Journal of the Serbian Chemical Society
JSCS@tmf.bg.ac.rs • www.shd.org.rs/JSCS
J. Serb. Chem. Soc. 83 (2) S137–S142 (2018)
Supplementary material

SUPPLEMENTARY MATERIAL TO

Synthesis of CaO/Fe_3O_4 magnetic composite for the removal of Pb(II) and Co(II) from synthetic wastewater

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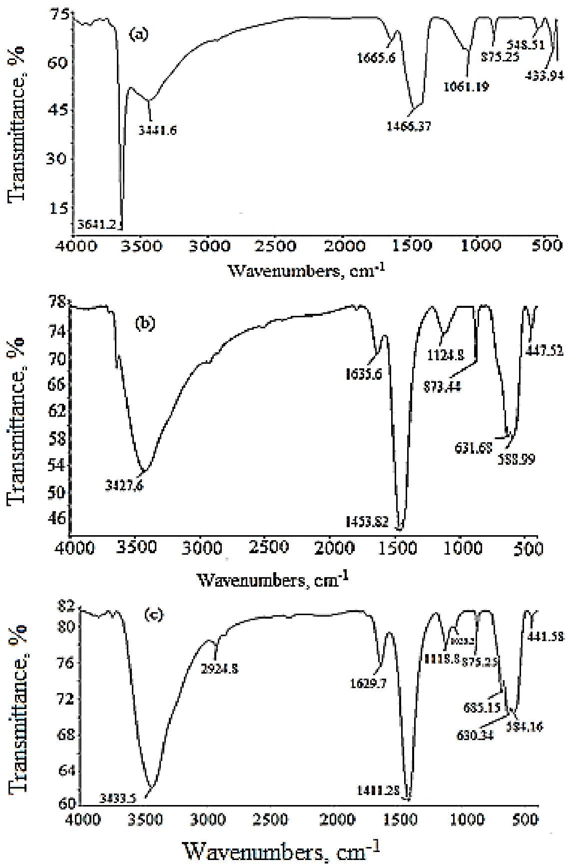
J. Serb. Chem. Soc. 83 (2) (2018) 237–249



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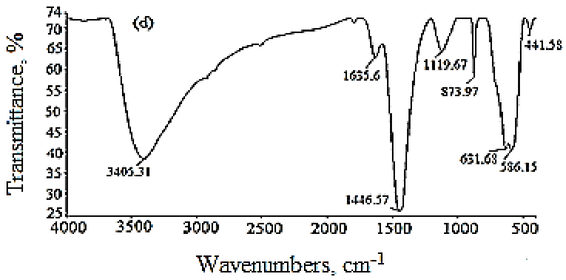

Fig. S-1. FT-IR analysis of: a) CaO, b) CaO/Fe_3O_4, c) $CaO/Fe_3O_4 + Pb^{2+}$ and d) $CaO/Fe_3O_4+Co^{2+}$.

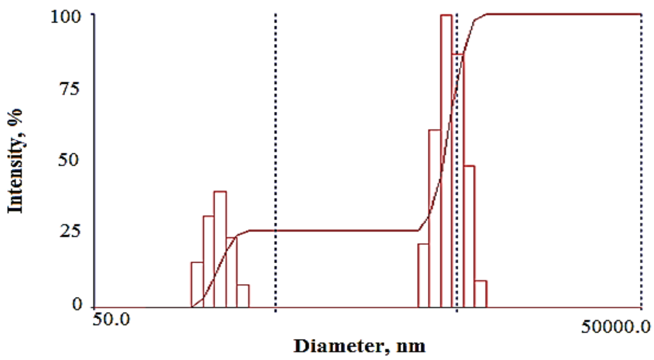

Fig. S-2. DLS analysis of CaO/Fe_3O_4.

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 linear form of the pseudo-first-order is shown in Eq. (S-1):[1]

$$\mathrm{Ln}(q_e - q_t) = \mathrm{Ln}\, q_e - k_1 t \qquad \text{(S-1)}$$

where k_1 is the pseudo-first-order rate constant of the equation (min^{-1}), q_e and q_t are the amounts of lead and cobalt ions adsorbed on adsorbent at equilibrium and time t, respectively (mg g^{-1}).[1-4]

By plotting of ln (q_e-q_t) versus t, the adsorption rate constant, k_1 and q_e for Pb^{2+} and Co^{2+} ions were calculated (Fig. S-3).

