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ORIGINAL PAPER

Multi-element modeling of heavy metals competitive removal from aqueous solution by raw and activated clay from the Aleg formation (Southern Tunisia)

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Abstract

The present study has been carried out for potential use of a raw clay from Gabes district (southern Tunisia) in wastewater treatment. A representative clay sample was collected from the outcropping feature of the Aidoudi area to the west of Gabes city; it followed a simple treatment to enhance its physicochemical properties. Adsorption experiments were performed by using a simple batch technique in single- and multi-element solution (Pb^{2+}, Cd^{2+}, Cu^{2+} and Zn^{2+}). The obtained results were fitted to different adsorption models, including extended and modified Langmuir, extended Freundlich and modified Redlich–Peterson. Our results indicated that the collected clay sample is mainly a smectite with high amounts of silica, alumina and iron. Adsorptive removal of single elements revealed encouraging efficiencies for most of the studied metals, reaching nearly 100%. Our results also indicated that lead removal reached 26.78 mg/g and 45.94 mg/g for natural and activated clay samples, respectively. Competitive adsorption showed strong dependence on the initial concentration and the metal properties, with preferential removal of lead that reached 41.71 mg/g in binary systems. In most of the mixed systems, metal removal substantially decreased in the presence of competing ions. It showed preferential removal of lead over other metals, regardless of the studied mixture. Further, the use of smectitic clay from southern Tunisia showed a good potential for metal ions removal in single and multi-element systems from aqueous solutions. Thus, it could be turned out to a viable material for the treatment of metal loaded waters.

Keywords Heavy metals · Activated clay · Competitive adsorption · Modeling · Extended Langmuir

Introduction

The presence of various toxic metal species such as lead (Pb), cadmium (Cd), copper (Cu) and zinc (Zn) in soil and industrial wastewater are the main sources of groundwater pollution; they harm every single component of either aquatic or terrestrial ecosystem. For instance, Afroze and Sen (2018) compiled an extensive literature review about the effects of toxic metals in water bodies and their deleterious health effects. They provided a comprehensive compilation of several adsorptive pollutant removal. Similarly, Hashim et al. (2011) mentioned that despite some heavy metals are essential microelements, they become poisonous once they exceed a threshold limit. In addition, their hazards are aggravated by their almost indefinite persistence in the environment (Ghrab et al. 2014; Ghorbel et al. 2014). Thus, their removal from contaminated water bodies is a compulsory step before the final discharge in the receiving ecosystem. There are several options to clean up soils and water contaminated with heavy metals like excavation, stabilization

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and use of clay minerals. The use of naturally occurring materials for heavy metals removal in aqueous system is one of the most efficient alternatives (Walker et al. 2003; Ayoub and Mehawej 2007; Sdiri et al. 2012b; Perassi and Borgnino 2014; Salameh et al. 2015; Sdiri 2018). Most of the above-mentioned works have concentrated on single-element systems. Industrial effluents are usually loaded by several contaminants that complicated the treatment process and lowered the removal efficiency. The issue needs to be properly solved for better protection of the ecosystem. That is why this work has been undertaken for an in-depth understanding of the removal mechanisms at the solid–liquid interface and deciphered the main processes involved in the competitive retention of metal ions (i.e., Pb^{2+}, Cd^{2+}, Zn^{2+} and Cu^{2+}) by using clayey adsorbents. Multi-metals modeling of simultaneous metal removal was seldom addressed by previous researches on the topic. Thus, our work is among the first studies that provide thorough evaluation and modeling of metal removal using low-cost natural deposits. Most of the experimental work has been performed at the University of Valencia, Spain, department of analytical chemistry during the training course of doctor Leila Khalfa et al. in 2016.

Materials and methods

Materials sampling and characterization

Raw clay was sampled from Jebel El Aidoudi, El Hamma, Gabes (southern Tunisia). Natural clay followed a physicochemical treatment to remove several impurities and retrieve the very fine particles whose textural properties are expected to be improved. Thus, the raw clay was suspended in distilled water for 24 h for total dispersion, and then washed several times. The obtained clay sample was vacuum dried at 105 °C for 24 h. Finally, it was crushed and sieved to 60 µm for further use as adsorbent.

Acid activation was undertaken with a solution of sulfuric acid in a jacketed glass reactor equipped with a reflux condenser, a thermometer and a stirrer. Powdered clay (100 g) was added to an aqueous H_2SO_4 solution (2 M) at 100 °C for 4 h under mechanical stirring at 200 rpm. Then, the activated sample was washed by distilled water several times until pH 6, dried at 60 °C for 24 h and stored for subsequent use as an activated clayey sorbent.

Henceforth, we used NC and AC to refer to the original and activated clay samples, respectively.

Physicochemical characteristics of the clays used were assessed by X-ray fluorescence technique for chemical analysis, loss on ignition and BET methodology. Specific surface area was measured using the standard BET technique as described elsewhere (Al-Degs et al. 2006; Sdiri et al. 2011) based on nitrogen gas adsorption on solid surface. Thus, powdered clay sample was introduced in a Micrometrics device equipped with cylindrical Dewar and glass sample holder (ASAP 2010, Micrometrics Instruments Corp.). After being degassed for 12 h at 150 °C, nitrogen adsorption/desorption isotherms were plotted.

Chemical analysis showed that the main constituents of these clays are silica, alumina and iron oxides.

The studied clays show high levels of iron, which may come from their octahedral layers or from an amorphous iron that has not been detected by XRD technique. Na_2O and K_2O are between 0.1 and 1% for both samples; they are mainly attributed to clay minerals and feldspars. A detailed description of the main chemical and structural properties was addressed by Khalfa et al. (2017). Table 1 summarizes the main physicochemical properties of studied clays.

Sorption experiments

Different sets of experiments have been conducted to study the influence of various adsorption parameters (time, pH, temperature, the mass of the adsorbent and the initial metal concentration) on the interactions of metal pollutants with the studied clays (i.e., NC and AC).

Effect of time on the adsorption of metal ions was studied at 20 °C as described by Khalfa et al. (2011, 2016). Briefly, 500 mL of the desired metal solution was shaken with 1 g/L of either NC or AC clay sample at 200 rpm; agitation time ranged between 5 and 240 min. Initial pH was adjusted by using 0.1 M NaOH or of 0.1 M HNO_3.

The influence of the temperature was ascertained at 20, 35, 50 and 65 °C; that of adsorbent mass ranged between 0.25 and 2 g/L. To establish the adsorption isotherms, the effect of initial metal concentrations was set at different values ranging from 10 to 80 mg/L.

Table 1 Chemical composition (% by weight) and structural properties of the studied clay samples

Sample	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	P_2O_5	SO_3	LOI	SSA	TPV	APD
NC	47.70	18.71	11.12	2.65	2.59	1.05	0.96	0.32	0.91	14	86	0.1394	40.53
AC	50.12	18.26	9.12	1.93	1.89	0.87	0.17	0.02	4.91	12	167	0.1986	49.03

LOI loss on ignition, *SSA* specific surface area (m^2/g), *TPV* total pores volume (cm^3/g), *APD* average pores diameter (Å)

We used acetylene flame atomic absorption spectroscopy (AAS) as an appropriate tool for the determination of metal concentrations.

