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Adsorption of binary and multi heavy metals ions from aqueous solution by amine functionalized SBA-15 mesoporous adsorbent in a batch system

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ABSTRACT

Mesoporous silica material Santa Barbara Amorphous-15 (SBA-15) and functionalized SBA-15 with amino functional group were synthesized in order to investigate its potential use as an adsorbent for adsorption of binary and multi heavy metals ions from aqueous solution. The characteristics of SBA-15 before and after functionalization were achieved, such as Brunauer-Emmett-Teller (BET) surface area and thermal gravimetric analysis (TGA). The adsorption of binary system consisting of Ni(II) and Co(II) on NH_2-SBA-15 was investigated, it was found that the percentage removal for Ni(II) ions in binary system was less than in single system by 64.67% which confirms the presence of competition between these ions, and the effect was much clearly in higher concentrations. The competitive adsorption for six metals ions on NH_2-SBA-15 was studied, and it was obtained that the adsorbent had an attraction toward metal ions in reducing order as follows: $Pb^{2+} > Cr^{3+} > Cu^{2+} > Cd^{2+} > Ni^{2+} > Co^{2+}$ which show that Pb was the most adsorbed metal at NH_2–SBA-15. It was also found that the Ni^{2+} adsorption efficiency acquired from the single-metal aqueous solution (99%) better than in multi-metals aqueous solution (42%), indicating the presence of competition between the metallic elements for adsorption by NH_2 groups.

Keywords: SBA-15; Functionalized SBA-15; Binary heavy metal ion removal; Metal ion adsorption; NH2-SBA-15; Multi metal ion removal

1. Introduction

A heavy metal is a public term used for the set of metals and metalloids with an atomic density above 5 g $(cm^3)^{-1}$ or whose molecular weight is higher than 40 [1]. As a rough generalization, the “Heavy metals” may be said to include all metals of the Periodic Table except those in Group I and II [2]. The heavy metals would become hazardous to living organisms and humans, when its concentration is above a toxic level, set by US Environmental Protection Agency (USEPA) and World Health Organization (WHO). The presence of these toxic ions is worried because of their toxicity to many life forms as they can enter the food chain when they are either discharged directly or indirectly into the environment [3]. Various technologies have been used for removing metals from aqueous solutions and each of them has several advantages and disadvantages, such as; ion exchange, chemical precipitation, membrane, flocculation, coagulation, flotation, electro dialysis and adsorption [4–6]. When planning to choose an appropriate technology for heavy metal removal, there are several points which must be taken into account, including the efficiency of the method, generation of secondary waste, and cost. In the light of the above, adsorption is a favorable choice for heavy metal removal [7]. Adsorption is generally applied technique for the metal ions removal from different industrial effluents [8]. Whether dealing with adsorption of heavy metal ions or any other contaminant, there is need to develop novel adsorbents that meet specific requirements. Many researchers have made their efforts for developing inexpensive, available and

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environmental friendly adsorbents based on agricultural and industrial wastes by-products such as tree fern [9], rice husk [10], hydrous titanium oxide [11], fly ash [12], sawdust [13], coconut shell [14], sugarcane bagasse [15], red mud [16], etc. However, all these adsorbents display many disadvantages due to their tight pore size, heterogeneous pore structure, wide pore size distribution, low selectivity and capacity due to their weak interactions with metallic ions, their difficult and very expensive reactivation process, and they need more chemical treatment before use [17]. Nowadays, nanoporous materials with ordered geometries are considered as ideal adsorbents that can effectively be used to remove toxic metals ions from aqueous media because of their extremely large and uniform pore sizes combined with high surface areas [18–20].

In this work, NH_2-SBA-15 amino functionalized mesoporous silica was applied as an effective adsorbent in order to adsorb a binary heavy metals ions Ni(II) and Co(II)) from metals solution in a batch system. The NH_2-SBA-15 adsorbent was applied to adsorbate the six heavy metals ions Ni(II), Co(II), Cu(III), Cr(II), Pb(II) and Cd(II) by the competitive adsorption investigation.

