



Synthesis of CaO/Fe₃O₄ magnetic composite for the removal of Pb(II) and Co(II) from synthetic wastewater

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Abstract: In this study, CaO was prepared from chicken egg shells. Then, to improve its properties, CaO/Fe₃O₄ magnetic composite was synthesized and was used for the removal of lead (Pb (II)) and cobalt (Co (II)) ions from aqueous solutions. For this purpose, the effects of several parameters including pH, contact time, temperature, adsorption dosage and initial concentration of ions on the adsorption were studied. The optimum conditions of pH, contact time, temperature, adsorption dosage and initial concentration of Pb and Co ions were determined to be 6, 30 min, 25 °C, 2 g L⁻¹ and 5 mg L⁻¹, respectively. The best efficiency for the adsorption of lead and cobalt ions was found to be 97.24 and 94.32 %, respectively. To investigate the equilibrium behaviour of adsorbent, Langmuir and Freundlich models were used. Also, pseudo-first order and pseudo-second order kinetic models were applied for the consideration of kinetic behaviours of experimental data. Additionally, the thermodynamic parameters including enthalpy, entropy and Gibbs energy were calculated for the adsorption of these heavy metal ions. The results showed that Freundlich isotherm model and the pseudo-second order kinetic model achieved the best match with the experimental data and the maximum adsorption capacities obtained from the Langmuir model were 227.27 and 217.39 mg g⁻¹ for lead and cobalt, respectively. Also, thermodynamics studies revealed that the adsorption process of lead and cobalt ions using CaO/Fe₃O₄ was suitable, spontaneous and exothermic.

Keywords: adsorption; heavy metals; CaO/Fe₃O₄ composite; equilibrium and thermodynamics study.

INTRODUCTION

Recently, water pollution has been a serious problem that affects human, animals, plants and every living organism. Among these contaminants, pollution from heavy metal is one of the most significant environmental problems through-

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out the world. Heavy metals are toxic, carcinogenic, non-biodegradable and lead to public health problems even at low concentration.¹

These metals exist in the natural water due to several industrial discharges such as, alloys, smelting, mining, paper industries, pesticides and etc.²⁻⁵

Lead (II) is known as one of the major environmental pollutants that can cause damage to liver, kidney, lungs, reproductive system, circulatory system and brain functions.⁶ Cobalt pollution comes from cobalt salts in nuclear medicine, semi-conductor production and electroplating.⁷ Although the low amount of cobalt is vital for living organisms, especially for human health,¹ it may cause genetic problems and cell mutations in the human body in high amount.⁷ Various methods for the removal of lead and cobalt from aqueous solution have been used, including: chemical precipitation, oxidation-reduction, evaporation, adsorption, ionic exchange, electrochemical treatment, membrane separation techniques, reverse osmosis processes, liquid-liquid extraction and resin cementation.^{2,4,8-10} At low metal concentration (less than 100 mg L⁻¹), these methods are costly, inefficient and difficult.¹¹ Among these methods, adsorption has been suggested as one of the most common process for small and medium scale heavy metal removal.¹²⁻¹⁴

Different adsorbents are reported in the literature.¹⁵ Recently, magnetic particles have gained special attention in water treatment,⁸ in terms of simplicity, high potential, high surface area and high efficiency to remove heavy metal ions from waste water.

Of these particles, Fe₃O₄ is the traditional particle that is extensively used in wastewater treatment; because it is highly active, hydrophilic, chemically stable, non-toxic and magnetic. Also, it's an environment-friendly adsorbent, cheap and available.^{4,16}

The main purpose of this work was to study the removal of heavy metals (lead and cobalt) from aqueous solutions by CaO/Fe₃O₄ as a magnetic adsorbent. Subsequently, the effects of several parameters including pH, temperature, contact time, initial concentration of Pb²⁺ and Co²⁺ and adsorbent dosage, on the adsorption, were studied. In addition, kinetic, thermodynamic and equilibrium behaviours of the adsorbent were studied, too.

EXPERIMENTAL

Chemical and materials

FeCl₃·6H₂O, FeCl₂·4H₂O, Pb(NO₃)₂ and Co(NO₃)₂·6H₂O were obtained from Merck company (Germany). All the materials were used in the analytical grade without any purification.