The quantity of heavy metal removed has been calculated as the difference between initial and equilibrium concentrations (Khalfa and Bagane 2011).

Multi-element modeling

Data collected from competitive sorption experiments were fitted to different competitive adsorption models. Table 2 summarizes the main theoretical assumptions provided by eminent researchers, including Freundlich, Langmuir, Redlich–Peterson and Sheindorf–Rebuhn–Sheintuch (Srivastava et al. 2006; Papageorgiou et al. 2009).

Results and discussion

Adsorption isotherms in binary system

Competitive adsorption of lead, copper, cadmium and zinc from aqueous solutions in binary systems (i.e., Pb–Zn, Pb–Cd; Pb–Cu; Zn–Cd; Zn–Cu and Cu–Cd) has been studied by varying the concentration of the desired elements in the range of 10–80 mg/L. Several possible combinations were studied incessantly, as described in the following text.

Competition with lead

The effect of initial lead concentration on the removal of the studied metals in binary systems (Pb–Cd, Pb–Zn and Pb–Cu) has been carried out under pH 6, shaking time of 3 h at 20 °C and clay concentration of 1 g/L. Adsorption isotherms of lead in the presence of competing ion are given in Fig. 1. These curves can be considered as L type in Langmuir classification; they showed a sharp decrease in the adsorbed amount as the initial concentration of the competing metal (cadmium, copper and zinc) increased. One can easily recognize the preferential removal of lead to the detriment of other cations (Qin et al. 2006; Naiya et al. 2009). For example, the maximum adsorbed amount of lead $q_{e,\mathrm{Pb}}$ (mg/g) on the activated clay has been significantly reduced from 45 mg/g to less than 20 mg/g as the concentration of cadmium rose from 0 to 80 mg/L due to the competitive effect of cadmium. Our results also showed that cadmium could not effectively compete with lead to the active sites, as copper and zinc did.

The inhibitory effects of cadmium, zinc and copper on the adsorptive capacity of lead are shown in Fig. 1. It appeared that variable concentrations of competing metal ions have undoubtedly affected the removal efficiencies of lead. Observably, an initial copper concentration of 10 mg/L decreased the adsorbed lead to 14.09 mg/g; the presence of cadmium to 23.5 mg/g (Fig. S1).

In all cases, the adsorption of lead onto activated clay was much higher than that onto natural clay, further confirming the enhanced adsorption in mono-element solution (Khalfa et al. 2017).

Competitive adsorption isotherms of lead Competitive adsorption isotherms of lead were studied by shaking a known metal concentration for 3 h with 10 mg/L of the desired competing metal (i.e., cadmium, copper or zinc). Maximum adsorbed amounts of lead cations in single and binary systems are given in Fig. 1.

Table 2 Multi-element adsorption isotherm models [after Srivastava et al. (2006), Papageorgiou et al. (2009)]

Model	Equation	Number	Description
Extended Freundlich	$q_{e,1} = \frac{k_{f,1} C_{e,1}^{(1/n_1)+x_1}}{C_{e,1}^{x_1} + y_1 C_{e,2}^{z_1}}$	(1)	k_{fi}: Freundlich isotherm constant for metal i (mg(1–1/n) L(1/n)/g) n_i, Freundlich isotherm constant for metal i
	$q_{e,2} = \frac{k_{f,2} C_{e,2}^{(1/n_2)+x_2}}{C_{e,2}^{x_2} + y_2 C_{e,1}^{z_2}}$	(2)	
Extended Langmuir	$q_{e,i} = \frac{q\max k_i C_{e,i}}{1 + \sum_{j=1}^{N} k_j C_{e,j}}$	(3)	$q_{\max}$: maximum adsorption capacity (mg/g). ki: extended Langmuir constant for component i (L/mg)
Modified Langmuir	$q_{e,i} = \frac{q_{m,i} k_{l,i} (C_{e,i} / \eta_{l,i})}{1 + \sum_{j=1}^{N} k_{l,j} (C_{e,j} / \eta_{l,j})}$	(4)	$\eta_{l,i}$: interaction factor for metal i in the presence of metal j
Modified Redlich–Peterson	$q_{e,i} = \frac{k_{R,i} (C_{e,i} / \eta_{R,i})}{1 + \sum_{j=1}^{N} a_{R,j} (C_{e,j} / \eta_{R,j})^{\beta j}}$	(5)	$\eta_{R,i}$: interaction Redlich–Peterson factor for metal i
Sheindorf–Rebuhn–Sheintuch (SRS)	$q_{e,i} = k_{f,i} C_{e,i} \left(\sum_{j=1}^{N} a_{ij} C_{e,j} \right)^{(1/n_i)-1}$	(6)	a_{ij}: competition coefficient of component i by component j

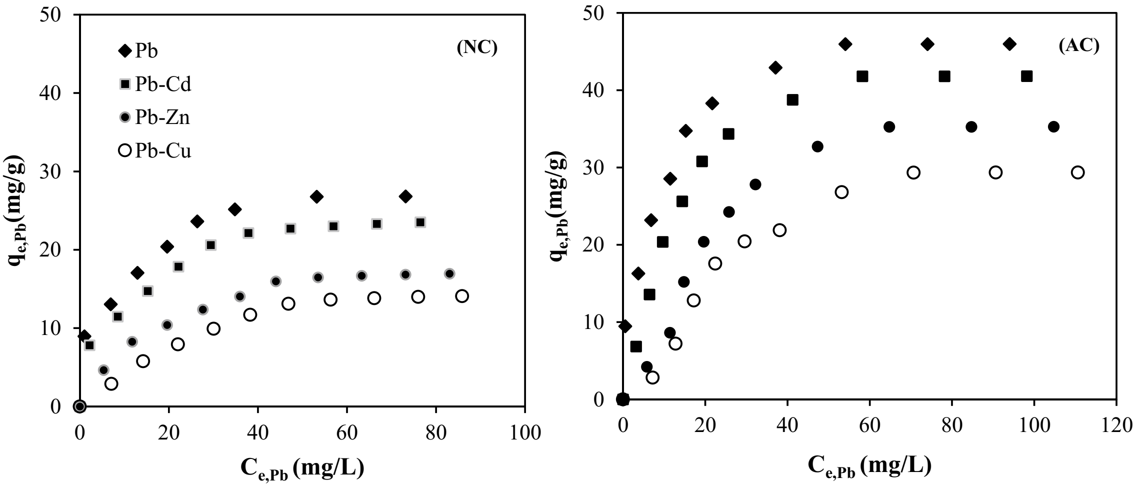

Fig. 1 Effects of initial concentration of different cations on the removal of lead by natural (NC) and activated (AC) clay (pH = 6; t_{eq} = 3 h; T = 20 °C, dose = 1 g/L)

According to the same figure, the adsorbed amount of lead dropped from 26.78 mg/g (single metal solution) to 13.83 mg/g in the presence of copper, and to 23.1 mg/g in the presence of cadmium.

