Nano spinels of copper-doped cobalt aluminate (Co$_x$Cu$_{(1-x)}$Al$_2$O$_4$) for removal of Cd(II) from aqueous solutions

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A B S T R A C T

The nano spinels of copper-doped cobalt aluminate (Co$_x$Cu$_{(1-x)}$Al$_2$O$_4$ ($x$ = 0–1)) have been synthesized by sol-gel method. The nano spinels were characterized by FTIR, X-ray diffraction, BET, transmission electron microscopy and scanning electronic microscopy methods. The adsorption of Cd(II) by nano spinels was studied. Results showed that adsorption efficiency of nano spinels is as follows: Co$_0.5$Cu$_0.5$AlO$_4$ > Co$_0.3$Cu$_0.7$AlO$_4$ > Co$_0.7$Cu$_0.3$AlO$_4$ > CuAl$_2$O$_4$ > CoAl$_2$O$_4$. Experimental results demonstrated that Cd(II) effectively removed by nano spinels in 90 min and solution pH of 6. Cd(II) removal was followed by the pseudo-first-order kinetic model. The equilibrium adsorption of Cd(II) was best described by the Langmuir isotherm model with maximum adsorption capacity ($q_{\text{max}}$) of 145 mg g$^{-1}$ for Co$_0.5$Cu$_0.5$AlO$_4$. Results of thermodynamic studies revealed that adsorption of Cd(II) on nano spinels is an endothermic process. The studies clearly demonstrated that the nano spinels of Co$_x$Cu$_{(1-x)}$Al$_2$O$_4$ could be an efficient and reusable sorbent for treatment of Cd(II) contaminated wastewaters. The desorption studies showed that the regeneration of Co$_0.5$Cu$_0.5$AlO$_4$ adsorbent can be easily achieved by inorganic acids. Results showed that the order of acids was as follows: nitric acid > hydrochloric acid > sulphuric acid > acetic acid.

Keywords: Adsorption; Cd(II); CoAl$_2$O$_4$; CuAl$_2$O$_4$; Nano spinel; Co$_x$Cu$_{(1-x)}$Al$_2$O$_4$

1. Introduction

Due to high development of industrial activity in recent years, the levels of heavy metals in water system have noticeably increased over time. This makes it essential to develop methods that allow one to detect, quantify and remove heavy metals from the wastewaters. The different industries such as electro-plating, dyeing, plastic, battery and refining industry release these metals into aquatic environments [1,2]. Among these metal ions, Cd, Zn, Hg, Pb, Cr, Cu, etc. gain importance due to their high toxic nature even at very low concentrations. Cadmium, one of the most toxic heavy metals usually found in contaminated ecosystems. Heavy metal ions are not biodegradable, and they tend to collect in the organisms and enter the food chains through various pathways. Therefore, development of economically feasible techniques to remove heavy metals from the environment is in order. Various methods are available to remove these heavy metals from the environment. The classical physico-chemical methods employed to remove toxic metals, viz. precipitation, evaporation, ion exchange, and oxidation/reduction, pose severe constraints associated with high capital and operating costs, in addition to generating several by-products [3–5]. Adsorption is known as an effective and economic method for heavy metal removal. Adsorption is one of the easiest, safe and cost-effective methods, being widely used in effluent treatment processes [6]. Recently, there is an increasing interest in the

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use of high efficient adsorbents, which are able to remove metallic ions from aqueous solutions [7]. Removal of heavy metals by different sorbents such as chitosan [8], leaves [9], rice husk [10], activated carbon [11], magnetite [12,13], MgO [14], coconut shell [15], bentonite nano composite [16], cobalt silicate [17], sawdust of walnut [18] and carbon nanotubes [19] was studied.

