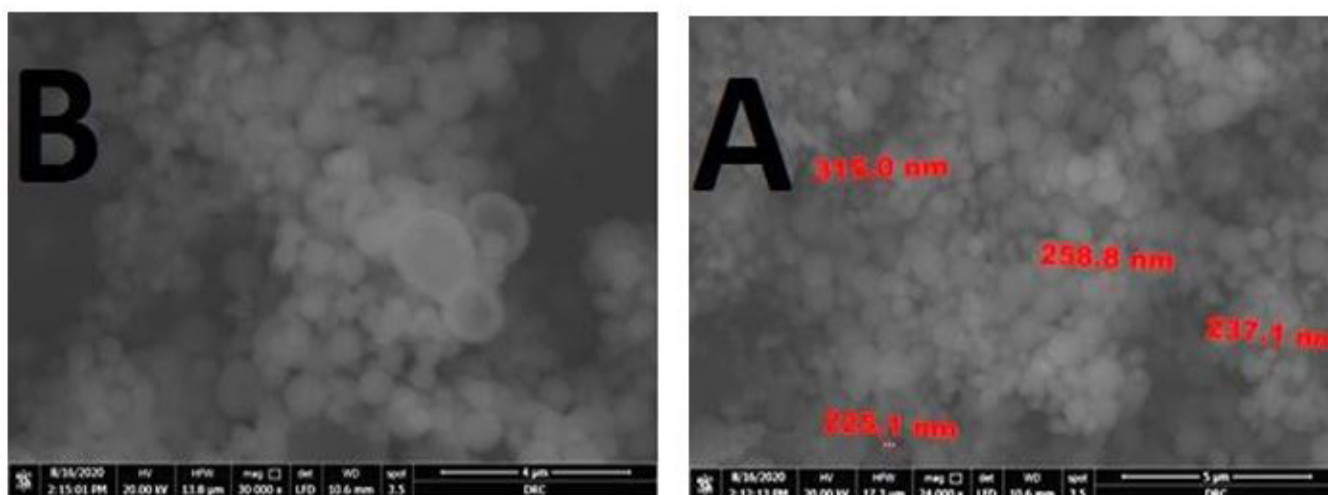


Figure 5: Scanning electron microscope images of MSNs (A) and NH<sub>2</sub>/MSNs (B)



stretching vibration peaks of Si-O-Si appear at  $1062\text{ cm}^{-1}$  and  $1347\text{ cm}^{-1}$ , and the asymmetry vibration peaks appear at  $797\text{ cm}^{-1}$ ; Si-OH has a symmetrical stretching vibration peak at  $895\text{ cm}^{-1}$  the absorption band at  $1635\text{ cm}^{-1}$  was attributed to the N-H bending vibrations. The absorbance peaks corresponding to the C-H stretching and bending vibrations appear in  $2205$  and  $2104\text{ cm}^{-1}$ ; these peaks became intense in all material containing amine. attributed to the vibrations N-H of  $-\text{NH}_3^+$ . The presence of N-H bending vibration around  $797\text{ cm}^{-1}$  and the symmetric  $-\text{NH}_2$  bending vibration confirm the incorporation of amino groups. The Si-OH vibration band decrease around  $895\text{ cm}^{-1}$

### Effect of pH

The pH of a solution strongly affects the adsorption capacity of the modified silica. So the effect of solution pH on metal ions removal after soaking of 24 hr. was studied at pH ranges of 2 - 5, by adjusting the solution pH using 0.1N HCl or 0.1N NaOH. It is important to mention that, modified silica is not stable at strong acidic medium, so its adsorption behavior was studied at pH ranges from 2-5.

Figure 7 shows the effect of pH on the individual adsorption of Cu (II) and Pb (II) by modified silica. The adsorption increases with increasing the pH value up to 5 where the maximum adsorption were obtained.

The low adsorption of metal ions in strong acidic pH solution (at low pH) could be mainly due to the electrostatic repulsion

between the positive metal ions ( $\text{M}^+$ ) in the medium and the positive charges in highly acidic solution ( $\text{H}^+$ ) which accumulate on the surface of modified silica. In the other words, the amino groups in modified silica is easily form protonation, reducing the number of binding sites available for the adsorption of heavy metal ions. This leads to the inducing an electrostatic repulsion of the different heavy metal ions. Therefore, the competition existed between protons and the metal ions ( $\text{M}^+$ ) for adsorption sites and adsorption capacity was decreased. Such repulsion prevents the approach of the metal ions to modified silica surface.