2. Materials and methods

2.1. Chemicals

Pluronic "P123" tetraethyl orthosilicate (TEOS, 98%), Hydrochloric acid (HCl), distilled water (H_2O), toluene ($C_6H_5–CH_3$), 3-aminopropyltriethoxysilane (APTES), ($H_2N(CH_2)_3Si(OC_2H_5)_3$, 99%), Nickel(II) nitrate hexahydrate ($Ni(NO_3)_2.6H_2O$, 99%), Cobalt(II) nitrate hexahydrate ($Co(NO_3)_2.6H_2O$, 99%), Copper(II) nitrate tri hydrate ($Cu(NO_3)_2.3H_2O$, 99%), Chromium(III) nitrate nona hydrate ($Cr(NO_3)_3.9H_2O$, 99%), Cadmium(II) nitrate tetra hydrate ($Cd(NO_3)_2.4H_2O$, 99%), Lead(II) nitrate ($Pb(NO_3)_2$, 99%), Sodium hydroxide (NaOH, 99%). All chemicals were purchased from Sigma Aldrich (Germany) and applied as acquired without additional purification.

2.2. Synthesis of SBA-15

SBA-15 was prepared by applying the standard method that has been mentioned by [21,22]. P123 template (6 g) was added in distilled water (45 g) and 2 M HCl solution (180 g) at 35°C until the surfactant was dissolved completely. Then, TEOS (12.75 g) was gradually dissolved to surfactant mixture and mixed for 20 h at 35°C. Then precipitated solution was aged in closed glass bottle for 24 h at 100°C under constant conditions. Then, white precipitate was permitted to cool at ambient temperature, filtered, washed with distilled water and then dried at ambient temperature for 12 h. The surfactant removal was performed by calcination for 6 h at 550°C, and then SBA-15 was acquired as white powder.

2.3. Functionalization of SBA-15

NH_2-SBA-15 was prepared by post grafting method followed procedure that described by [23]. First, 1 g of calcined SBA-15 was dried for 3 h at 100°C then stirred under reflux with 40 ml of Toluene and 10 ml of 3-aminopropyltriethoxysilane (APTES) for approximately 6 h. The colloidal solution was then cooled, filtered, washed with toluene and dried at 60°C, and then white powder of amino-SBA-15 (NH_2-SBA-15) would be obtained.

2.4. Characterization

The mesoscopic order for mesoporous silica SBA-15 before and after functionalization was identified. The total pore volume and the specific surface area of SBA-15 and NH_2-SBA-15 were measured by BET method using surface area analyzer [Type: Q-surf 9600, Origin: USA]. A TGA was achieved to confirm the incorporation of functional group after functionalization and also obtained information concerning the thermal stability. The powder was heated from ambient temperature to 600°C, at heating rate of 10°C min^{-1} using TG-DSC [Type: STA PT1000, origin: USA]. The characterization includes the FTIR, SEM and BET was achieved in our previous study [19,22].

2.5. Preparation of metals solutions

The stock solutions (1,000 mg L^{-1}) of metals (Ni, Co, Cu, Cr, Pb and Cd) were prepared by dissolving required quantities of metals salts (all in nitrate form) in distilled water. Then required concentration of metal solution was prepared by dilution with distilled water. The concentrations of metals ions before and after adsorption were measured by atomic absorption spectrophotometer [Type: SHIMADDZU AA-7000, origin: Japan].

2.6. Batch adsorption

2.6.1. Effect of surface functionalization of SBA-15

In order to examine the effect of amino functional group on the removal efficiency of metal ions, a comparison between amino-SBA-15 and pure SBA-15 was made in terms of the removal of Ni^{2+} and Co^{2+} in single metal solutions. A 0.1 g of adsorbent was added to 100 ml of varied metal ion concentrations (from 20 to 100 mg L^{-1}) at pH = 5. These solutions were agitated by electrical shaker [Type: Unimax 1010 DT Heidolph, Origin: Germany].

2.6.2. Binary and multi heavy metal ions adsorption

Binary adsorption of Ni(II) and Co(II) was studied by stirring 1 g of amino-SBA-15 with 1 L solution of equimolar concentration of metal ions (0.51 and 1.7 mmol L^{-1}) and pH 5 using magnetic stirrers at room temperature. The samples were analyzed at different time intervals. The adsorbent was separated by filtration using filter paper [Type: Whatman 542, origin: England] and then the samples were analyzed by atomic absorption spectrophotometer for metals analysis.

Competitive adsorption for six metal ions (Ni^{2+}, Co^{2+}, Cu^{2+}, Cr^{3+}, Cd^{2+} and Pb^{2+}) was studied, where 1 g of amino-SBA-15 was added to 1 L solution of equimolar concentration (0.5 mmol L^{-1}) of metals ions at pH 5 then stirred by using a magnetic stirrer at room temperature.