Moreover, the adsorption capacity of lead in single-element system was much higher than that in multi-element systems for both natural and activated clay. Similar results have been recorded by Futalan et al. (2011) who used the chitosan-immobilized bentonite as adsorbent. These authors attributed the decrease to the competitive adsorption of lead in the presence of copper. Ionic hydrated radius and electronegativity seemed to be the most influencing factors in the competition (Sdiri et al. 2012a). Higher electronegativity of lead (2.33) compared to that of copper (1.9) may encourage the preferential removal of lead over the other competing cations (i.e., Cu; Fig. 1). Similar statement can be adopted for both cadmium and zinc, but to a much lower extent.

Modeling competitive adsorption of lead The adsorption isotherms of Pb^{2+} in the presence of cadmium, copper or zinc on the natural and activated clay samples were fitted by several nonlinear models including modified Langmuir (ML), extended Langmuir (EL), extended Freundlich (EF) and modified Redlich–Peterson model (MRP). Model parameters were determined by minimizing the differences between the experimental and theoretical data calculated using an optimization function under MATLAB R2017a (The MathWorks Inc. Suisse; Fig. 1). The obtained parameters, given in Table 3, showed that both modified Redlich–Peterson and extended Freundlich models best describe the adsorption isotherms.

In addition, modified Langmuir model provided lower coefficient of determination and larger values of root-mean-square error (RMSE) and the Marquardt's percent standard deviation (MPSD) for all of the binary systems, indicating clear discrepancies between measured and calculated data. Therefore, modified Langmuir model did not describe well the isotherms of competitive adsorption of lead in binary systems. Maximum adsorbed quantities determined by the extended Langmuir model are in concordance with those determined experimentally illustrating a well-suited model for the description of mixed system adsorption of lead. The differences of the affinities of some metal ions to the active sites of the adsorbent can be explained by some physicochemical properties of the adsorbates such as the ionic radius, the ionic radius hydrated and the electronegativity (2.33 for Pb, 1.9 for Cu, 1.65 for zinc and 1.69 for Cd) (Kinraide and Yermiyahu 2007).

Competition with cadmium

Competition with cadmium was studied in binary systems including different concentrations of Pb^{2+}, Cu^{2+} and Zn^{2+} (10, 30, 50 and 80 mg/L); Cadmium concentrations was varied between 10 and 100 mg/L following the experimental procedure described earlier in the text. Recall that 1 g/L of clay sample (NC or AC) was suspended in metal solution of desired concentration. The dispersion was shaken for 3 h under constant shaking speed of 200 rpm and 20 °C. The adsorption isotherms of cadmium are shown in Fig. 2. A quick look to the isotherms showed that both clay samples removed low amounts of cadmium in single-element solution, reaching 19.84 mg/g in the highly efficient activated clay; this was much higher than the natural clay removal

Table 3 Model parameters for competitive adsorption of heavy metals ions in binary systems into natural and activated clay

Fitting models	Parameters	Pb–Cd	Pb–Zn	Pb–Cu	Cu–Cd	Cu–Zn	Cu–Pb	Zn–Cd	Zn–Cu	Zn–Pb	Cd–Pb	Cd–Zn	Cd–Cu
Natural clay (NC)													
Extended Langmuir	q_m (mg/g)	27.645	21.067	15.83	19.153	14.145	11.978	17.87	10.50	13.82	18.610	19.257	15.55
	$k_{EL,Pb}$	0.092	0.086	0.07	0.04	0.060	0.035	0.031	0.022	0.020	0.022	0.024	0.202
	$k_{EL,j(Cd,Zn,Cu)}$	0.001	0.122	0.001	0.001	0.005	0.002	0.011	0.0015	0.0082	0.026	0.001	0.001
	R^2	0.9746	0.9876	0.9876	0.9992	0.994	0.9935	0.9784	0.987	0.9713	0.9894	0.9880	0.9868
	RMSE	5.650	2.229	0.630	0.130	1.097	0.619	2.772	0.939	2.526	2.069	1.964	1.630
	MPSD	14.272	9.486	3.815	5.0699	23.256	26.728	13.767	25.607	21.192	31.164	25.772	51.283
Extended Freundlich	x_{Pb}	0.556	0.440	0.428	0.691	0.483	0.334	0.002	0.065	0.119	1.023	0.809	1.067
	y_{Pb}	0.796	1.997	3.677	4.156	2.433	2.600	0.208	1.83	0.622	1.014	0.001	0.900
	z_{Pb}	0.489	0.001	0.114	0.056	0.044	0.024	0.113	0.011	0.411	1.999	5.037	3.994
	R^2	0.9935	0.9962	0.9706	0.9955	0.9789	0.9788	0.9848	0.9753	0.9655	0.9880	0.9931	0.9634
	RMSE	1.012	0.341	1.468	0.432	2.904	1.548	1.728	1.680	2.943	1.146	1.348	2.264
	MPSD	3.407	4.421	5.664	8.278	31.718	35.657	8.908	57.606	23.157	19.264	25.838	55.388
Modified Langmuir	$\eta_{LM,Pb}$	1.745	4.630	7.367	1.386	2.371	3.400	1.406	4.859	2.627	1.498	1.022	1.787
	$\eta_{LM,j}$	0.5370	0.490	0.251	1.658	2.308	1.814	2.28	1.160	2.98	5.237	2.821	0.965
	R^2	0.9725	0.9943	0.9872	0.9920	0.9873	0.9931	0.9830	0.9881	0.9753	0.9859	0.9882	0.9852
	RMSE	5.4996	0.6384	0.6441	2.138	1.300	0.577	1.200	0.844	2.145	1.531	2.783	1.389
	MPSD	13.966	4.910	3.902	18.835	23.582	27.117	10.247	23.150	16.734	23.214	30.629	27.378
Modified Redlich–Peterson	$\eta_{RPM,Pb}$	1.531	1.627	0.261	1.020	2.153	1.670	1.183	4.758	0.802	1.670	0.108	1.282
	$\eta_{RPM,j}$	0.633	0.536	0.165	0.057	0.109	0.063	0.470	1.562	0.438	0.380	0.124	0.313
	R^2	0.9944	0.9933	0.9684	0.9965	0.9891	0.971	0.9626	0.9834	0.9655	0.9792	0.9876	0.9810
	RMSE	1.708	9.641	5.305	4.695	2.095	2.929	3.099	1.255	4.977	2.322	1.872	1.330
	MPSD	5.221	25.091	13.069	31.833	34.840	57.094	13.681	33.0925	33.2044	20.736	27.979	23.703
Activated clay (AC)													
Extended Langmuir	q_m (mg/g)	46.501	39.027	36.398	30.927	26.244	21.636	25.25	16.33	20.79	22.542	24.996	17.37
	$k_{EL,Pb}$	0.097	0.067	0.043	0.033	0.031	0.031	0.046	0.046	0.047	0.023	0.040	0.023
	$k_{EL,j(Cd,Zn,Cu)}$	0.001	0.001	0.024	0.001	0.001	0.003	0.012	0.001	0.012	0.002	0.072	0.001
	R^2	0.9986	0.9888	0.9878	0.9959	0.9950	0.9919	0.9935	0.9918	0.9873	0.9938	0.9979	0.9932
	RMSE	19.291	54.258	26.400	1.622	1.387	1.642	2.221	1.373	3.088	0.972	0.327	1.820
	MPSD	26.027	66.374	81.646	9.2882	7.3817	9.6922	12.476	14.771	11.185	14.700	2.188	16.500
Extended Freundlich	x_{Pb}	0.464	0.368	0.223	0.349	0.233	0.116	0.597	0.352	0.499	0.058	0.765	0.887
	y_{Pb}	0.01	0.589	0.123	0.145	0.115	0.106	0.285	0.279	0.452	0.004	0.109	0.007
	z_{Pb}	0.014	0.111	0.011	0.626	0.894	0.984	0.128	0.374	0.116	2.935	4.074	4.679
	R^2	0.9807	0.9511	0.9551	0.9857	0.9862	0.9831	0.9953	0.9763	0.9924	0.9842	0.9930	0.9961
	RMSE	28.482	54.980	38.518	5.649	3.886	3.493	1.426	5.264	1.968	2.096	1.041	0.864
	MPSD	33.965	53.318	97.057	17.912	18.421	14.966	4.615	28.746	10.254	17.370	5.236	15.218