The mixed metal oxides such as spinel structure oxides (AB₂O₄) constitute one of the most interesting classes of inorganic metalloid materials. They have fundamental physical and chemical properties. Among the spinel oxides, copper and cobalt aluminates possess interesting properties for technological application. Cobalt aluminate oxide (Co₃Al₂O₄) has been employed in various fields such as ceramic pigment, optical properties, catalysts in reactions; photo catalyst for degradation of pollutants such as carbon monoxide, sensors for gas and volatile organic compounds, hydrogenation, and removal of H₂S and NH₃ [20–26]. Some of the altered spinel ferrites were used as adsorbent [27–30]. The spinels mostly were used for dye removal. The same metal oxides and their composites were used for Cd removal [31–33]. Recently the composite of NiFe₂O₄ spinel was used for Cd removal [34].

The aim of this study was to prepare the nano spinels of copper-doped cobalt aluminates. The usage and adsorptive properties of nanocrystals for Cd(II) removal from aqueous solutions was the second aim.

2. Experimental

2.1. Materials and methods

All of the compounds were analytical grade and were used as received without any purification. All of the chemicals were purchased from Merck Chemical Co., (Germany). Distilled water was used in all of experiments.

The stock solution 1,000 mg L⁻¹ of Cd(II) ions was prepared by dissolving metal salt from Cd(NO₃)₂·6H₂O. The required diluted solutions with different concentrations were prepared by this stock solution.

CuAl₂O₄ and Co₃Al₂O₄ powders were prepared from aluminum nitrate (Al(NO₃)₃·9H₂O), cobalt nitrate (Co(NO₃)₂·6H₂O) and copper nitrate (Cu(NO₃)₂·3H₂O).

Appropriate amount of Co(NO₃)₂·6H₂O and Al(NO₃)₃·6H₂O with molar ratio of Co²⁺:Al³⁺ 1:2 was dissolved in the distilled water and then titrated drop wise by 1 M NH₃ till the pH was 8.5 under fast magnetic stirring at 25°C. Then the prepared sample was filtered off, washed with distilled water and then dried in a furnace at 150°C for 6 h [5]. For preparation of CoₓCu₁–ₓAl₂O₄ different moles of Co:Cu (x = 0.0–1) were used. The preparation method was the same.

Adsorption experiments were conducted to investigate the influence of adsorption parameters such as contact time and ratio of Co:Cu, pH, adsorbent mass and initial concentration of Cd(II) by using nanocrystals of copper-doped cobalt aluminate (CoₓCu₁–ₓAl₂O₄) as adsorbent.

0.05 g of adsorbent was added in 50 mL Cd(II) sample on rotary shaker at a constant speed of 150 rpm. After different contact times (0–180 min), the sorbent was removed from the solution and the equilibrium concentration of the Cd(II) in the solution was determined with atomic absorption spectrometer. All experiments were carried out at room temperature (25°C ± 1°C). The adsorbent was separated by centrifugation in 10,000 rpm for 10 min and residual cadmium was analyzed.

The FTIR transmission spectra were taken with a tensor-27 of Bruker Co. (Germany), Infrared spectrometer using the KBr pellet from 4,000 to 400 cm⁻¹. All pH measurements were carried out with an ISTEK-720P (Germany) pH meter. The powder X-ray diffraction (XRD) studies were made on a Philips PW1840 (Netherlands) diffractometer using Ni-filtered Cu ka radiation and wavelength 1.54 Å. The average particle size and morphology of samples were observed by SEM using a Hitachi S-3500 (Japan) scanning electron microscopy. The transmission electron microscopy (TEM) was employed using transmission electron microscope (Zeiss - EM10C - 80 kV, Germany).

The amount of adsorbed Cd(II) was calculated from the difference between the initial and final solution concentrations. The concentration of cation in solution was measured by an atomic absorption spectroscopy, Varian AA240. All the experiments were repeated four times, and the average results were given. Relative standard deviation (% RSD) was determined between 1.82% and 2.5% for every point at all the tests. The removal efficiency and adsorption capacity of Cd(II) were calculated according to the below equations, respectively. The percentage removal of Cd(II) by the hereby adsorbent is given by:

\[
\% \text{Removal} = \left( \frac{C_0 - C_e}{C_0} \right) \times 100
\]

where \(C_0\) and \(C_e\) are denoted as the initial and equilibrium concentration (mg L⁻¹) of Cd(II), respectively.