Stock solution

In this study, a stock solution of Pb²⁺ and Co²⁺ with a concentration of 1000 mg L⁻¹, were prepared by dissolving of Pb(NO₃)₂ and Co(NO₃)₂·6H₂O salts in deionised distilled water. Other solutions with the desired concentrations were prepared by dilution of the stock sol-

ution. In order to adjust the initial pH of the solutions, HCl (0.1 Mol L⁻¹) and NaOH (0.1 mol L⁻¹) were used. For measuring the pH of the solutions, digital pH-meter (model Metrohm 744) was applied. All batch experiments were carried out in an Erlenmeyer flask with 250 ml volume, including 50 ml solution, containing lead and cobalt ions.

Preparation of CaO

Calcium oxide was synthesized from egg shells. Collected egg shells were washed several times with water and then they were kept for 10 h in an oven, at 105 °C, until completely dry. Afterwards they were calcined in Furnace at 800 °C for 4 h.

After being cooled, the egg shells were crushed using mortar and pestle for 30 min, and then were stored in the plastic air tight containers.

Preparation of CaO/Fe₃O₄ magnetic composite

In order to support the Fe₃O₄ nanoparticles on CaO, a solution containing Fe³⁺ and Fe²⁺ in a 2:1 mole ratio was prepared. Then, under vigorous magnetic stirring at 60 °C, CaO (1.0 g) was added and mixed for 20 min, with 400 rpm speed.

After that, NaOH (3 M) was added dropwise into the solution until the colour of solution changed to black and the oxidation reaction was carried out. Then the prepared magnetic composite was washed several times with distilled water. After washing, the obtained adsorbent was separated from water and was dried in an oven at 105 °C for 24 h.

Characterization of adsorbent

The surface area of CaO and CaO/Fe₃O₄ was determined by Brunauer–Emmet–Teller (BET, instrument model ASAP 2020). X-ray powder diffractometer (XRD, Broker AXS-D8 Advance) was used to determine the crystal structure of the adsorbent and X-ray fluorescence (XRF, Spectro iQ) was used for elemental analysis.

Raman and Fourier transform infrared spectroscopy (FTIR, Perkin Elmer, model Spectrum two) were also used to characterize the functional groups of the CaO and CaO/Fe₃O₄. To study the morphology and surface characterizations of adsorbents after and before adsorption, scanning electron microscopy (SEM, model Hitachi 4160) was used. Additionally, dynamic light scattering (DLS, Zeta Plus, Brookhaven) was used for the determination of the particle size of adsorbent.

To determine pH_{pzc} (point of zero charge), 0.1 M KCl first was prepared. Afterwards 2.0 g of CaO/Fe₃O₄ adsorbent was added to 10 ml of the aqueous solution where the initial pH (pH_i) was adjusted from 2 to 10 by the addition of either HCl (0.1 mol L⁻¹) or NaOH (0.1 mol L⁻¹). This solution was placed in a shaker at room temperature for 24 h. After that, the final pH (pH_f) was recorded and a plot of the initial solution pH *versus* the final pH gives the pH_{pzc} value for the adsorbent.^{5,16-18}

Adsorption experiment

In this study, the effect of parameters including pH (2.0–11.0), temperature (25–55 °C) contact time (5–50 min), adsorbent dosage (0.25–5 g L⁻¹) and the initial concentration of metal ions (5–50 mg L⁻¹) on the adsorption of cobalt and lead ions, were investigated. Each experiment was repeated twice, and the average result was reported.

After experiments, CaO/Fe₃O₄ particles were separated by an external magnetic field from the solution, and the absorbance amounts of metal ions were measured in an atomic absorption spectrophotometer (Plus Specter AA-10 model, Varian Company).

In all cases, the amounts of lead and cobalt adsorbed (*R*) are calculated by Eq. (1):

$$R = 100 \frac{c_i - c_0}{c_i} \quad (1)$$

where c_0 and c_i are the initial and equilibrium concentration of metal ions, respectively.