Table 3 (continued)

Fitting models	Parameters	Pb–Cd	Pb–Zn	Pb–Cu	Cu–Cd	Cu–Zn	Cu–Pb	Zn–Cd	Zn–Cu	Zn–Pb	Cd–Pb	Cd–Zn	Cd–Cu
Modified Langmuir	$\eta_{LM,Pb}$	1.079	4.733	3.5	2.918	1.818	1.855	1.031	2.831	1.436	2.545	1.336	2.966
	$\eta_{LM,j}$	0.238	2.218	0.094	2.781	0.424	0.565	0.838	0.76	0.986	1.865	0.362	0.266
	R^2	0.9983	0.5408	0.9719	0.9956	0.9945	0.9902	0.9944	0.9914	0.9948	0.9934	0.9976	0.9858
	RMSE	24.632	23.905	32.5413	1.963	1.523	1.976	1.863	1.409	1.223	1.006	0.371	1.185
	MPSD	33.934	36.778	79.163	12.967	7.924	9.605	11.477	15.531	9.180	15.488	2.396	11.844
Modified Redlich–Peterson	$\eta_{RPM,Pb}$	1.279	2.571	2.689	0.609	1.161	3.197	1.072	4.12	2.615	2.654	0.666	2.793
	$\eta_{RPM,j}$	6.080	0.133	0.133	0.579	1.576	0.075	0.464	0.192	0.075	0.667	0.312	0.179
	R^2	0.9983	0.9666	0.9673	0.9905	0.9895	0.9795	0.9952	0.9824	0.9932	0.9898	0.9862	0.9888
	RMSE	20.900	51.775	21.775	5.493	3.945	6.029	1.539	3.687	1.799	1.463	2.359	1.204
	MPSD	25.815	59.967	59.967	26.310	21.594	14.992	5.7089	20.9172	9.1048	18.210	6.726	14.265

efficiency (12.89 mg/g). In mixed solutions, it appeared that the adsorbed cadmium was undoubtedly inhibited by the presence of other competing cations. Copper was the most influencing metal compared to lead and zinc. Further investigation can easily point out that the removal efficacy decreased when the concentration of the competing cations increased from 10 to 80 mg/L. At those concentrations, metals may compete with cadmium to the active sites. The inhibition of cadmium cations can be explained by the physicochemical properties of both cations (Sdiri et al. 2012a). On the other hand, the decrease in the adsorbed quantity of cadmium was observed on both natural and activated clay with a bigger variation in the AC sample. This is ubiquitous for all binary mixtures.

The decay of the adsorbed cadmium on natural and activated clay was clearly observed in the presence of other competing metal ions (zinc, copper and lead; Figure S2). The highest removal of cadmium was observed in the Zn–Cd binary system for both AC and NC clay. NC clay removed 12.48 mg/L of cadmium in the presence of 10 mg/L of zinc and only 8.75 mg/g when zinc concentration rose to 80 mg/L. As expected, acid-activated clay sample (AC) removed higher amounts of cadmium form Zn–Cd solution, reaching 19.84 mg/g for 10 mg/L of zinc. The removal substantially decreased for 80 mg/L of zinc to 13.49 mg/L, but still higher than that of original clay (i.e., 12.48 mg/g).

Competitive adsorption isotherms of cadmium Adsorption isotherms of cadmium in the presence of 10 mg/L in lead, zinc and copper on the natural and activated clay are shown in Fig. 2. Adsorption isotherms of cadmium showed similar trends with increasing adsorbed amounts in the low initial concentrations to reach a plateau when reproaching higher cadmium concentrations. In terms of adsorbed quantities, cadmium removal by NC sample was lower than AC sample, as mentioned before. Addition of competing cations influenced the removal of cadmium in both NC and AC samples. Thus, cadmium was slightly influenced by the existence of zinc, but strongly inhibited by the presence of lead and copper.

Modeling competitive adsorption isotherms of cadmium Adsorption isotherms of the binary systems Cd–Pb, Cd–Cu, Cd–Zn were analyzed by the above-mentioned models (i.e., modified Langmuir, extended Langmuir, extended Freundlich and modified Redlich–Peterson). Comparisons between the experimental and predicted data for cadmium in all possible combinations of binary systems are given in Fig. 2. The models tested may not

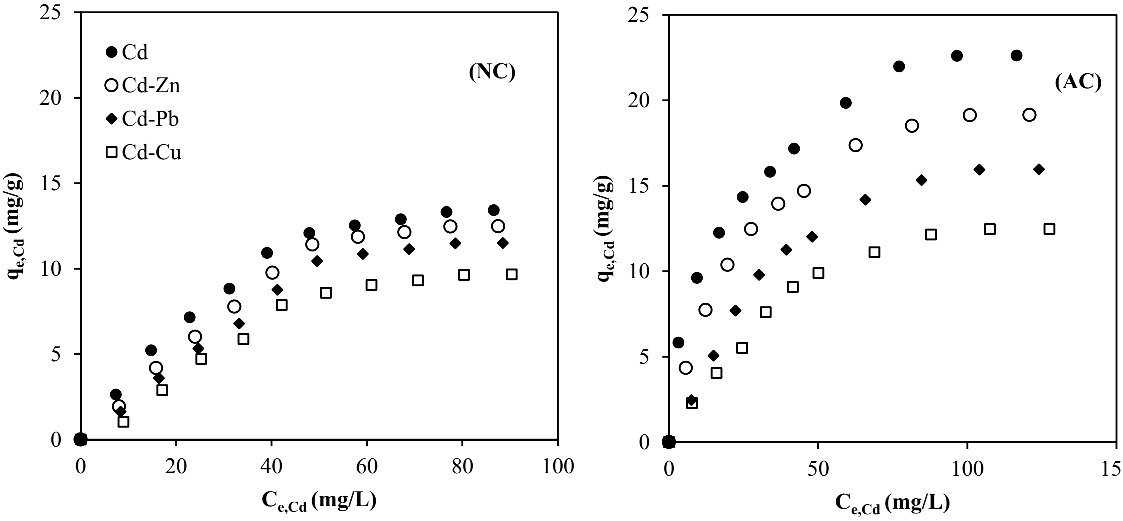

Fig. 2 Effects of initial concentration of different cations on the removal of cadmium by natural (NC) and activated (AC) clay (pH = 6; t_{eq} = 3 h; T = 20 °C, dose = 1 g/L)