The amount of equilibrium adsorption, \(q_e\) (mg g⁻¹), was calculated by:

\[
q_e = \frac{(C_0 - C_e)V}{W}
\]

where \(C_0\) and \(C_e\) (mg L⁻¹) are the liquid-phase concentrations of Cd(II) at initial and equilibrium, respectively. \(V\) (L) is the volume of the solution and \(W\) (g) is the mass of dry sorbent used.

3. Results and discussions

3.1. Characterization

X-ray powder diffraction analysis was used to identify the crystal structure of CoₓCu₁–ₓAl₂O₄ samples. First effect of calcination temperature on the crystallinity of sample was experienced; therefore, cobalt aluminate sample was heated at different temperatures (100°C, 300°C, 600°C and 900°C). The XRD patterns are shown at Fig. 1. The results are shown with increasing of calcination temperature, cobalt aluminate sample had more crystal order and at 900°C cobalt aluminate had the highest crystallinity form. At this temperature cobalt aluminate sample showed the characteristic diffraction peaks at 20 values of 31.19°, 36.74°, 44.69°, 55.49°, 59.19° and 65.4° corresponding to the [220], [311], [400], [422], [511] and [440] planes, respectively. These planes are associated
with the spinel type of CoAl₂O₄ with cubic structures in agreement with the Joint Committee on Powder Diffraction Standards (JCPDS) cards no. 44–0160. The XRD showed the formation of spinel phase at 900°C (2θ of 36.74° corresponding to d = 2.444) [35]. Cobalt aluminate sample also showed face centered cubic (FCC) with Fd-3m space group. However the spinel sample confirmed that the intensity of the peaks increases with increase in calcination temperature to 900°C.

The nanocrystals of spinel copper-doped cobalt aluminate CoₓCu₁₋ₓAl₂O₄ (x = 0–1) were prepared and heated to 900°C. Typical XRD pattern for the samples of CoₓCu₁₋ₓAl₂O₄ (where x = 0.0, 0.3, 0.5, 0.7 and 1.0) is shown in Fig. 2. Results of Fig. 2 show that the doping of copper on the cobalt aluminate did not change crystal spinel phase. The results of X-ray crystallography showed the cubic unite cell (a = b = c = 8.02 Å) for CoAl₂O₄. Doping of Cu increases the lattice parameters of CoAl₂O₄ from 8.02 Å for CoAl₂O₄ to 8.08, 8.14, 8.18 and 8.2 Å for Co₀.₇Cu₀.₃Al₂O₄, Co₀.₅Cu₀.₅Al₂O₄, Co₀.₃Cu₀.₇Al₂O₄ and CuAl₂O₄, respectively. It is observed that the lattice parameters increase linearly with increase in copper concentration. The reason for this increase of lattice parameter values may be due to the larger ionic radii of Cu²⁺ (73 pm) as compared with Co²⁺ (70 pm).

The mean crystallite size (D) of the particles was calculated from the XRD line broadening measurement using the Scherrer equation:

\[ D = \frac{0.89\lambda}{\beta \cos \theta} \]  

where \( \lambda \) is the wavelength (Cu-Kα), \( \beta \) is the full width at the half maximum of the CoₓCu₁₋ₓAl₂O₄ (311) line and \( \theta \) is the diffraction angle. On the basis of the Scherrer equation, the main crystallite size was calculated 52, 35 and 46 nm for CoAl₂O₄, Co₀.₅Cu₀.₅Al₂O₄ and CuAl₂O₄, respectively.