While at higher pH value, the adsorption of heavy metal ions increases due to the weaker electrostatic repulsion, and with the increase of pH value, the amino groups are free from protonation. Such positive charge density decreases allowing the metal ions to approach the different sorbent beads surface which result in higher adsorption values. The adsorption mechanism may be partially replaced by a chelation mechanism on the amino groups of modified silica. Further increase in the pH value more than 5 would transform the dissolved metal into precipitated hydroxide form thus the adsorption capacity is decreased. This is well agreement with the previous works [26]

### Effects of contact time

The effects of contact time on the removal of Cu(II) and Pb(II) by modified silica are depicted in Fig. 8. Initially the metal uptake was fast due to the many vacant adsorption sites, all the active sites were occupied by target Cu(II) or Pb(II) within 2hrs after

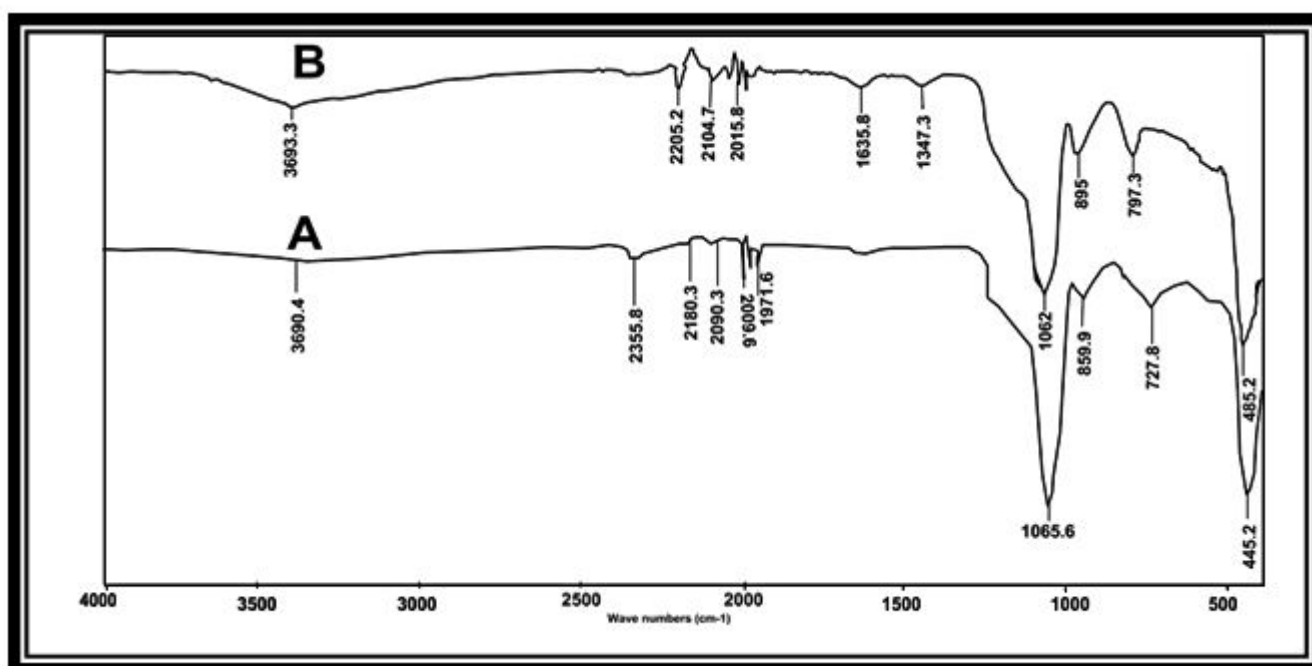


Figure 6: IR shows of the samples (A)Si and (B) NH<sub>2</sub>-MS

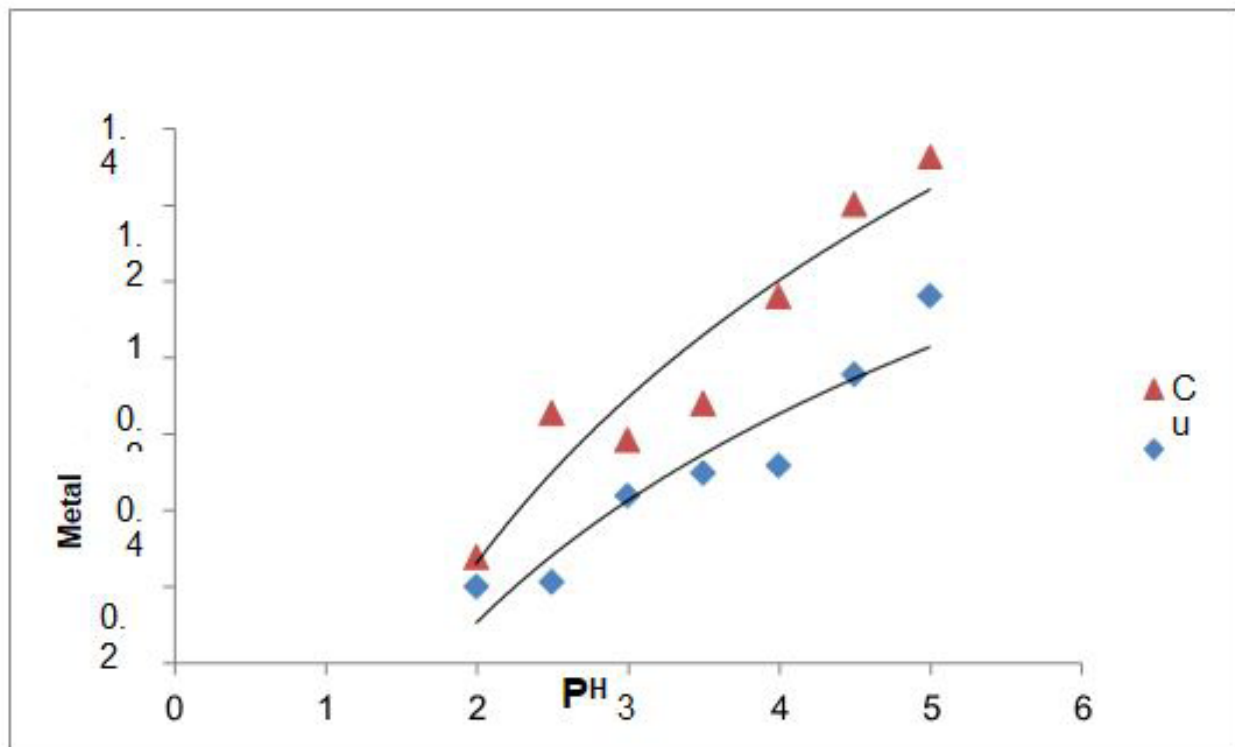


Figure 7: pH-dependent metal uptake of metal ion

which the adsorption rate gradually decreased and became constant at equilibrium to attain equilibrium conditions where the concentration of adsorbate in the bulk solution was in dynamic balance with that at the interface.

It is possible that some of the adsorption sites of modified silica

were easily obtained due to increases of the functional groups on its surface. This was also seen from the higher kinetics of copper adsorption by modified silica compared to lead ions. Due to the small increase of the adsorption capacity after 2hrs of mixing, contact time of 24 h was selected for all the equilibrium tests.