perfectly describe all of the experimental results. One can interpret from the results of Table 3 that modified Langmuir model (ML) presents a good correlation with the experimental data; also, extended Langmuir model (EL) showed low MPSD values; the calculated adsorption capacities for different binary systems containing cadmium were very close to those determined experimentally. Thus, we concluded that extended Langmuir model best fitted the experimental data with low values of MPSD and RMSE. According to Table 3, we define a coefficient of competition n_{ij} for MRP model to express the inhibition element i (e.g., cadmium) caused by the competing element j (i.e., lead, zinc or copper). A comparison n_{ij} and n_{ji} shows that the coefficient of competition $n_{\mathrm{Cd},j}$ follows the ascending order: $n_{\mathrm{Cd,Zn}} < n_{\mathrm{Cd,Cu}} < n_{\mathrm{Cd,Pb}}$. Therefore, the adsorption of cadmium was not significantly affected by the presence of zinc as copper and lead did.

Srivastava et al. (2006) studied the competitive adsorption of cadmium and zinc on fly ash of bagasse (BFA) which are the solid wastes released by the industries of sugar production. They have proved that Sheindorf–Rebuhn–Sheintuch (SRS) model best described the experimental data of zinc and cadmium adsorption on the BFA. On the other hand, they have studied the effect of initial concentration of zinc from 10 to 100 mg/L on the adsorption of cadmium; they observed that the adsorbed cadmium regularly decreased with the initial concentration of zinc, as was the case in the present clay samples.

Competition with copper

The adsorption of copper in binary system at different initial concentrations of zinc, cadmium and lead was studied to determine the effects of the competitor element initial concentration on the removal of copper. Adsorption isotherms of copper in all binary systems are similar to those determined in single element with high removal efficiencies (Fig. 3).

Addition of cadmium has decreased slightly the adsorbed amount of copper compared to that of the mono-solute. As for zinc and lead, the presence of competing metal has strongly influenced copper removal. For instance, Cu^{2+} adsorbed onto activated clay has decreased from 26.39 to 11.12 mg/g in the presence of 80 mg/L of the Pb^{2+}.

Amounts of the Cu^{2+} removal have been determined for all binary systems in the presence of different initial concentrations of competing metal ions (Fig. S3). The maximum capacity of Cu^{2+} removal was measured in the presence of 10 mg/L of Cd^{2+}, ascertained to 23.5 mg/g. The lowest amount of Cu^{2+} was observed for the system Cu–Pb to be 5.52 mg/g and 11.12 mg/g in the case of NC and AC, respectively, in the presence of 80 mg/L of Pb^{2+}. Such an observation may further confirm the importance of using activated clay to improve the retention of toxic pollutants. It also proved that both zinc and lead are the most competitive elements to the active sites of the studied clay surface.

Figure 3 shows a comparison between the removal efficiencies of copper in single and binary systems. Our results

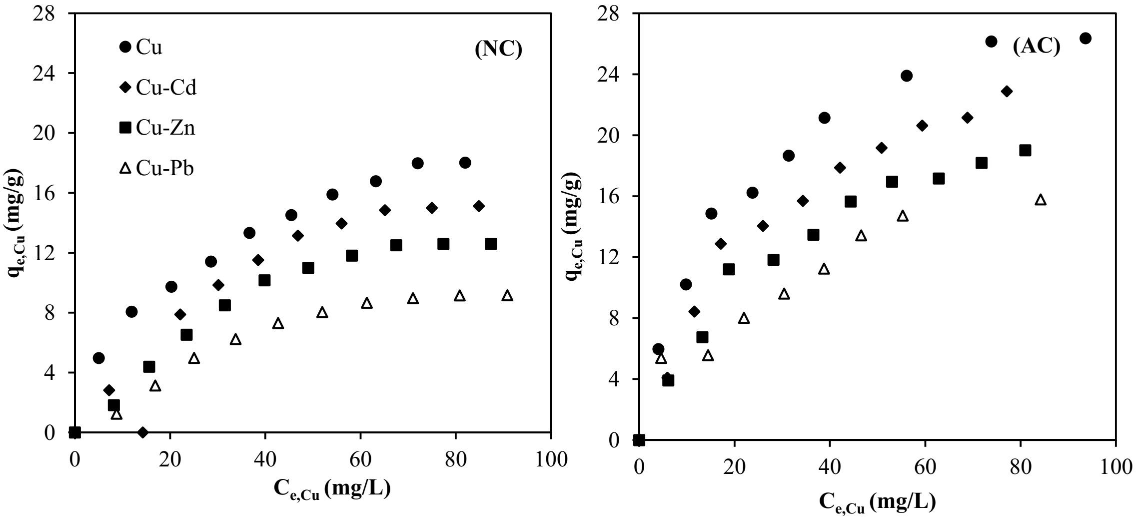

Fig. 3 Effects of initial concentration of different cations on the removal of copper by natural (NC) and activated (AC) clay. (pH = 6; t_{eq} = 3 h; T = 20 °C, dose = 1 g/L)

indicated that the activated clay adsorbed higher amounts than that of the natural sample. Moreover, the affinity toward copper in the presence of other competing metals followed a sequence of Cu–Cd ≫ Cu–Zn ≫ Cu–Pb, confirming the lower adsorption of copper in the presence of zinc or lead. This finding corroborated well with the findings of Sdiri et al.(2012a), who studied the competition between those element to montmorillonite and calcareous clay surface.

Modeling competitive adsorption of copper

Prediction of the adsorption isotherms in the Cu–Cd, Cu–Pb and Cu–Zn systems is given in Fig. 3; model parameters, including the coefficients of determination (R^2), root-mean-squared error (RMSE) and the maximum amount of adsorbed copper in binary systems, are given in Table 3.

Experimental data better fitted ML and EL models as confirmed by the calculated maximum adsorbed quantities, similar to those determined experimentally. Thus, it was concluded that both ML and EL adsorption models correctly predicted the adsorption of Cu^{2+} for the binary systems.