FTIR spectra of as prepared spinels of CoₓCu₁₋ₓAl₂O₄ were recorded from 4,000 to 500 cm⁻¹. The two main broad metal-oxygen bands are important in the IR spectra of all spinels. The highest IR band, \( V_1 \), is generally observed in the lower frequency range of 630–670 cm⁻¹, and the intrinsic stretching vibrations of the metal-oxygen bond at the tetrahedral site (M tetra-O). The lowest IR band, \( V_2 \), is usually observed in the frequency range of 450–385 cm⁻¹, assigned to stretching vibrations of the metal oxygen bond at the octahedral site (M octa-O). In the FTIR spectra, \( V_1 \) (640 cm⁻¹) for CoAl₂O₄ shifted slightly to higher frequencies (670 cm⁻¹) by replacing Co²⁺ ion with a Cu²⁺ ion. Small shifts of the \( V_1 \) peak positions indicate that changes due to the Co²⁺ substitution has slightly affected the metal-oxygen force constants in the tetrahedral site. This can be explained by the very small difference in both the atomic mass and ionic radii of the Cu and Co ions.

The surface morphology of CoₓCu₁₋ₓAl₂O₄ (x = 0, 0.5, 1) was studied by scanning electronic microscopy (SEM) and results are shown in Fig. 3. The SEM micrographs showed spherical homogenous phase, uniformly distributed particles and highly porous morphology. Copper particles are brighter and CoAl₂O₄ nanoparticles are darker color in Fig. 3b.

The N₂ adsorption–desorption isotherm of CoₓCu₁₋ₓAl₂O₄ nanoparticles is determined. The BET results of CoₓCu₁₋ₓAl₂O₄ nanoparticles are shown in Table 1. Results also shown the surface area of nanoparticles was increased with increasing different amounts of Cu in doped cobalt aluminate.

### 3.2. Adsorption study

Foreknowledge of optimal conditions would allow a better design and modeling of the process. Thus the effect of some major parameters such as pH, contact time and amount of copper, amount of adsorbent and concentration of adsorbate was studied using the batch experiments.

#### 3.2.1. Effect of contact time and copper contain of cobalt aluminate

To find an appropriate contact time between the sorbent and Cd metallic ion solution, adsorption capacities of metal
ion were measured as a function of time. The effect of equilibration time on the adsorption of Cd(II) ions was analyzed over a range of 0–240 min (Fig. 5). The plot reveals that the rate of the percentage of Cd removal is higher at the beginning. That is probably due to the larger surface area of the spinel sorbent being available at the beginning of process for the adsorption of metal. This shorter time indicates easier approachability of the binding sites for metal ions at the surface of nanoparticles of spinel sorbent. The removal of Cd(II) ions increased rapidly with time up to 90 min and thereafter increased slowly. According to the results, the equilibrium reached at 90 min and was taken as optimal contact time for the subsequent experiments, thereafter; it reached a constant value indicating that no more Cd(II) ions were further removed from solution as shown in Fig. 5.

Effect of copper contain of cobalt aluminate also was investigated. From Fig. 4, it looks copper had catalytic effect for CoAl2O4 and existence of copper increased the adsorption property of cobalt aluminate for Cd removal. The results showed that adsorption capability of nano spinel particles for Cd(II) was as follows: Co0.5Cu0.5AlO4 > Co0.3Cu0.7AlO4 > Co0.7Cu0.3AlO4 > CuAl2O4 > CoAl2O4.