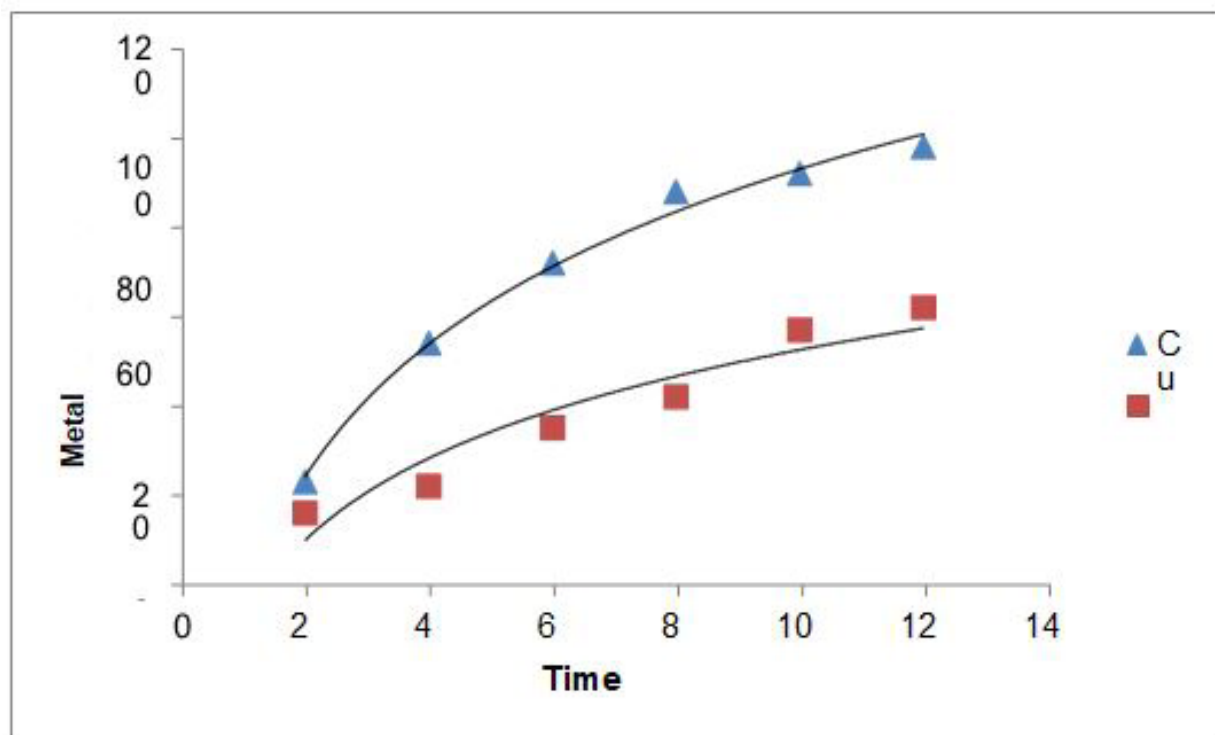


Figure 8: Metal uptake of metal ion with time

### Adsorption kinetics

Modeling of adsorption kinetics was conducted by using the pseudo-first-order and pseudo-second-order models. These originally empirical models have been used extensively to describe the sorption kinetics.

The pseudo-first-order model is expressed as  $\log(q_e - q_t) = \log q_e - t$  (1)

The dependence from Cu (II) and Pb(II) adsorption on NH<sub>2</sub>-MS

against contact time is shown in Figure 9.

The pseudo second-order model has usually been adopted to describe mass transfer processes.

where,  $q_e$  (mg/g) is the adsorption amount at equilibrium,  $q_t$  (mg/g) is the adsorption amount at time  $t$ ,  $k_1$  (min<sup>-1</sup>) and  $k_2$  (gmg<sup>-1</sup> min<sup>-1</sup>) are the pseudo-first-order and pseudo-second-order rate constants. Simulation results were obtained from Cu (II) and Pb(II) adsorption based on the pseudo second-order kinetics model. As shown in Figure 10