The linear equation of the pseudo-second-order model is expressed in Eq. (S-2):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad \text{(S-2)}$$

where k_2 is the pseudo-second-order rate constant of the equation (g mg^{-1}min^{-1}), and q_e and k_2 calculated by plot of t/q_t versus t (Fig. S-3).[1,2]

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

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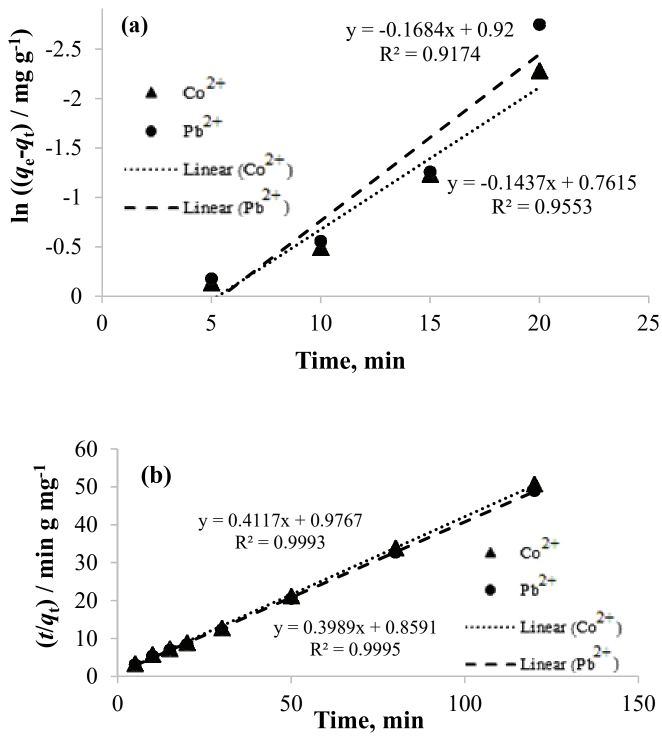

Fig. S-3. The adsorption kinetic curves related to: a) pseudo-first order and b) pseudo-second order model for the adsorption of Pb^{2+} and Co^{2+} at various contact time

Isotherm study

The adsorption isotherm model describes the interaction between the amount of metal ions adsorbed on adsorbent and metal ion concentration at equilibrium.[1,4,5] The experimental data from the study of Pb^{2+} and Co^{2+} adsorption by CaO/Fe_3O_4 are analyzed using Langmuir and Freundlich equations. The Langmuir isotherm assumes that the adsorbent surface is homogeneous, the number of active sites on the adsorbent is constant, and the adsorption process is reversible.[1,4]

The Langmuir isotherm is expressed by:

$$\frac{c_e}{q_e} = \frac{1}{K_L q_m} + \frac{c_e}{q_m} \tag{S-3}$$

where q_e / mg g^{-1}, q_m / mg g^{-1}, c_e / mg L^{-1} and k_L / L mg^{-1} are metal uptake capacity at equilibrium state, maximum uptake capacity, concentration of adsorbate at equilibrium state and Langmuir constant, respectively.

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Feasibility and shape of a Langmuir isotherm are calculated by following equation of equilibrium parameter:

$$R_L = \frac{1}{1 + K_L c_e} \tag{S-4}$$

where c_e is the initial metal ion concentration in the solution (mg L^{-1}) and K_L is Langmuir constant. The values of R_L indicate conditions and qualities of adsorption isotherm model.[28] If R_L>1, R_L=1, 0<R_L<1 and R_L=0, the adsorption process is unsuitable, linear, suitable and irreversible, respectively.[2]

The Freundlich isotherm assumes that the adsorbent surface is heterogeneous and the active sites on the adsorbent have different energy.[1] The linear form of the Freundlich can be depicted as below:

$$\mathrm{Ln}\, q_e = \mathrm{Ln}\, k_f + \frac{1}{n} \mathrm{Ln}\, c_e \tag{S-5}$$

where k_f / mg g^{-1} and $1/n$ are Freundlich constants which are determined from Fig. S-4. The n represents an adsorption deviation from linearity. If n = 1, it

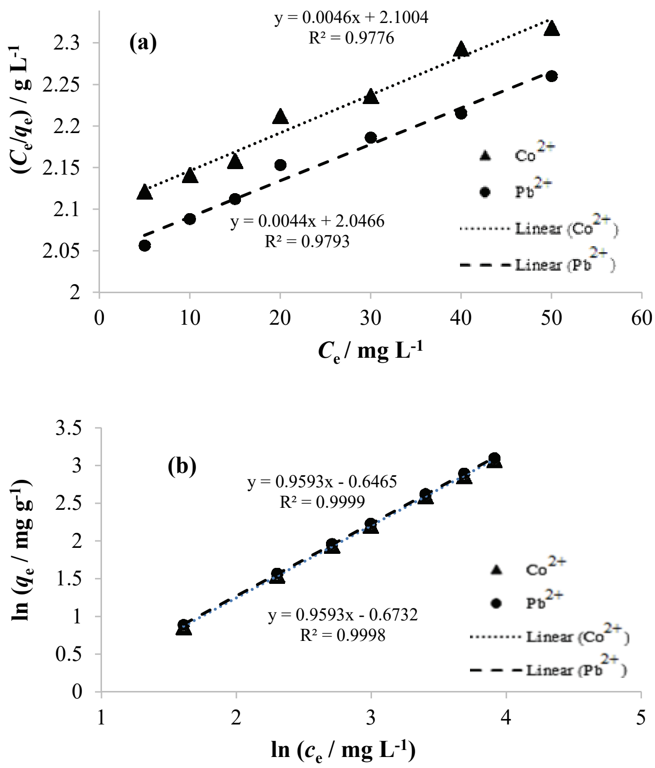

Fig. S-4. The adsorption isotherm curves related to a) Langmuir and b) Freundlich model for adsorption of Pb^{2+} and Co^{2+} on CaO/Fe_3O_4 magnetic composite.