3.2.2. Effect of pH on adsorption of Cd(II)

It is well known that adsorption of heavy metal ions depends on pH of aqueous solution. The pH of aqueous media is an important parameter controlling adsorption processes of heavy metals. The percentage removal of cadmium as a function of equilibrium pH was investigated for contact time of 90 min. pH was adjusted by adding 1.0 M HCl or 1.0 M NaOH. Fig. 6 indicates the effect of pH on the adsorption of
Cd(II) by CoCu_{1-x}Al_{2}O_{4} nano spinels. At pH < 4.0, the Cd removal is low whereas it increased abruptly in the pH range from 4.0 to 6.0. At pH ≤ 3.0, H^+ ions compete with Cd(II) ions for adsorption on the sites in the adsorbent, which would hinder Cd(II) ions from reaching the binding sites of the sorbent caused by the repulsive forces. However, the metal removal is minimum presumably due to the enhanced competition of proton with cadmium ions. The removal of Cd(II) increased rapidly at pH values between 4.0 and 6.0. The increase in metal removal as pH increased can be explained on the basis of a decrease in competition between proton (H^+ or H_3O^+) and positively charged metal ions [M^{2+} and M(OH)^+] at the surface sites. The percentage removal of Cd^{2+} ions reached to 95% at pH 6 for Co_{0.5}Cu_{0.5}Al_{2}O_{4}. At pH > 6.0, the Cd(II) ions get precipitated due to hydroxide anions forming a cadmium hydroxide precipitate. For this reason, the optimal pH value was selected to be 6.0 [36,37].

3.2.3. Effect of initial Cd(II) concentration

The effect of initial Cd concentration on the adsorption process was investigated. Fig. 7 indicates the effect of initial metal concentration on the adsorption of Cd(II) from 25 to 250 mg L\(^{-1}\) by spinel sorbents. By increasing the initial concentration of Cd(II) solution from 25 to 50 mg L\(^{-1}\), the amount adsorbed increased. This may be attributed to an increase in the driving force of the concentration gradient with the increase in the initial Cd(II) concentration in order to overcome all mass transfer resistance of Cd(II) ions between the aqueous and solid phases. The initial concentration of Cd(II) solution from 50 to 250 mg L\(^{-1}\) decreased the present removal. Therefore, higher initial concentration of Cd(II) ions may decrease the adsorption capacity [38]. The initial concentration of 50 mg L\(^{-1}\) for next experiments was selected.

3.3. Adsorbent dosage effect

Adsorbent dosage is one of the important parameter of adsorption. The effect of adsorption dosage from 0.01 to 0.3 g was determined at initial metal ions concentration of 50 mg L\(^{-1}\) and pH 6. The results of the investigations of cadmium removal are presented in Fig. 8. With the increase in dosage of spinel adsorbent, the percentage of adsorption increased from 0.01 to 0.1 g. This effect can be due to some of the adsorption sites remaining unsaturated during the adsorption reaction. At the initial step usually, there is fast increase in adsorption of Cd^{2+} with corresponding increase in adsorbate concentration which may be attributed to the increasing presence of adsorption sites. However, as the binding sites of the sorbent get saturated the curves level off due to the independence of the adsorption on concentration of the adsorbate. Therefore, best dosage of spinel sorbent was 0.05–0.1 g.

3.4. Adsorption isotherms, kinetics and mechanism

Various adsorption kinetic models have been used to describe the adsorption of metal ions. The first-order kinetic process has been used for reversible reaction with an equilibrium being established between liquid and solid phases. The pseudo-first-order rate by Lagergren has also widely been used. The adsorption rate expression of Lagergren is [39] as follows:

\[
\ln (q_t - q_e) = \ln q_e - k_1 t
\]
where \( q_e \) is the amount adsorbed (mg g\(^{-1}\)) at equilibrium, \( q_t \) is the amount adsorbed (mg g\(^{-1}\)) at time \( t \) and \( k_2 \) is the adsorption rate constant (min\(^{-1}\)). The rate constants \( k_2 \) and correlation coefficients \( R^2 \) were calculated from the linear plots of \( \ln(q_e - q_t) \) vs. \( t \) (Fig. 9a).