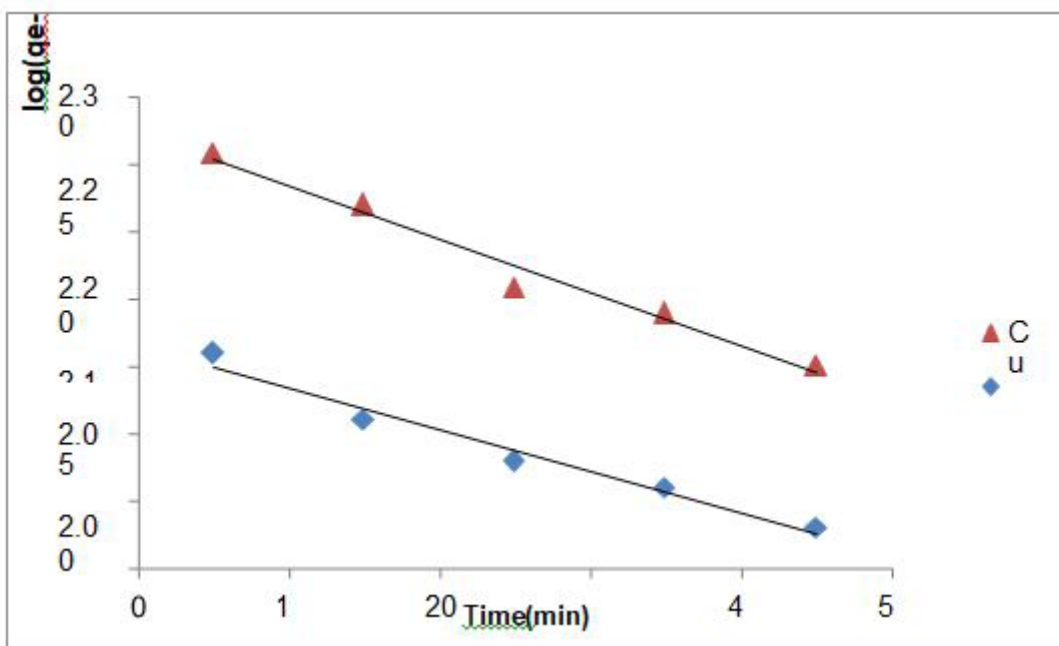


Figure 9: Plots of  $\log(q_e - q_t)$  against time for the exchange of Cu (II) and Pb(II) ions on NH<sub>2</sub>-MS

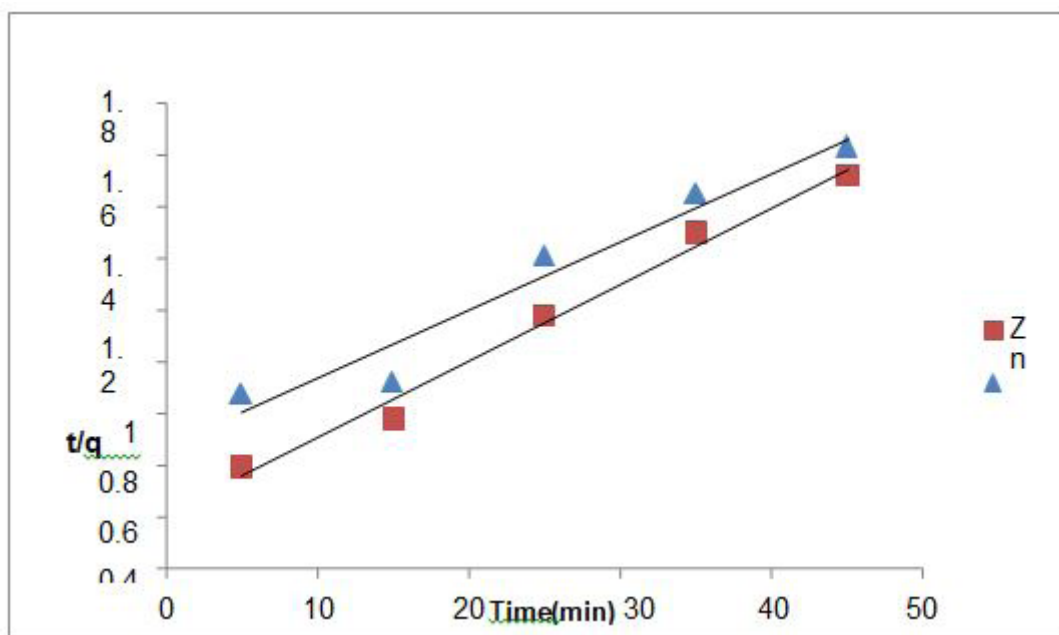


Figure 10: Pseudo second order model for the exchange of Cu (II) and Pb(II) ions on NH<sub>2</sub>-MS



pseudo second-order kinetics present a linear relation with  $R^2$  higher than 0.98. Moreover, Cu(II) and Pb(II) adsorption amounts obtained from data (39.50 and 31 mg/g). while pseudo first- order kinetics present a linear relation with  $R^2$  not more 0.95. Thus, Cu (II) and Pb(II) adsorption processes on NH<sub>2</sub>-MS obeyed pseudo second-order kinetics. The adsorption rate constants of Cu (II) and Pb(II) calculated based on the pseudo second order kinetics were  $0.72 \times 10^{-2}$  and  $0.61 \times 10^{-2}$  g/(mg·min). There were two steps for the heavy metal adsorption by NH<sub>2</sub>-MS. First, a large amount of heavy metals was rapidly adsorbed by the exterior surface and amino groups of NH<sub>2</sub>-MS. When the adsorption of exterior surface reached saturation, heavy metals entered into the pores and were absorbed by the interior surface of NH<sub>2</sub>-MS. The fitted results are presented in Table 1.