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shows that the adsorption process is linear, $n<1$ indicating chemical adsorption process and $n>1$ shows that the adsorption of metal ions on CaO/Fe_3O_4 is a physical process at studied conditions.[1] In Table S-I, the calculated parameters related to Langmuir and Freundlich equations are listed.

TABLE S-I. Isotherm model parameters for the adsorption of Pb^{2+} and Co^{2+} using CaO/Fe_3O_4 magnetic particles

Isotherm model	Parameter	Pb^{2+}	Co^{2+}
Freundlich	n	1.0424	1.0424
	K_f / mg g^{-1} L$^{-1/n}$ min$^{1/n}$	0.523	0.510
	R^2	0.9999	0.9998
Langmuir	q_m / mg g^{-1}	227.27	217.39
	K_L / L mg^{-1}	0.00214	0.00219
	R^2	0.979	0.977
	R_L	0.002-0.085	0.002-0.083

The values of R_L in different initial concentrations of metal ions are shown in Fig. S-5. The values of R_L in initial ion concentration 5–50 mg/L of lead and cobalt ions were between 0 to 1. It indicates that CaO/Fe_3O_4 adsorbent is a suitable adsorbent to adsorption Pb^{2+} and Co^{2+} from aqueous solution.

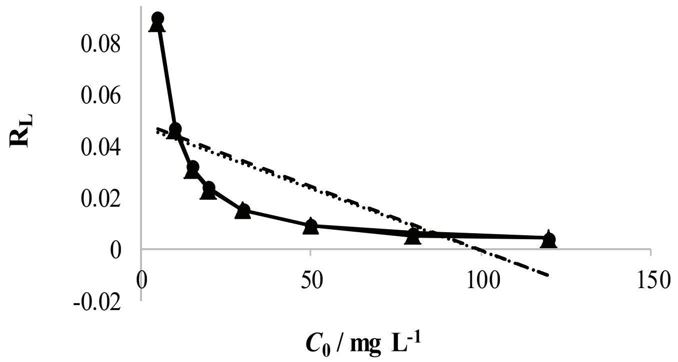

Fig. S-5. Plot of adsorption intensity (R_L) versus initial metal concentration (c_0, mg/L) for the determination of R_L values.

Thermodynamic study

The values of the thermodynamic parameters of the adsorption, such as the Gibbs energy change, ΔG / kJ mol^{-1}, enthalpy change, ΔH / kJ mol^{-1}, and the entropy change, ΔS / J mol^{-1} K^{-1}, change were analyzed. These parameters were estimated by Eqs. (S-6)–(S-8):

$$\Delta G = -RT \ln K_c \quad \text{(S-6)}$$

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$$\frac{\Delta S}{R} - \frac{\Delta H}{RT} = \ln K_c = \frac{-\Delta G}{RT} \quad \text{(S-7)}$$

$$\Delta G = \Delta H - T\Delta S \quad \text{(S-8)}$$

where K_c, is the equilibrium constant, T, is the absolute temperature (K) and R is the universal gas constant (8.314 J mol^{-1} K^{-1}), respectively.[1,4] The thermodynamic parameters for the adsorption of lead and cobalt ions are listed in Table S-II. Also, ln K_c *versus* T^{-1} for the determination of thermodynamic parameters is shown in Fig. S-6.

TABLE S-II. Thermodynamic parameters for the adsorption of Pb^{2+} and Co^{2+} on CaO/Fe_3O_4 magnetic particles

Metal ion	ΔS / kJ mol^{-1} K^{-1}	ΔH / kJ mol^{-1}	ΔG / kJ mol^{-1}			
			298.15 K	308.15 K	318.15 K	328.15 K
Pb^{2+}	84.58	–33.90	–8.82	–7.63	–6.97	–6.25
Co^{2+}	60.08	–24.94	–6.94	–6.57	–5.62	–5.26

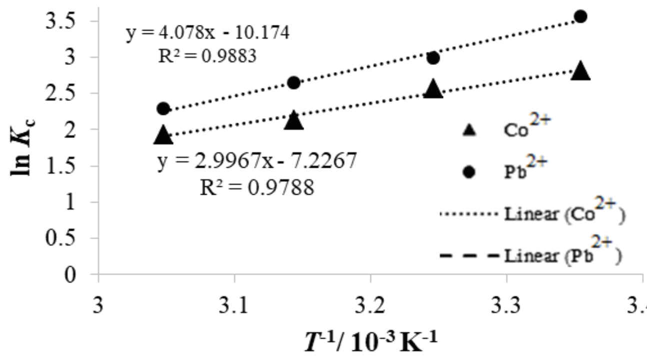

Fig. S-6. Plot of ln K_c *vs*. T^{-1} for the determination of thermodynamic parameters for the adsorption of Pb^{2+} and Co^{2+} onto CaO/Fe_3O_4 magnetic composite.

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