The kinetic data were further analyzed with Ho and McKay’s [40] pseudo-second-order kinetics model. This model is based on the assumption that the adsorption follows second-order chemiadsorption. Its integrated linear form can be expressed as:

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}
\]

(5)

where \( q_e \) and \( q_t \) (mg g\(^{-1}\)) are the adsorption capacity at equilibrium and time \( t \), \( k_2 \) (g mg\(^{-1}\) min\(^{-1}\)) is the rate constant of the pseudo-second-order adsorption. The rate constants \( k_2 \), \( q_e \) and correlation coefficients \( R^2 \) were calculated from the linear plots of \( \ln(q_e - q_t) \) vs. \( t \) (Fig. 9b). The \( R^2 \) value was significant in this case, which showed that adsorption of Cd(II) followed a pseudo-second-order kinetic model. This implied that adsorption in this case took place through chemical bond formation (chemisorption). Table 2 shows the kinetic parameters of Cd removal by spinel sorbents.

### 3.5. Adsorption isotherms

In order to recognize the design of an adsorption method, it is important to perform the study of equilibrium curves. In this study, two adsorption isotherms such as Langmuir and Freundlich adsorption isotherm models were used to describe the obtained equilibrium data.

Langmuir isotherm can be arranged in its linear form as following [41]:

\[
\frac{C_{eq}}{q_{eq}} = \frac{1}{q_{max} K_l} + \frac{C_{eq}}{q_{max}}
\]

(6)

where \( q_{eq} \) is the amount of adsorbed Cd(II) in the adsorbent (mg g\(^{-1}\)). \( C_{eq} \) is the equilibrium ion concentration in solution (mg L\(^{-1}\)). \( K_l \) (L mg\(^{-1}\)) is the equilibrium constant related to the adsorption energy, and \( q_{max} \) is the maximum adsorption capacity (mg g\(^{-1}\)).

The Freundlich isotherm assumes heterogeneous surface energies, in which the energy term in the Langmuir equation varies as a function of the surface coverage [38]. The adsorption data were also fitted to Freundlich isotherm, which is described by the linear form following the equation [42]:

\[
\log q_{eq} = \log K_f + \frac{1}{n} \log C_{eq}
\]

(7)

where \( K_f \) and \( n \) are the Freundlich constants; \( C_{eq} \) is the equilibrium ion concentration in solution (mg L\(^{-1}\)). According to Eq. (7), the values of \( K_f \) and \( n \) can be determined experimentally by plotting \( \log q_{eq} \) vs. \( \log C_{eq} \). The high value of the regression correlation coefficient of Langmuir adsorption isotherm was obtained, which indicated a good agreement between the experimental values.

Table 3 shows the Langmuir and Freundlich equilibrium parameters for the adsorption of cadmium on Co Cu\(_{x}\) AlO\(_4\) nano spinels. It would be seen from the table that the Langmuir isotherms are linear with correlation coefficient \( R^2 \) in the range of 0.95–0.98. The maximum adsorption capacity observed for Co Cu\(_{0.5}\) Cu\(_{0.5}\) AlO\(_4\) was 145 mg g\(^{-1}\).

### Table 2

<table>
<thead>
<tr>
<th>Sample</th>
<th>First order</th>
<th>Second order</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( R^2 )</td>
<td>( k_1 ) (s(^{-1}))</td>
</tr>
<tr>
<td>CoAlO(_4)</td>
<td>0.777</td>
<td>3.46 \times 10(^{-2})</td>
</tr>
<tr>
<td>Co(<em>{0.5}) Cu(</em>{0.5}) AlO(_4)</td>
<td>0.863</td>
<td>2.85 \times 10(^{-2})</td>
</tr>
<tr>
<td>Co(<em>{0.5}) Cu(</em>{0.5}) AlO(_4)</td>
<td>0.803</td>
<td>4.32 \times 10(^{-2})</td>
</tr>
<tr>
<td>Co(<em>{0.5}) Cu(</em>{0.5}) AlO(_4)</td>
<td>0.823</td>
<td>3.12 \times 10(^{-2})</td>
</tr>
<tr>
<td>CuAlO(_4)</td>
<td>0.868</td>
<td>4.15 \times 10(^{-2})</td>
</tr>
</tbody>
</table>
3.6. Thermodynamic studies