### Adsorption isotherms

The adsorption isotherm is important for determining the adsorption behavior of an adsorbent. The Cu (II) and Pb(II) adsorption isotherms of the NH<sub>2</sub>-MS were compared at pH 5. The maximum Cu (II) and Pb(II) adsorption amounts on NH<sub>2</sub>-MS within the tested concentration range were substantially enhanced by functionalization, as shown in Figure 11,12 which was achieved through the complexation of metal ions by amino groups [27].

The equilibrium data were fitted by the Langmuir (Eq. (3)) and Freundlich (Eq. (4))

$$\text{models: } \log q_e = \log k_f + (1/n) \log C \quad (4)$$

pseudo first-order				pseudo second-order		
Metal Ions	$q_e$	$K_1 \times 10^{-2}$	$R^2$	$q_e$	$K_2 \times 10^{-2}$	$R^2$
Cu <sup>2+</sup>	179	0.92	0.94	39.5	0.72	0.983
Pb <sup>2+</sup>	172.5	0.72	0.95	31	0.61	0.985

Table 1: Pseudo - First and second order parameters for the adsorption of Cu(II) and Pb(II) on NH<sub>2</sub>-MS.

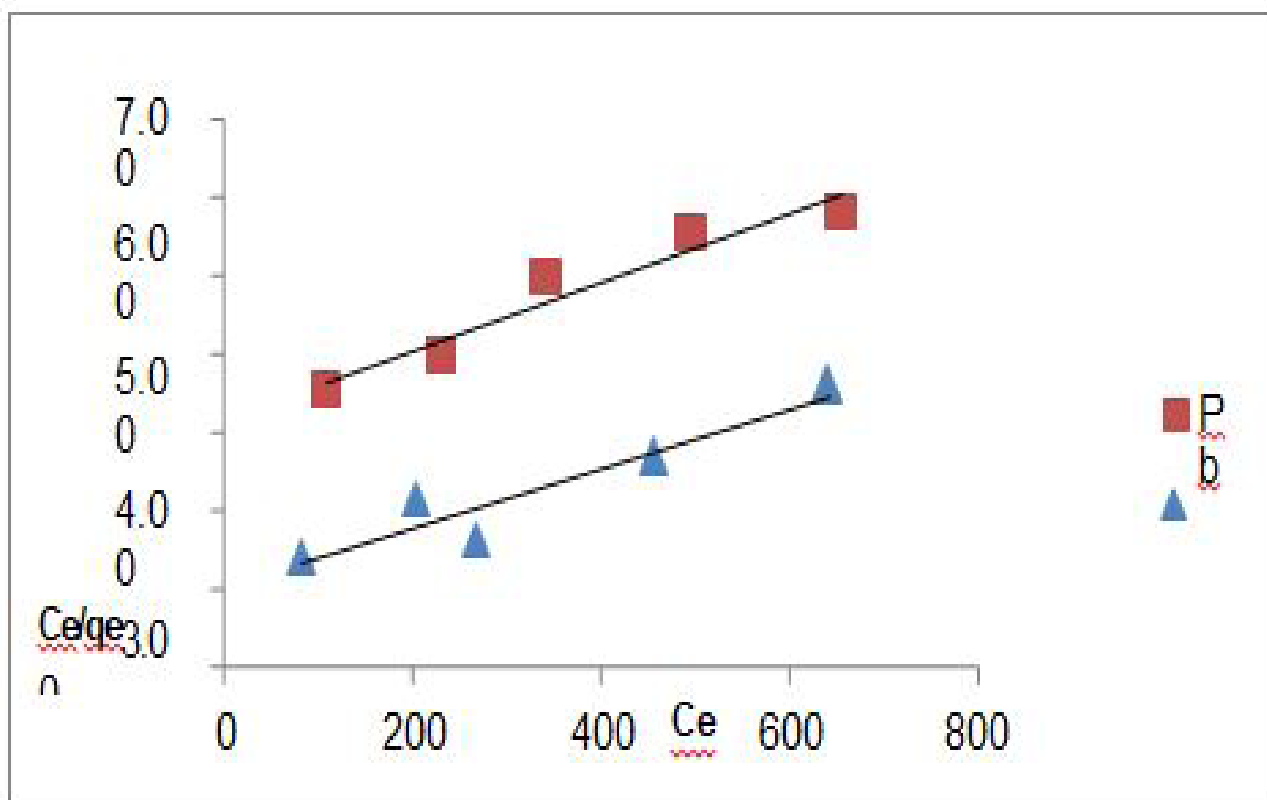


Figure 11: plot of  $(C_e/q_e)$  ainst  $C_e$  for Cu (II) and Pb(II) metals ions