RESULTS AND DISCUSSION

Characterization

As shown in Fig. 1, from the SEM images with the same resolution, before adsorption, there are heterogeneous surfaces with high roughness, both in case of CaO and CaO/Fe₃O₄. (Fig. 1a and b, respectively). After adsorption, as it is shown in Fig. 1c and d, it can be clearly observed that many ions are located on CaO/Fe₃O₄ surface.

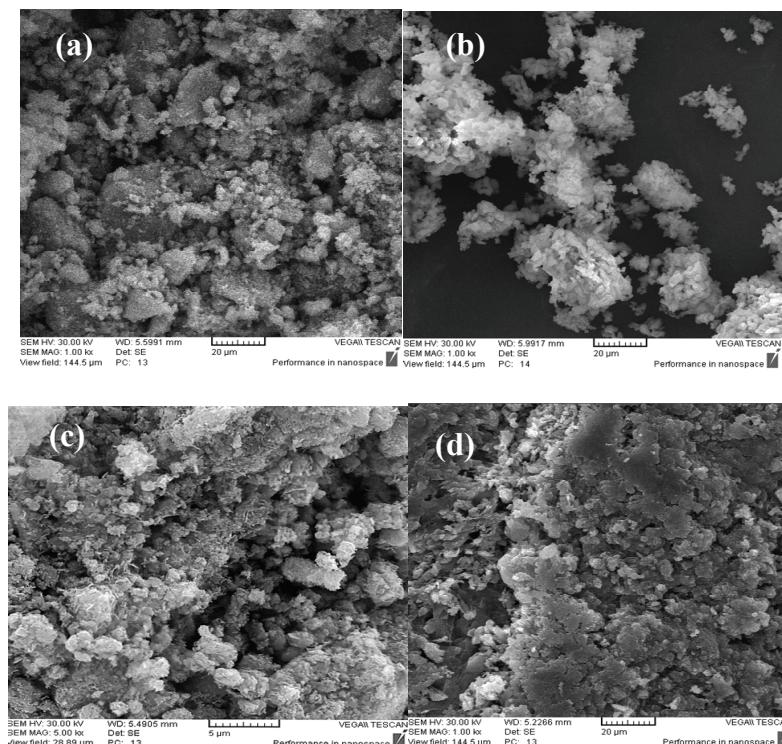


Fig. 1. SEM images of: a) CaO, b) CaO/Fe₃O₄, c) CaO/Fe₃O₄+Pb²⁺ and d) CaO/Fe₃O₄+Co²⁺.

Also, the BET analysis shows that the adsorbents have the surface area of 41.47 and 71.23 m² g⁻¹, the average pore diameter (APD) of 50.38 and 96.14 Å and the total pore volume (TPV) of 0.094 and 0.178 cm³ g⁻¹ for CaO and CaO/Fe₃O₄, respectively.

Additionally, the chemical compositions of CaO and CaO/Fe₃O₄ obtained by XRF are shown in Table I, which shows the presence of CaO and Fe₃O₄ as original compounds and other compounds with low percentages as impurities.

TABLE I. XRF analysis of CaO and CaO/Fe₃O₄

Sample	SiO ₂	Al ₂ O ₃	Fe ₃ O ₄	CaO	Na ₂ O	MgO	K ₂ O	TiO ₂	MnO	P ₂ O ₅	LOI
CaO	12.557	None	0.434	63.598	0.012	0.49	None	0.012	0.015	0.206	21.9
CaO/Fe ₃ O ₄	None	None	59.978	22.394	0.69	1.121	None	0.013	0.151	0.144	7.6

Fig. S-1 of the Supplementary material to this paper displays FTIR spectra of CaO, CaO/Fe₃O₄, CaO/Fe₃O₄+Pb²⁺ and CaO/Fe₃O₄+Co²⁺ composite. Extracted information from the spectra are shown in Table II.