The thermodynamic parameters for Cd adsorption onto spinel sorbents have been calculated. The thermodynamic parameters, change in the standard free energy ($\Delta G^\circ$), enthalpy ($\Delta H^\circ$) and entropy ($\Delta S^\circ$) associated with the adsorption process. The Gibbs free energy change $\Delta G^\circ$ of adsorption process can be calculated from classic Van’t Hoff equation [43]:

$$\Delta G^\circ = -RT\ln K_c$$  (8)

where $R$ is the universal gas constant (8.314 J mol$^{-1}$ K$^{-1}$), $T$ is the absolute temperature, and $K_c$ is the equilibrium constant. The apparent equilibrium constant of the sorption, $K_c$ is the equilibrium constant of Van’t Hoff equation. $K_c$ is obtained from:

$$K_c = \frac{C_s}{C_0}$$  (9)

where $K_c$ is the equilibrium constant, $C_s$ is the amount of Cd(II) adsorbed on the adsorbent of solution at equilibrium (mg L$^{-1}$), and $C_0$ is the equilibrium concentration of Cd(II) in the solution (mg L$^{-1}$).

The enthalpy change ($\Delta H^\circ$) (i.e., heat of adsorption) and entropy change ($\Delta S^\circ$) is related with the Gibbs free energy by the equation:

$$\ln K_c = \frac{\Delta G^\circ}{RT} = \frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$$  (10)

A plot $\ln K_c$ vs. $(1/T)$ gives a straight line, $\Delta H^\circ$ and $\Delta S^\circ$ can be determined from intercept and slope, respectively.

The negative values of $\Delta G^\circ$ indicated thermodynamically feasible and spontaneous nature of the adsorption of Cd(II) by nanoparticles of spinel sorbent. The decrease in negative $\Delta G^\circ$ values together with an increase in temperatures shows an increase in feasibility of sorption at higher temperatures. The negative $\Delta H^\circ$ indicates the exothermic nature of the sorption process. The $\Delta H^\circ$ and $\Delta S^\circ$ values for Co$_{0.5}$Cu$_{0.5}$Al$_2$O$_4$ were found $-7.3$ kJ mol$^{-1}$ and 46 J mol$^{-1}$ K$^{-1}$, respectively. The positive values of entropy disclosed the increasing of randomness at the solid/liquid interface, suggesting the affinity of Cd ions on the surface of ferrite adsorbents [44]. Table 4 shows thermodynamic parameters for Cd adsorption onto Co$_{0.5}$Cu$_{0.5}$Al$_2$O$_4$ sorbents.

### Table 3
Langmuir and Freundlich constants for the adsorption of Cd(II) onto Co$_{x}$Cu$_{1–x}$Al$_2$O$_4$ ($x = 0–1$) nanoparticles

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>$K_f$</th>
<th>$N$</th>
<th>$R^2$</th>
<th>$q_m$ (mg g$^{-1}$)</th>
<th>$K_C$ (L mg$^{-1}$)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoAl$_2$O$_4$</td>
<td>325</td>
<td>1.2</td>
<td>0.83</td>
<td>92</td>
<td>34.7</td>
<td>0.95</td>
</tr>
<tr>
<td>Co$<em>{0.5}$Cu$</em>{0.5}$Al$_2$O$_4$</td>
<td>345</td>
<td>2.8</td>
<td>0.86</td>
<td>145</td>
<td>38</td>
<td>0.98</td>
</tr>
<tr>
<td>Co$<em>{0.7}$Cu$</em>{0.3}$Al$_2$O$_4$</td>
<td>463</td>
<td>3.8</td>
<td>0.80</td>
<td>124</td>
<td>36.2</td>
<td>0.97</td>
</tr>
<tr>
<td>CuAl$_2$O$_4$</td>
<td>542</td>
<td>6.4</td>
<td>0.82</td>
<td>98</td>
<td>34.3</td>
<td>0.97</td>
</tr>
</tbody>
</table>