where,  $q_{max}$  (mg/g) is the theoretical maximum heavy metal adsorption amount,  $q_e$  (mg/g) is the equilibrium adsorption amount at heavy metal equilibrium concentration  $C_e$  (mg/L),  $k_f$  is the Freundlich coefficient characteristic of the adsorption affinity of the adsorbent, and  $n$  is the linearity index. Langmuir and Freundlich equations are employed to describe the adsorption process in heterogeneous systems. The Langmuir models assume monolayer adsorption on the solid surface while Freundlich model is empirical in nature. The fitted results are presented in Table 2.

The results showed that the Langmuir model with  $R^2$  higher than 0.98 fitted better than the Freundlich model, indicating that Cu (II) and Pb(II) adsorption on NH2-MS can be considered to be a monolayer adsorption process. The amino groups had a strong affinity towards metal ions, and the possible adsorption mechanism could be explained by the coordinate interactions [27]. In addition, all the Freundlich adsorption intensity variables supported the favorable adsorption of metal ions with NH2-MS. The adsorption capacities of Cu (II) and Pb(II) were 163.16 and 147.79 mg/g respectively. By comparison, the adsorption capacity of Cu(II) was higher than that of Pb(II), which could result in a higher utilization of amino groups in the adsorbent in Cu (II) adsorption, leading to its larger saturation adsorption capacity [27].

## Application

In the 10<sup>th</sup> of Ramadan, waste water contains heavy metals. From

the chemical analysis of the five waste water samples it is clear that, the soluble heavy metals of waste water samples such as Lead is more than the permissible limit (0.1 mg/l). To overcome this problem, two of waste water samples were chosen for the treatment process. The efficiency of the treatment was measured by chemical analysis samples before and after this process using NH2-MS. It was found that the soluble Lead in samples was 0.052 ppm before treatment and 0.09 ppm after treatment, and 0.03 ppm before treatment and 0.007 ppm after treatment. It can be concluded that the surfaces of NH2-MS had adsorption sites that were able to bind Cu(II) ions.

## Conclusions

NH2-MS were found to effectively adsorb Cu(II) and Pb(II) from aqueous solutions. The maximum metal uptake by the NH2-MS were 147.79 and 163.16 mg/g for Pb(II) and Cu(II), respectively. The selectivity sequence of both ions uptake as follow; Cu(II)-NH2-MS > NH2-MS > Pb(II) were in accordance with the stability constants of the metal chelates of NH2-MS. Adsorption kinetics followed a pseudo-Second-order model for NH2-MS, but the rate of the adsorption was also affected by intraparticle diffusion. Modeling of adsorption equilibrium required not only the choice of isotherm equation but also the error function. The quality of the fit was judged by a few statistical tests as well as accurate approximation of the real adsorption capacity ( $q_e$ ). Langmuir model should better describe the two metal ions adsorption on aminated mesoporous materials than Freundlich model where the  $R^2$  values are compared.

Metals	Langmuir constants (NH2-MS)			Freundlich constants (NH2-MS)		
	$Q_{max}$ (mg/g)	$K_L$	$R^2$	$K_F$	1/n	$R^2$
Cu(II)	163.16	0.38	0.988	1.4	0.79	0.93
Pb(II)	147.79	0.44	0.989	1.2	0.71	0.92

Adsorbent	$q_m$ (mg/g)	Ref.
Silica-Activated Carbon	178.5	2
Metal oxide nanoparticles $Fe_3O_4$	127.4	3
Rice husk ash	39.87	4
Poly(ethyleneimine)- Functionalized Silica	36.8	21
NH2-MS	179	This study

Table 3: Comparison of the maximum adsorption capacity of heavy metals onto different adsorbents

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