TABLE II. Information extracted from the FTIR analysis of CaO, CaO/Fe₃O₄, CaO/Fe₃O₄+Pb²⁺ and CaO/Fe₃O₄+Co²⁺ (wave number, cm⁻¹)

Bond	Material			
	CaO/Fe ₃ O ₄ +Co ²⁺	CaO/Fe ₃ O ₄ +Pb ²⁺	CaO/Fe ₃ O ₄	CaO
Ca–O	441	441	447	433
Fe–O	586	584	588	–
O–C–O	873	875	873	875
	1119	1053	1124	1061
	1446	1411	1453	1466
C=O	1635	1629	1635	1635
O–H	3405	3433	3427	3441
N–H Bending	–	–	–	548
N–H Amide	–	–	–	3641

Moreover, X-ray diffraction analysis was done on the powder samples of CaO and CaO/Fe₃O₄. X-ray diffraction patterns were plotted by the X-pert software and X-ray diffraction lines were indexed. Peaks of MgO, CaO, Ca(OH)₂ and Fe₃O₄ compounds were matched with the reference card numbers: 00-004-0829, 01-070-4068, 00-044-1481 and 01-075-0449 that is shown in Fig. 2.

Eventually, the DLS measurements (Fig. S-2 of the Supplementary material) reveal the dimensions of the synthesized material (219.5 nm).

Effect of pH

The initial pH of the solution during adsorption is considered as one of the most important parameters, because hydrogen ions themselves are highly competing with the adsorbate.¹⁹ Also, it has an effect on the change in surface charge and the ionization degree of the adsorbed material (metal ions), during the adsorption process.

Point of zero charge (pH_{pzc}) of the CaO/Fe₃O₄ has shown in Fig. 3. As shown, pH_{pzc} is obtained 6.8.

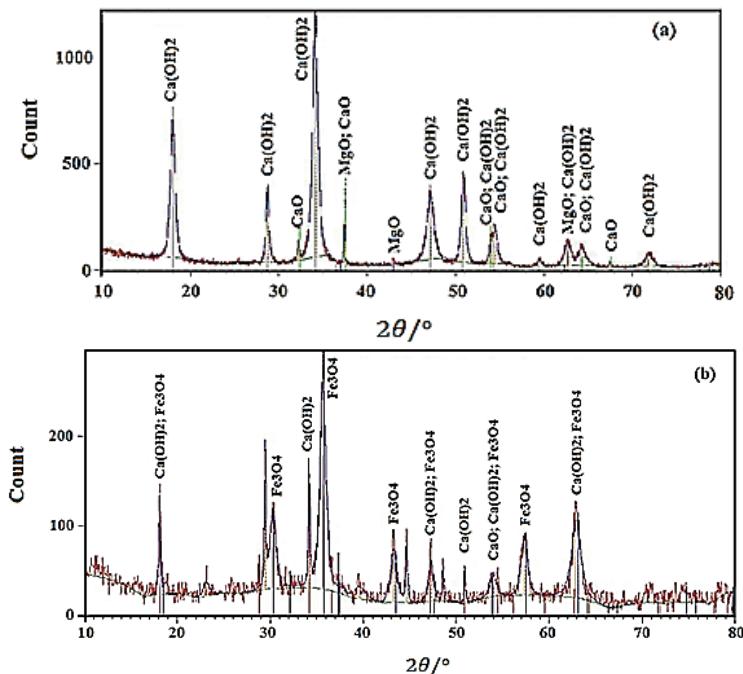


Fig. 2. XRD analysis of: a) CaO and b) CaO/Fe₃O₄.

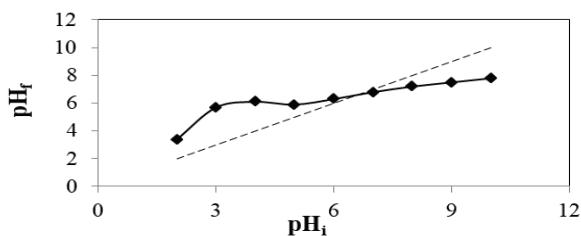


Fig. 3. Point of zero charge (pH_{pzc}) of the $\text{CaO}/\text{Fe}_3\text{O}_4$.