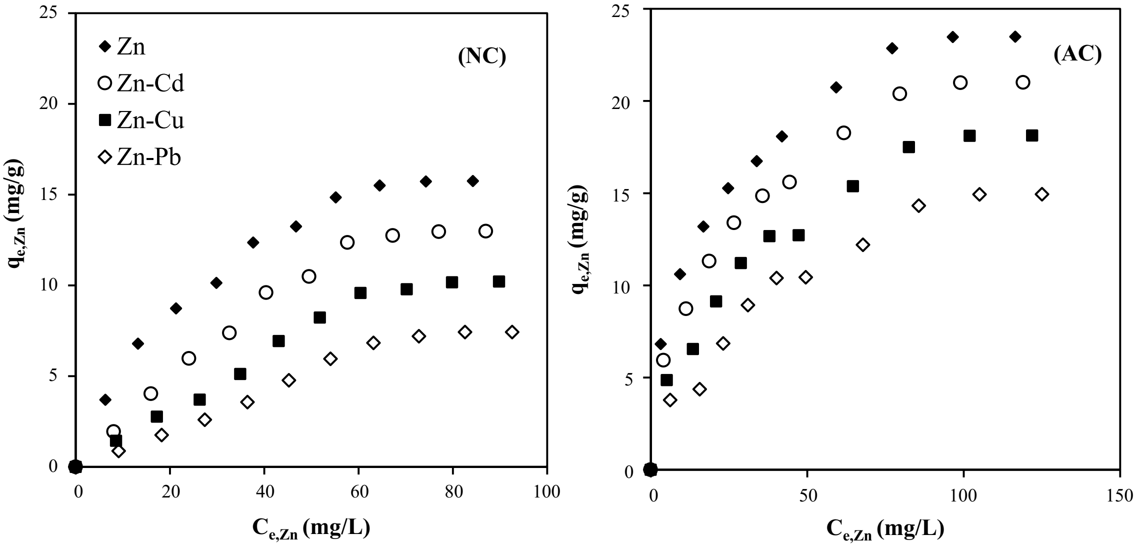

Fig. 4 Effects of initial concentration of different cations on the removal of zinc by natural (NC) and activated (AC) clay.(pH = 6; t_{eq} = 3 h; T = 20 °C, dose = 1 g/L)

Competition with zinc

Here, we varied the initial concentration of zinc while keeping the initial concentration of competing metal (i.e., lead, cadmium and copper) constant. Initial concentration of the competing cations was set to 10, 30, 50 and 80 mg/L (Fig. 4). Inhibitory effects of those metals on the adsorption of Zn^{2+} can be easily recognized. We noticed that the adsorbed quantity of Zn^{2+} in single-element system reached 15.51 mg/g and 20.74 mg/g for natural and activated clay, respectively. Those values dropped to 4.66 mg/g and 9.17 mg/g in the presence of 80 mg/L of Pb^{2+}. Similarly, the presence of copper exerted a high inhibition of zinc sorption by both clay samples; a decrease from 15.51 mg/g to 1.80 mg/g and from 20.74 mg/g to 6.74 mg/g was observed in the case of NC and AC, respectively. Cadmium also competes strongly with zinc to the active sites, leading to substantial decrease in zinc removal (Fig. S4).

Competitive adsorption isotherms of zinc Adsorption isotherms of Zn^{2+} on the natural and activated clay for the different binary systems (i.e., Zn–Cu, Zn–Cd and Zn–Pb) are given in Fig. 4.

The addition of copper fact decreased the amount of zinc removed. This can be explained by the fact that copper has a strong competitive effect with zinc to the active sites; similar effect is obtained in the presence of cadmium. Moreover, lower adsorption efficiencies of zinc on both samples in Zn–Pb and Zn–Cu binary systems are shown in Fig. 4.

Depci et al. (2012) studied the adsorption of metal ions in mono- and multi-systems on the active coal prepared from waste pulp of apple. They have proved that the maximum adsorption capacity decreased in the order Pb^{2+} (15.96 mg/g) > Pb^{2+} (Pb–Zn; 13.23 mg/g) > Zn^{2+} (11.72 mg/g) > Zn^{2+} (Zn–Pb; 7.54 mg/g). The adsorption capacity of zinc is more affected by the presence of Cu^{2+} rather than Pb^{2+}, indicating the great affinity to copper and lead in comparison with zinc.

Modeling competitive adsorption isotherms of zinc Adsorption isotherms of zinc in the presence of 10 mg/L of a competing metal (cadmium, lead or copper is smoothed by using extended Freundlich, extended Langmuir, modified Langmuir and modified Redlich–Peterson models (Table 3). The experimental and calculated values of zinc removal in the presence of other metal cations were compared. It was found that extended Langmuir model correctly predict the experimental results, contradicting other models that fitted only the first part of the isotherm (only for the less than 30 mg/L concentration).

One can easily conclude that among the four models tested, only modified Langmuir and extended Langmuir models described well the experimental data. This is well-confirmed by the values of MPSD below 5% (Table 3). Other models, particularly the modified Redlich–Peterson, did not correctly predict the adsorption of zinc on activated clay. Thus, both modified Langmuir and extended Freundlich that apply in the case of natural clay are in perfect agreement with the adsorption of zinc in the presence of cadmium (Fig. 5).

Ternary and quaternary systems adsorption of heavy metals by natural and activated clay

Experiments of competitive sorption have also been carried out for the simultaneous elimination of three heavy metals with 45 mg of natural or activated clay, 45 mL of metal solution at ambient temperature and contact time of 180 min. We studied the effects of initial concentration with addition of 10 mg/L of competing ions. We varied the initial concentration of the desired metal from 10 to 100 mg/L; initial pH of the mixture was set to 6.

We illustrate that the activated clay has removed higher quantities of heavy metals, while the natural clay has retained lower amounts regardless of the cation removed and the mixture studied (ternary or quaternary). In addition, the affinity of the metal cations in the ternary system followed the order $Pb^{2+} > Cd^{2+} > Cu^{2+} > Zn^{2+}$ like those in mono-solute and binary system.

On the whole, we can say that in ternary systems, metal ions (Pb^{2+}, Zn^{2+}, Cd^{2+} and Cu^{2+}) are more competitive than in binary systems.

These results indicate that in the ternary systems, the removed quantities have decreased compared to single and binary systems. This was expected because of the higher electrostatic repulsion between the studied metals, and the greater affinities of the studied clay samples for Pb^{2+} and Cu^{2+} Usman 2008).

Metal ion removal was lowered with the presence of two other metal ions. For example, the adsorbed amount of lead on natural clay has decreased from 29 mg/g in mono-solute to 14.65 mg/g in ternary system Pb–Cu–Zn.

Simultaneous presence of the metal ions (Zn^{2+} and Cu^{2+}) in the solution creates a strong competition with Pb^{2+} to the clay active sites. A drop of more than 50% of the adsorption of lead is noted; it is reduced to 16.36 mg/g in competition with copper and zinc.