The uptake of heavy metals ions was calculated from the mass balance, which was stated as the amount of metals adsorbed onto the solid which is equal the amount of metals removed from the solution, and mathematically represent by the equation:

$$q_e = \frac{V\left(C_o - C_e\right)}{W} \tag{1}$$

where q_e is the adsorbent equilibrium adsorption capacity, C_o and C_e are the initial and equilibrium concentration respectively in (mg L^{-1}), V is the volume of solution in (L) and W is the adsorbent weight in (g). The uptake of metal ions at any time was calculated from Eq. (2).

$$q_t = \frac{V\left(C_o - C_t\right)}{W} \tag{2}$$

where q_t and C_t are the adsorption capacity in (mg g^{-1}) and metal ion concentration in solution in (mg L^{-1}) respectively at time t. The removal efficacy was calculated by the following equation [24]:

$$\%R = \frac{C_o - C_e}{C_o} \times 100\% \tag{3}$$

The distribution ratio (K_d) was calculated using the equation:

$$K_d = \frac{\text{Amount of metal in adsorbent}}{\text{Amount of metal in solution}} \times \frac{V}{m} \tag{4}$$

where V is the volume of the solution (ml) and m is the weight of the adsorbent (g). K_d is the distribution coefficient which was determined from the following equation [24–29]:

$$K_d = \frac{q_e}{C_e} \tag{5}$$

Substitution Eq. (1) in Eq. (5) yields the following equation:

$$K_d = \frac{V\left(C_o - C_e\right)}{W * C_e} \tag{6}$$

3. Result and discussions

3.1. Adsorbent characterization

The surface area of SBA-15 and NH_2-SBA-15 are summarized in Table 1. The prepared mesoporous silica has high surface area and pore volume, falls within the range of surface area (400–900 m^2 g^{-1}) and pore volume (0.56–1.23 cm^3 g^{-1}) for SBA-15 [30]. Also, the results show that there is a dramatic decrease in surface area (406.779 to 170.511) and total pore volume (1.2243 to 0. 412) after functionalization; this confirms that the functional group is located not only on the outer surface but also inside the mesoporous channels [31,32].

The weight loss of thermal gravimetric analyses is plotted in Fig. 1, both samples SBA-15 and NH_2–SBA-15 was heated from ambient temperature to 600°C, at a rate of 10°C min^{-1}. Thermal gravimetric results are showed mass losses of 20% and 13.6% for SBA-15 and NH_2–SBA-15 respectively, this indicates that NH_2–SBA-15 is more thermostable. Therefore; after functionalization, the thermal stability is enhanced greatly and this is very important. The weight loss for SBA-15 up to 200°C was occurred because the loss of physically and chemically adsorbed water molecule.

At high temperature (above 200°C) the residual weight loss was occurred because of the existences dehydroxylation by silanol groups condensation, while for NH_2–SBA-15, there is an extra weight loss in the range of temperature 200°C–300°C because of the decomposition of organic moiety as a result of amino functional group loading on the surface of SBA-15 [33].

3.2. Comparison between SBA-15 and NH_2–SBA-15

A comparative study was done between SBA-15 and NH_2–SBA-15 so as to study the effectiveness of amino functional group on removal of Nickel and Cobalt ions from its aqueous solutions and the findings are shown in Fig. 2. This figure shows that SBA-15 has weak affinity to adsorb both metals ions, while the Ni(II) and Co(II) percentage removal have been doubled after SBA-15 functionalization with amino group (NH_2) even it reached 100% (for Ni(II)). In addition to the successful functionalization with amino functional group, these results confirm that NH_2–SBA-15 is an efficient adsorbent for Ni(II) and Co(II) adsorption from aqueous solutions in various concentrations in the order: Ni(II) > Co(II) because the existences of activity amine group [19].

Table 1
Physical properties before and after functionalization

Sample	(BET) surface area (m^2 g^{-1})	Total pore volume (cm^3 g^{-1})
SBA-15	406.779	1.2243
NH_2-SBA-15	170.5110	0.412

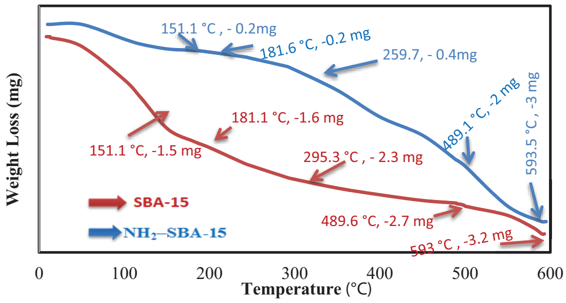

Fig. 1. Thermal gravimetric analysis for SBA-15 and NH_2–SBA-15.