Then, the effect of pH with varying values (2.0–11.0) was investigated on the adsorption of Co^{2+} and Pb^{2+} by means of $\text{CaO}/\text{Fe}_3\text{O}_4$ and keeping all other parameters constant (adsorbent dosage 2 g L^{-1} , contact time 80 min, temperature 25°C , initial metal ion concentration 5 mg L^{-1}).

In Fig. 4, the percentage of metal removed by $\text{CaO}/\text{Fe}_3\text{O}_4$ versus initial solution pH has been plotted. The results indicate that, by increasing the initial pH from 2.0 to 6.0, metal ion adsorption efficiency increases, so that, the optimum uptake of the Co^{2+} and Pb^{2+} take place at around pH 6.0. After that, the adsorption of lead and cobalt was decreased; so that, the highest amounts of removal of these metal ions were 97.84 and 94.52 %, for lead and cobalt respectively.

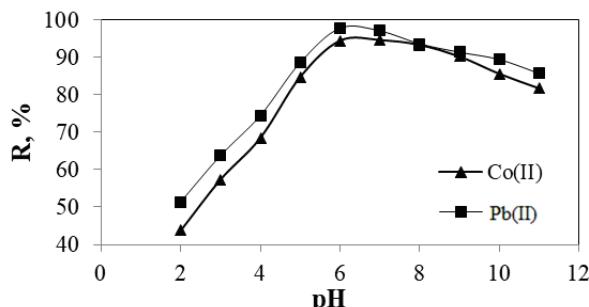


Fig. 4. The effect of pH on the removal of Pb²⁺ and Co²⁺ using CaO/Fe₃O₄ (contact time 80 min, adsorbent dosage 2 g/l, initial metal ion concentration 5 mg/l, mixture rate 200 rpm, and temperature 25 °C).

At pH < 6.8 (pH_{pzc} 6.8), there is a competition effect between heavy metal and hydrogen ions. So, as the result of the high amount of hydrogen ions in the solution, functional groups on the adsorbent are protonated and the CaO/Fe₃O₄ surfaces have positive charges.

With the increasing pH, the amount of hydrogen ions (H₃O⁺) in the solution is decreased and the competitive effects also reduce. At pH 6.8, the functional groups have negative charges, which leads to the electrostatic attraction between positively charged ions, (metal ions), and negatively charged functional groups.²⁰

Also at higher pHs (pH > 6.8), the percentage of the removal of metal ions was decreased again, because lead and cobalt ions get out of the solution due to formation of hydroxide.

Namely, it can be said that the optimum pH for adsorption by CaO/Fe₃O₄ is 6.

Effect of contact time and temperature

The contact time is one of the most significant parameter that plays an important role in batch adsorption experiments. In order to investigate the effect of contacting time on the adsorption of metal ions, further experiments were performed at pH 6, by varying the contact time from 5 to 120 min. Fig. 5 shows the effect of the contact time on the adsorption percentage of lead and cobalt ions at different temperatures (25–55 °C). According to the Fig. 5, it can be assumed that the adsorption process consists of two stages: a fast and a slow one.

Initially, the adsorption percentage of the metal ions onto CaO/Fe₃O₄ increased quickly, so that the maximum adsorption percentages of lead and cobalt of 97.24 and 94.32, respectively, were obtained within 30 min. Afterwards, the adsorption process was reduced and this reduction was done slowly.

It is obvious that there were a large number of unsaturated active sites for adsorption at the initial stage. In the next step, with gradual occupation of these sites, the adsorption efficiency started to decrease.²¹

Rapid adsorption can be attributed to the mutual attraction between the negatively charged surface of the adsorbent and positively heavy metal ions. With the increasing time, the repulsive forces between the heavy metal ions, (lead and cobalt) lead to a slow down in the adsorption process.^{21,22}