A similar study published by Xue et al. (2009) for the competitive adsorption of several metals on the slag gave an order:

$Pb^{2+} > Cu^{2+} > Zn^{2+} > Cd^{2+}$, as the case of the present clay samples. By comparing the data obtained for lead, cadmium, copper and zinc, a strong relationship between the

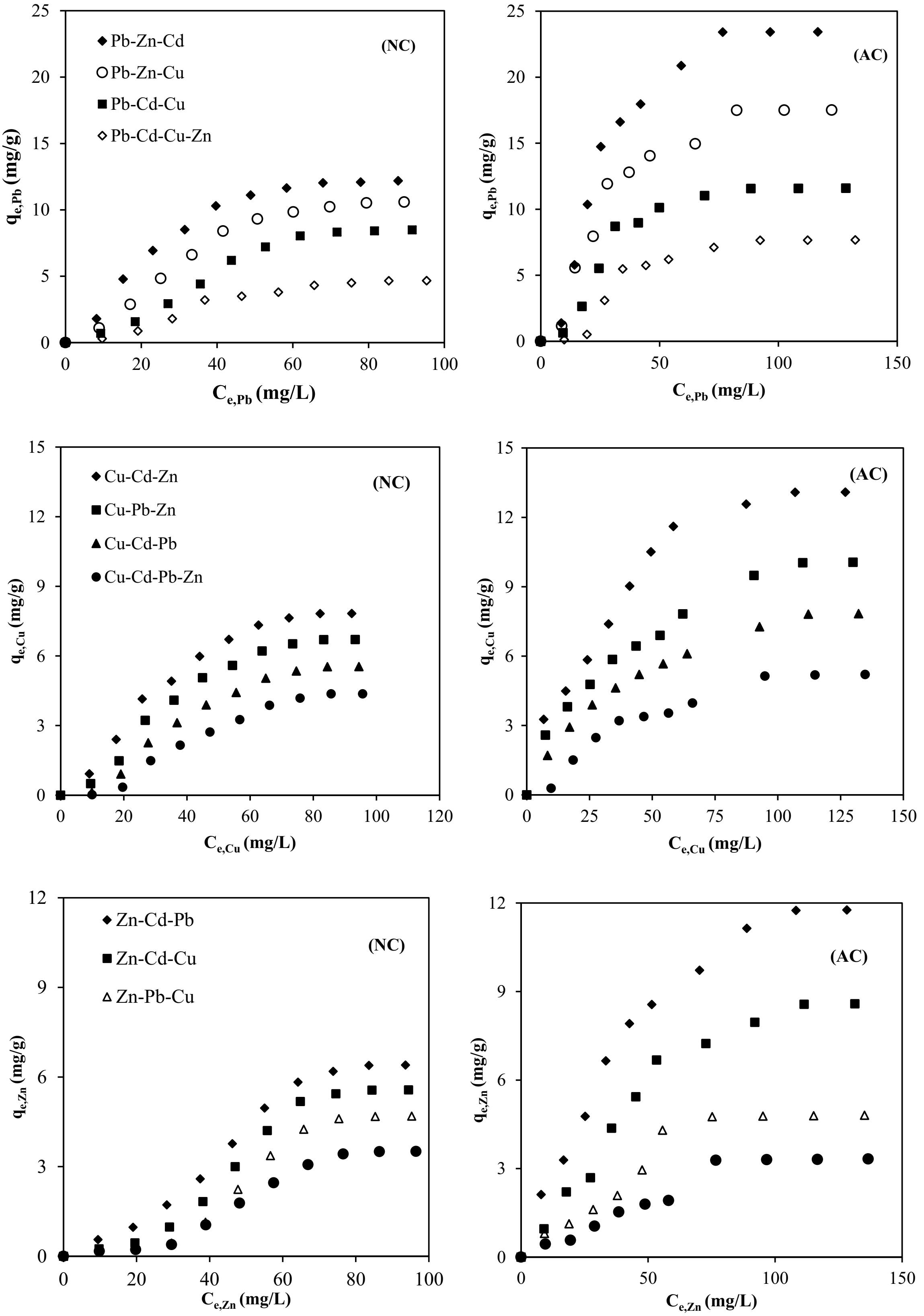

Fig. 5 Ternary and quaternary systems adsorption isotherms

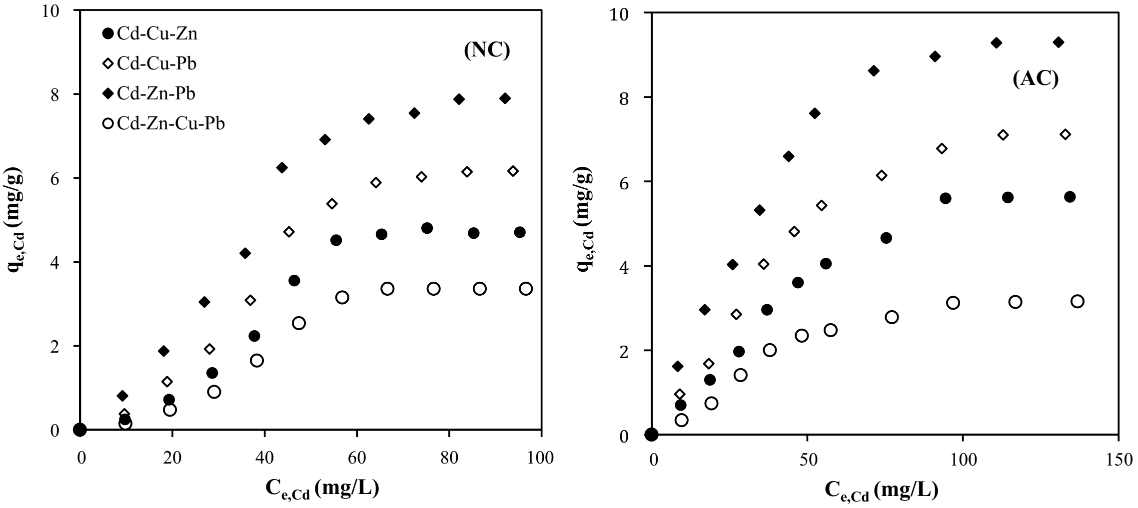

Fig. 5 (continued)

percentage of metal removal and its hydrolysis constant is proven (Kinraide and Yermiyahu 2007; Sdiri et al. 2012a).

According to the results shown in Table 4, elimination of lead by natural clay showed an increased removal from 12.26 mg/g in Pb–Zn–Cu to 16.43 mg/g in Pb–Cd–Zn. Similar results were also observed in the case of activated clay (16.36 mg/g and 29.38 mg/g).

For the system Pb–Cu–Zn, the removed quantities of lead were higher than those observed in the system Pb–Cu–Cd, but much lower than those recorded in the mixture Pb–Cd–Zn.

Given that copper has grealy inhibited the adsorption of Pb^{2+}, it was anticipated that the elimination of lead was lower. In the presence of Zn^{2+}, the removal of lead was reduced for all samples in the system Pb–Cd–Zn, but it has further decreased in the Pb–Cu–Zn mixture.

On the other hand, one can consider that the elimination capacity can be attributed to the porous texture of the adsorbent (specific surface area and volume of pores).

In Pb–Cu–Zn and Pb–Cd–Cu systems, the activated clay sample has eliminated similar quantities of Pb^{2+}, but much lower than those found in the case of Pb–Cd–Zn system.