### Table 4
Thermodynamic parameters for adsorption of Cd(II) by adsorption onto Co$_{x}$Cu$_{1–x}$Al$_2$O$_4$ ($x = 0–1$) nanoparticles

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T$ (K)</th>
<th>$\Delta G^\circ$ (kJ mol$^{-1}$)</th>
<th>$\Delta H^\circ$ (kJ mol$^{-1}$)</th>
<th>$\Delta S^\circ$ (J mol$^{-1}$ K$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoAl$_2$O$_4$</td>
<td>303</td>
<td>-15.387</td>
<td>-5.6</td>
<td>32.3</td>
</tr>
<tr>
<td>Co$<em>{0.7}$Cu$</em>{0.3}$Al$_2$O$_4$</td>
<td>303</td>
<td>-19.36</td>
<td>-6.6</td>
<td>42</td>
</tr>
<tr>
<td>Co$<em>{0.5}$Cu$</em>{0.5}$Al$_2$O$_4$</td>
<td>303</td>
<td>-21.24</td>
<td>-7.3</td>
<td>46</td>
</tr>
<tr>
<td>CoAl$_2$O$_4$</td>
<td>313</td>
<td>-19.74</td>
<td>-6.6</td>
<td>38</td>
</tr>
<tr>
<td>Co$<em>{0.7}$Cu$</em>{0.3}$Al$_2$O$_4$</td>
<td>313</td>
<td>-20.167</td>
<td>-7.3</td>
<td>46</td>
</tr>
<tr>
<td>Co$<em>{0.5}$Cu$</em>{0.5}$Al$_2$O$_4$</td>
<td>313</td>
<td>-18.8</td>
<td>-6.9</td>
<td>38</td>
</tr>
</tbody>
</table>

3.7. Regeneration of spinel sorbent

The adsorption capacity of the Co$_{0.5}$Cu$_{0.5}$Al$_2$O$_4$ nano spinel for Cd(II) after its regeneration has also been studied. The spent nano spinel was regenerated following the process mentioned above. Experiments on adsorption desorption and regeneration of nano spinel was performed with batch method. Thus, the Cd(II) ions are recovered and the nano spinel can be reused many times for desorption. Once the adsorption process had been finished, the centrifuged solids were washed with some drops of double distilled water to dilute and remove residual solution. Commonly, it is known that heavy metals can be separated from nano spinel by desorption in an inorganic acid or alkaline medium. Therefore, nitric acid, hydrochloric acid, sulphuric acid and acetic acid 0.1 M were verified for desorption. 50 mL of 50 mg L$^{-1}$ of Cd solution at pH 6 stirred for 90 min for Co$_{0.5}$Cu$_{0.5}$Al$_2$O$_4$ nanoparticles. The mixture was stirred at 150 rpm in an orbital shaker at 25°C for 90 min. After the filtration, the residue was treated with different acids. Among them 0.1 M nitric acid gave the most effective result releasing about 90% of metal ions onto the solution in four successive cycles. Results are shown in Fig. 10. Results showed that the order of acids was as follows: nitric acid > hydrochloric acid > sulphuric acid > acetic acid. Therefore, HNO$_3$ was selected as a regenerating agent [45].

4. Conclusion

In this work, the nanosized spinels of Co$_{x}$Cu$_{1–x}$Al$_2$O$_4$ were successfully prepared. The XRD patterns and FTIR
Adsorption of Cd(II) ions depends on their initial concentrations, pH and contact time. Adsorption process was followed by the pseudo-first-order kinetic model and isothermal data of adsorption on sorbent can be modeled by Langmuir isotherm. Desorption order kinetic model and isothermal data of adsorption on these spinel ferrites are very efficient for removal of Cd(II).

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