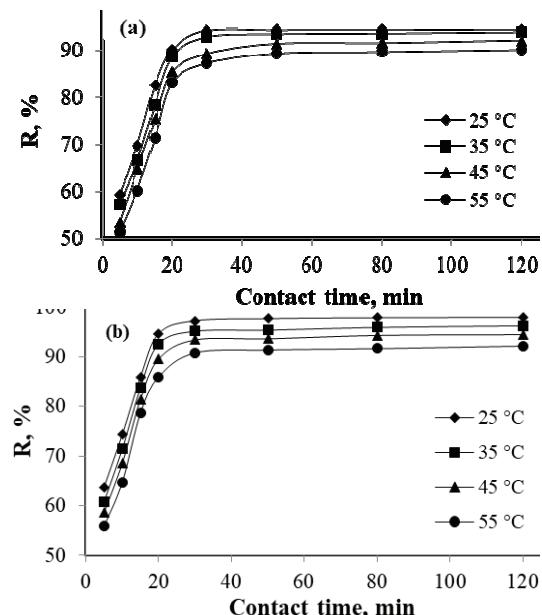


Fig. 5. The effect of time and temperature on the removal of: a) Co^{2+} and b) Pb^{2+} using $\text{CaO}/\text{Fe}_3\text{O}_4$ (pH 6, adsorbent dosage 2 g L^{-1} , initial metal ion concentration 5 mg L^{-1} , mixture rate 200 rpm).

Another important parameter in the metal ion adsorption process is the temperature.²³ The percentage removal was decreased with the increasing temperature. It may be due to the high tendency of metal ions to separate from the adsorbent and release in the solution with the increase of the temperature of the solution.²⁴ So, the adsorption of Pb^{2+} and Co^{2+} by $\text{CaO}/\text{Fe}_3\text{O}_4$ was exothermic.

The optimum temperature for further adsorption experiments was taken to be 25°C .

Effect of metal ions concentration

In the adsorption process, the initial metal ion concentration plays a key role as a driving force to provide essential energy for the mass transfer between the solution and adsorbent.²⁵

Fig. 6 indicates the effect of different concentrations of Pb^{2+} and Co^{2+} on the adsorption percentage and adsorption capacity per gram of dry adsorbent under the optimized conditions of initial pH 6.0, contact time 30 min, temperature 25°C , adsorbent dosage 2 g L^{-1} and mixing rate 200 rpm . The concentrations of lead and cobalt ions varied from $5\text{--}120 \text{ mg L}^{-1}$. The percentage adsorption of lead and cobalt decreased with the rise of the lead and cobalt concentration.

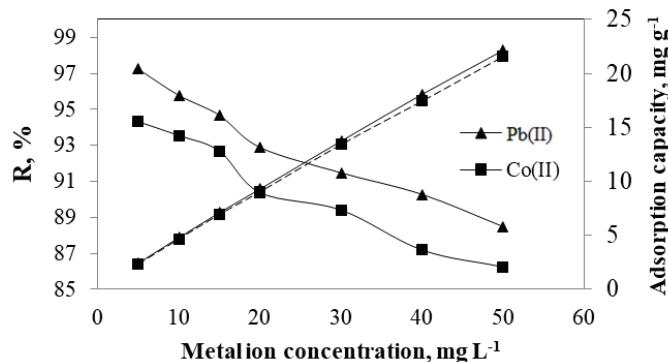


Fig. 6. The effect of initial metal ion concentration on the removal of Pb²⁺ and Co²⁺ using CaO/Fe₃O₄ (initial pH 6, temperature 25 °C, contact time 30 min, adsorbent dosage 2 g L⁻¹, mixture rate 200 rpm).

At low concentrations of Pb²⁺ and Co²⁺, there were a lot of active sites on the adsorbent to react with metal ions, while at higher concentration of Pb²⁺ and Co²⁺, the number of active sites on the adsorbent surface was not adequate to complex with metal ions.¹²

Also, it was found that with the increasing of lead and cobalt ion concentration, the uptake capacity of the adsorbent increased because of higher availability of lead and cobalt ions in the aqueous solution for the adsorption.

So, the maximum adsorption capacities (q_{\max}) of Pb²⁺ and Co²⁺ using CaO/Fe₃O₄ adsorbent are 22.1 and 21.6 mg g⁻¹, for 5 mg L⁻¹ Pb²⁺ and Co²⁺, respectively.