3.3. Effect of pH

The most important factor that affects adsorption processes (particularly metals adsorption) is the effect of pH solution. The best pH at which the bonding process for Ni(II) and Co(II) ions at NH_2–SBA-15 has been studied was in the range 1–6. The results obtained are presented in Fig. 3, which shows that the removal efficiency for both metals increases gradually as the solution pH increased. At lower pH (less than 3), the amino group is protonated and the surface would become more positively charged leading to strong repulsive forces which inhibit the approach of positively charged Nickel and Cobalt cations to the binding sites, and consequently the interaction between metals ions and adsorbent surface would decrease. Moreover, as the pH of the solution increases (up to 5) the repulsion between the surface and metals cations decreases due to the decreasing in amine group protonation, and consequently, the extent of formation of complex between metals ions and the amine groups increases, leading to increasing the removal efficiency up to 99.27% and 48.96% for Ni(II) and Co(II), respectively. When the pH increased more than 5 (at pH 6) a slight decrease in removal efficiency was observed (98.7% and 43.487% for Ni(II) and Co(II), respectively), this is due to the precipitation of the metal ions as its hydroxides would be formed. Therefore, pH 5 is the better value of pH for the adsorption of Ni(II) and Co(II) from solution at which neither precipitation of the metal hydroxide nor protonation of the amine groups occurs [34,35].

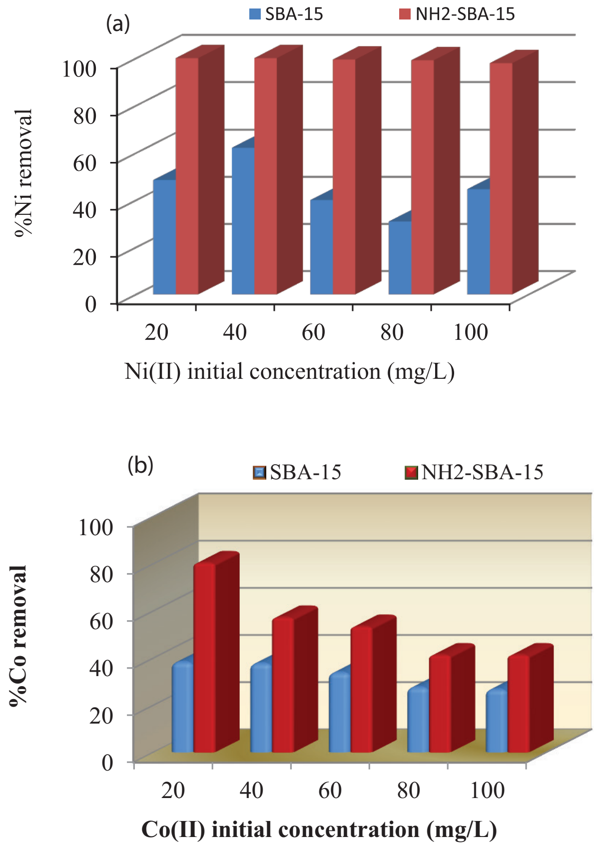

Fig. 2. Comparison between SBA-15 and NH_2–SBA-15, (a) Ni (II) removal and (b) Co (II) removal.

3.4. Binary adsorption

Binary mixture of 100 mg L^{-1} of Ni(II) and Co(II) was equilibrated to figure out the effect of each one on the adsorption of other and compared between both metals as shown in Fig. 4. It is obvious from this figure that Ni(II) equilibrium adsorption capacity in binary solution is much less than in single metal solution (64.67%), Which confirms that these ions (Ni(II)) are affected by the presence of Co(II) ions in solution that competes with the first one to reach the active sites.

The rate of adsorption for binary solutions which consist of equimolar initial concentration of Ni(II) and Co(II) ions was also studied as shown in Fig. 5. At low initial concentration the effect of competition was not much clear because there is more active sites are available for binding metals ions. While at higher initial concentration the effect is much clear as shown in Fig. 6.