Effect of adsorbent dosage

The another important parameter in adsorption studies is the adsorbent dosage. This parameter determines the potential of an adsorbent to adsorb the metal ions for a standard concentration of the adsorbates.²⁶

The effect of adsorbent dosage on the equilibrium adsorption of Pb (II) and Co (II) was studied in the conditions: initial pH 6, contact time 30 min, mixture rate 200 rpm and initial metal ions concentration 5 mg L⁻¹. The results are indicated in Fig. 7.

As shown in Fig. 7, with the increase in adsorbent dosage from 0.25 to 2 g L⁻¹, the percentage removal increased from 58.83 to 97.24 for Pb (II) and from 55.58 to 94.32 for Co (II).

This increase is mainly the result of the larger surface area and also more numbers of active sites available to react with metal ions. By increasing the adsorbent dosage from 2 to 5 g L⁻¹, the metal ion adsorption efficiently was maintained almost constant and with no significant differences.

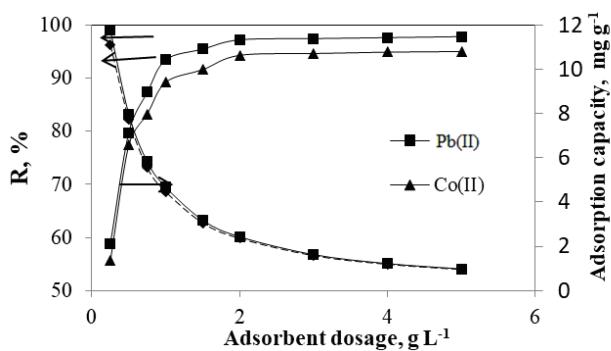


Fig. 7. The effect of adsorbent dosage on the removal of Pb^{2+} and Co^{2+} using $\text{CaO}/\text{Fe}_3\text{O}_4$ (pH 6, temperature 25 °C, initial metal ion concentration 5 mg/l, contact time 30 min, mixture rate 200 rpm).

In addition, with the increase in adsorbent dosage the adsorption capacity was decreased. It may be because of the lack of availability of the more active sites due to overlapping and aggregation.

The optimum percentages removal of Pb^{2+} and Co^{2+} obtained were 97.24 and 94.32 for 2 g L^{-1} of adsorbent, respectively. Also, the highest adsorption capacities obtained were 11.766 and 11.116 mg g^{-1} for 0.25 g L^{-1} of the adsorbent for lead and cobalt ions, respectively.

Kinetic study

In this study, pseudo-first-order and pseudo-second-order kinetic models were employed to predict the kinetic rate of Pb^{2+} and Co^{2+} adsorption. The details are given in Supplementary material.

For the adjusting of laboratory data with kinetic models the correlation coefficient (R^2) was used.

The values of calculated ($q_{e,\text{cal}}$) and experimental ($q_{e,\text{exp}}$) equilibrium adsorption capacity, the correlation coefficients and the rate constants related to the kinetic plots are presented in Table III. It can be seen that the correlation coefficients for the second-order model are more close to 1, for both metal ions. Moreover, the values of calculated and experimental q_e are in the best match with pseudo second-order model.

Consequently, based on the result, the pseudo-second-order kinetic model is more capable and reliable to explain the kinetic behaviour of adsorbent.

Isotherm study

The adsorption isotherm model describes the interaction between the amount of the metal ions adsorbed on the adsorbent and the metal ion concentration at equilibrium.^{21,27,28} The experimental data from the study of Pb^{2+} and Co^{2+}

adsorption by CaO/Fe₃O₄ are analyzed using Langmuir and Freundlich equations. The details are given in Supplementary material.

TABLE III. Kinetic model parameters for the adsorption of Pb²⁺ and Co²⁺ onto CaO/Fe₃O₄ magnetic particles

Kinetic model	Parameter	Co ²⁺	Pb ²⁺
Pseudo-first order	k_1/min^{-1}	0.143	0.168
	$q_{e,\text{cal}}/\text{mg g}^{-1}$	2.140	2.509
	R^2	0.955	0.917
Pseudo-second order	$k_2/\text{g mg}^{-1}\text{min}^{-1}$	0.173	0.184
	$q_{e,\text{cal}}/\text{mg g}^{-1}$	2.433	2.512
	R^2	0.999	0.999
	$q_{e,\text{exp}}/\text{mg g}^{-1}$	2.358	2.431

The results show the Freundlich isotherm model have greater correlation coefficient values (R^2), compared with the Langmuir isotherm model. So the adsorption data achieved the best fitted to the Freundlich adsorption model.

Moreover, the value of n obtained from the Freundlich isotherm for Pb²⁺ and Co²⁺ adsorption was 1.0424. It shows the physical nature of adsorption.

Thermodynamic study

In order to determine the thermodynamic behaviour of the adsorption of lead and cobalt ions in the aqueous solution, the effect of temperature on the adsorption of these ions by CaO/Fe₃O₄ was evaluated at four different temperatures (25, 35, 45 and 55 °C). The details are given in Supplementary material. The negative values of Gibbs energy and enthalpy changes confirmed that the removal of Pb²⁺ and Co²⁺ metals onto CaO/Fe₃O₄ is spontaneous and exothermic. Also, the positive values of entropy change means that the random encounters at the solid/solution interface were increased during the adsorption process of these heavy metal ions.

CONCLUSION

In this investigation, the adsorption characteristics of lead and cobalt ions from aqueous solutions using CaO/Fe₃O₄ were studied in a batch system. The effects of useful parameters such as pH, temperature, contact time, initial metal ion concentration and adsorbent dosage were studied, and pH 6.0, temperature 25 °C contact time 30 min, adsorbent dosage 2g L⁻¹ and initial metal ion concentration 5 mg/L were determined to be the optimal experimental parameters for lead and cobalt ions. To characterize the behaviour of the metal ion adsorption isotherm using CaO/Fe₃O₄, the Langmuir and Freundlich isotherm models were used. As the results showed, the Freundlich isotherm model fitted well with the experimental data. The pseudo-first order and pseudo-second order kinetic models were also used to describe the kinetic behaviours of the adsorption pro-

cess. Based on the result, the pseudo-second order achieved the best fit with the experimental data. Finally, the thermodynamic parameters including entropy, enthalpy and Gibbs energy changes for the adsorption process of lead and cobalt ions were calculated. The results show that the adsorption of these metal ions is favourable, spontaneous and exothermic.

SUPPLEMENTARY MATERIAL

Additional experimental details and details related to kinetic and adsorption studies are available electronically at the pages of journal website: <http://www.shd.org.rs/JSCS/>, or from the corresponding author on request.

ИЗВОД
СИНТЕЗА МАГНЕТОГ КОМПОЗИТА CaO/Fe₃O₄ ЗА УКЛАЊАЊЕ Pb(II) И Co(II) ИЗ
СИНТЕТИЧКЕ ОТПАДНЕ ВОДЕ

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У овој студији, CaO је припремљен из љуски од јаја. За побољшање његових особина синтетисан је магнетични CaO/Fe₃O₄ композит, који је употребљен за уклањање јона олова и кобалта из водених растворова. Проучени су утицаји неколико параметара, укључујући pH, време контакта, температуру, дозу адсорбента и почетну концентрацију јона на адсорпцију. Оптимални услови за pH, време контакта, температуру, дозу адсорбента и почетну концентрацију јона Pb и Co су били 6,0, 30 min, 25 °C, 2 g L⁻¹ и 5 mg L⁻¹, редом. Најефикаснија адсорпција је била 97,25 % за олово и 94,32 % за кобалт. Равнотежно понашање адсорбента је испитивано Лангмировим и Фројндлиховим моделима. Такође, експериментални подаци су апроксимирани кинетиком псеудо-првог и псеудо-другог реда. Додатно, за адсорпцију ових тешких метала израчунате су промене енталпије, ентропије и Гибсове енергије. Резултати су показали да се модел Фројндлихове изотерме и псеудо-други ред реакције најбоље слаже са експерименталним подацима, а максимални капацитети адсорпције добијени из Лангмировог модела су били 227,27 и 217,39 mg g⁻¹ за олово и кобалт, редом. Такође, термодинамичко испитивање је показало да је адсорпциони процес јона олова и кобалта уз коришћење CaO/Fe₃O₄ повољан, спонтан и егзотерман.

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