Fig. 6 shows that after the first 25 min the adsorption capacity of Co(II) are increased gradually more than Ni(II) capacity, this could be attributed to the ionic radius for Co(II) (0.745 A°) is larger than Ni(II) (0.69 A°) and with the time a layer of Co(II) will consist on NH_{2-}SBA-15 surface that prevent the passage of Ni(II) ions to the inner surface [25].

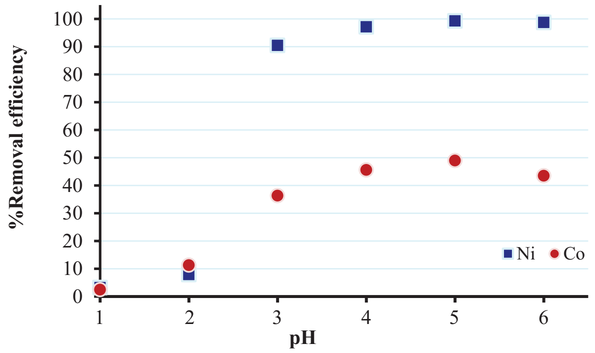

Fig. 3. Effect of pH on the removal efficiency of Ni(II) and Co(II) ions (C_o = 100 mg L^{-1}, contact time = 60 min, NH_2–SBA-15 dosage = 0.1g, and at room temperature).

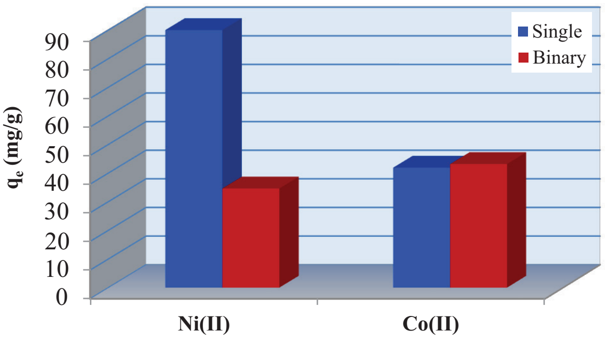

Fig. 4. Effect of binary metal ion on the equilibrium adsorption capacity of Co(II) and Ni(II) on to NH_2–SBA-15 (pH = 5, C_o = 100mg L^{-1}, volume = 100 ml, dose = 0.1 g, time = 90mi, and at room temperature).

3.5. Competitive adsorption

The selectivity of NH_2–SBA-15 toward six metal ions (Ni(II), Co(II), Cu(II), Cd(II), Cr(III) and Pb(II)) was studied by equilibrating 1 g of NH2–SBA-15 with 1 L of solution containing equimolar concentrations of these metals ions. The equal initial molar concentrations were used for all studied metal ions in the solution to acquire equitable controlled selectivity metal ions of different atomic weights [36]. Fig. 7 shows the extent of metal ions adsorption on NH_2–SBA-15.

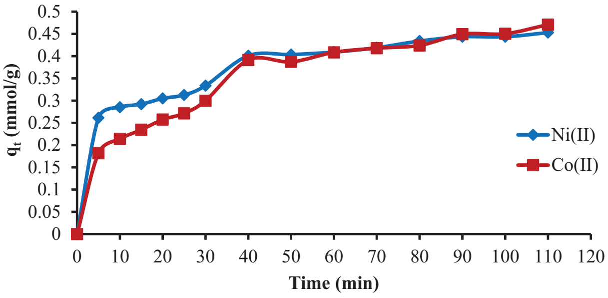

Fig. 5. Binary adsorption for Ni(II) and Co(II) (pH = 5, C_o = 0.51 mmol L^{-1}, dosage = 1 g L^{-1}, and at room temperature).

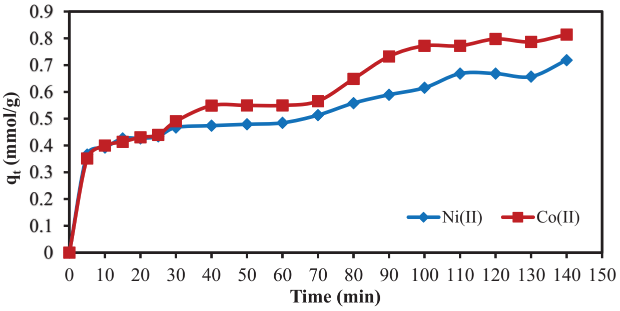

Fig. 6. Binary adsorption for Ni(II) and Co(II) (pH = 5, C_o = 1.7 mmol L^{-1}, dosage = 1 g L^{-1}, and at room temperature).

The distribution coefficient K_d is the measure of adsorbent affinity for metal ions and the high magnitude of K_d values refer to the high selectivity of adsorbent of metal ions, so depending on the results as shown in Table 2, NH_2–SBA-15 has an ability for metal ions in removing order as follows: –$Pb^{2+} > Cr^{3+} > Cu^{2+} > Cd^{2+} > Ni^{2+} > Co^{2+}$ which shows that Pb is the most adsorbed metal at NH_2–SBA-15. It is also noted that the Ni^{2+} adsorption efficacy obtained from single-metal solutions is 99% higher than multi-metals solutions 42% as shown in Fig. 4, supporting the presence of competition between metallic elements for adsorption by amine groups. Table 3 presents removal selectivity acquired from multi-metals solutions on SBA-15 functionalized with different groups from some previous studies [37,38].

4. Conclusions

Mesoporous material SBA-15 was synthesized, functionalized with 3-aminopropyltriethoxysilane by post synthesis method, characterized and used as adsorbent of heavy metals from aqueous solution in batch system. Functionalization of the surface of SBA-15 material with amino group is very efficient in increasing the percentage removal of Ni(II) and Co(II), where NH_2-SBA-15 increases the percentage removal to the double as compared with pure SBA-15. Binary

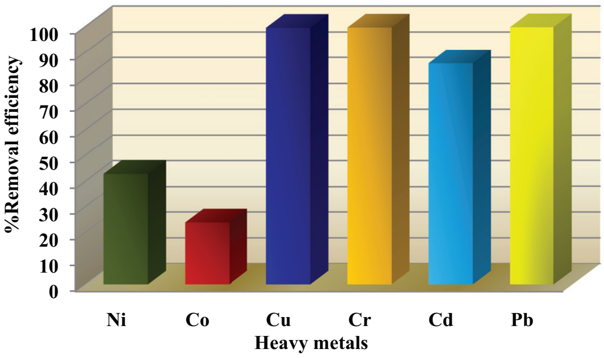

Fig. 7. Competitive adsorption of metals ions at the same initial concentration.

Table 2
Competitive adsorption (pH = 5, volume = 1 L, dose = 1 g, room temperature, C_o = 0.51 mmol L^{-1}, and agitation speed = 300 rpm)

Heavy metal	Pb	Cr	Cu	Cd	Ni	Co
C_e (mmol L^{-1})	0.000585	0.00123	0.0017	0.071	0.2854	0.38
% Removal	99.88	99.754	99.66	85.8	42.92	24
K_d	853700.85	405504.065	293117.6	6042.25	751.93	315.79

Table 3
Adsorption selectivity obtained from multi-metals solutions for previous studies

Adsorbent	Functional group	Metals order	Reference
SBA-15	N-propylsalicylaldimine	$Cu^{+2} > Ni^{+2} > Co^{+2} > Zn^{+2}$	[37]
SBA-15	3-aminopropyltriethoxysilane	$Cr^{3+} > Cu^{2+} > Zn^{2+} > Pb^{2+} > Co^{2+} > Cd^{2+} > Ni^{2+}$	[17]
SBA-15	bis(2,4,4-trimethylpentyl) phosphinic acid	$Zn^{2+} > Cu^{2+} > Co^{+2}$	[38]
SBA-15	3-aminopropyl triethoxysilane	$Pb^{+2} > Cr^{+3} > Cu^{+2} > Cd^{+2} > Ni^{+2} > Co^{+2}$	This work

adsorption for both Ni(II) and Co(II) ions shows that these metals competed between each other to reach the active sites. The competitive adsorption of six metals ions (Pb^{2+}, Cr^{3+}, Cu^{2+}, Cd^{2+}, $Ni^{2+}$and Co^{2+}) on NH_2-SBA-15 shows that these metals ions have the affinity for adsorption in the decreasing order as follows: –$Pb^{2+} > Cr^{3+} > Cu^{2+} > Cd^{2+} > Ni^{2+} > Co^{2+}$, which show that Pb is the most adsorbed metal at NH_2-SBA-15.

It is also found that the Ni^{2+} adsorption efficiency acquired from the single-metal aqueous solution (99%) better than in multi-metals aqueous solution (42%), indicating the presence of competition between the metallic elements for adsorption by NH_2 groups.

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