Table 4 Extended Langmuir parameters for competitive adsorption in ternary and quaternary systems

Metal ion	System	NC						AC					
		q_m (mg/g)	K_{l-Cd}	K_{l-Pb}	$K_{l-}Cu$	K_{l-Zn}	R^2	q_m (mg/g)	K_{l-Cd}	K_{l-Pb}	$K_{l-}Cu$	K_{l-Zn}	R^2
Pb^{2+}	Pb–Zn–Cd	16.43	0.021	0.039	–	0.001	0.9912	29.39	0.002	0.038	–	0.017	0.9699
	Pb–Cu–Cd	14.65	–	0.029	0.011	0.001	0.9880	24.17	–	0.029	0.011	0.012	0.9782
	Pb–Cu–Zn	12.26	0.001	0.023	0.016	–	0.9704	16.36	0.002	0.026	0.001	–	0.9640
	Pb–Cu–Cd–Zn	6.92	0.001	0.022	0.010	0.011	0.9843	11.19	0.012	0.022	0.011	0.009	0.9441
Cd^{2+}	Cd–Zn–Pb	13.00	0.018	0.008	–	0.001	0.9848	15.42	0.015	0.001	–	0.0003	0.9832
	Cd–Pb–Cu	11.16	0.013	0.001	0.001	–	0.9767	13.37	0.011	0.005	0.002	–	0.9832
	Cd–Zn–Cu	8.38	0.015	–	0.005	0.003	0.9640	10.38	0.011	–	0.008	0.002	0.9881
	Cd–Zn–Cu–Pb	4.82	0.023	0.009	0.011	0.002	0.9672	5.36	0.028	0.014	0.010	0.012	0.9779
Zn^{2+}	Zn–Cd–PB	11.28	0.009	0.003	–	0.021	0.9405	16.97	0.006	0.003	–	0.020	0.9953
	Zn–Cd–Cu	9.00	0.009	–	0.001	0.01	0.9520	13.51	0.005	–	0.001	0.015	0.9878
	Zn–Pb–Cu	4.88	–	0.005	0.018	0.011	0.9405	6.64	–	0.002	0.015	0.023	0.9602
	Zn–Pb–Cu–Cd	3.87	0.010	0.011	0.016	0.017	0.9343	4.41	0.017	0.011	0.010	0.013	0.9751
Cu^{2+}	Cu–Cd–Zn	11.45	0.011	–	0.027	0.012	0.9873	17.91	0.011	–	0.028	0.009	0.9912
	Cu–Pb–Zn	9.46	–	0.007	0.026	0.011	0.9748	13.84	–	0.013	0.023	–	0.9963
	Cu–Pb–Cd	8.55	0.017	0.012	0.021	–	0.9729	12.14	0.018	0.014	0.019	0.005	0.9985
	Cu–Pb–Cd–Zn	6.91	0.016	0.016	0.018	0.006	0.9602	9.90	0.013	0.011	0.012	0.016	0.9847

This was expected given that the presence of Cu^{2+} strongly inhibited the adsorption of Pb^{2+}, whereas the ions Zn^{2+} and Cd^{2+} have weakly affected the elimination of Pb^{2+}. Therefore, the elimination of Pb^{2+} has shown augmented efficiencies for all the samples in the system Pb–Cd–Zn, but it decreased in Pb–Cu–Zn mixture indicating the antagonistic effect of Zn^{2+} and Cu^{2+}. With regard to copper, the efficiencies in the Pb–Cu–Zn and Pb–Cd–Cu were similar because of ionic properties very close to Zn^{2+}, and Cd^{2+}, which implies that the both ions would compete with copper in a similar manner. In addition, the highest removal of Cu^{2+} by the studied clay samples was recorded in Cd–Cu–Zn mixture due to the poor effects of Cd^{2+} and Zn^{2+} on the adsorption of Cu^{2+}.

Finally, it is to be noted that the studied clay samples have eliminated low amounts of Zn^{2+} and Cd^{2+} with regards to Pb^{2+} and Cu^{2+}, in all cases, because of their low electronegativities combined with strong hydrolysis constants and high hydrated radii.

Similar results have been proposed by Srivastava et al. (2009), who studied the competitive adsorption of cadmium, nickel and zinc in ternary systems. Experimental study was carried out at pH 6, 30 °C, agitation for 5 h under 150 rpm. They have proven that the adsorbed cadmium decreased with the initial concentration of nickel and zinc. Also, they have shown that SRS model is the most adequate model to describe the adsorption isotherms in ternary system.

Adsorption of four metal mixture was also ascertained (Fig. 5). Note that both samples (NC and AC) have a strong affinity for the ions Pb^{2+} in quaternary system, leading to the highest removal quantities. For example, elimination of lead was of 6.92 mg/g and 11.19 mg/g for the natural and activated clay, respectively. The sorption capacity of Cd^{2+} is approximately 4.82 mg/g and 5.35 mg/g, respectively, for the both materials.

According to these results, it can be stated that the elimination of metal pollutants (Pb^{2+}, Cd^{2+}, Cu^{2+} and Zn^{2+}) by the clay materials is influenced by the properties of the studied metals (e.g., the strength of relative binding, the hydrated radius and the hydrolysis constant, as well as the properties of textural properties of the adsorbent; Kinraide and Yermiyahu 2007).

Finally, it is interesting to mention that the retention of cadmium and zinc is low for all systems compared to other metal ions (lead and copper) because of their low electronegativities and high enthalpies of hydration (Sdiri et al. 2012a).

Analysis of the retention mechanism of metal ions in multi-element systems

According to our study, the presence of a metal ion may cause a strong inhibitory effect on the adsorption of other metal ion in the multi-element system.

Maximum adsorbed amount of each metal ion in binary systems is linked to its affinity vis-a-vis the active sites of the adsorbent. When two metal ions are competing for the same active sites of adsorption, the metal which presents a greater affinity could preferably adsorb to the available site (Karabulut et al. 2000; Kinraide and Yermiyahu 2007; Antoniadis and Tsadilas 2007; Vidal et al. 2009; Alqadami et al. 2017).

The adsorption capacity of a given metal ion to the surface of clay is related to its electronegativity. The electronegativity and the hydrated ionic radius of Pb^{2+} are a much more important than for Cd^{2+}; this indicates that lead ions have an stronger electrostatic attraction to the surface of the adsorbent.

By comparing the properties of lead, cadmium, copper and zinc, a strong relationship between the adsorption capacity of metal and the hydrolysis constant can be illustrated (Kinraide and Yermiyahu 2007). This hypothesis can give a reasonable explanation for the elimination of Pb^{2+} and Cu^{2+} over Cd^{2+} and Zn^{2+}. Srivastava et al. (2006) found that lead has a higher affinity than that of copper, in turn greater than that of cadmium and zinc. They stated that cadmium could not effectively compete with other metals due to its limited adsorption. Pb^{2+} has a strong affinity for the surface of the clayey adsorbent. The presence of Pb^{2+} in the system has strongly influenced the adsorption capacity of Cu^{2+}, Cd^{2+}, and Zn^{2+}. These metals, especially cadmium and zinc, have had only a minor effect on competitive adsorption of Pb^{2+}. Both Cd^{2+} and Zn^{2+} have very close ionic radii of 4.26 and 4.30 Å, respectively, and low electronegativity.

The order of affinity for a metal is usually associated to its physicochemical properties, as stated earlier. The hydrated ionic radius of metals increases in the following order: Pb (4.01 Å) < Cu (4.19 Å) < Cd (4.26 Å) < Zn (4.30 Å).

According to Padilla-Ortega et al. (Padilla-Ortega et al. 2014), the gaps in the adsorption capacities of metals cannot be attributed to the accessibility of those metal cations to the pores of clay because the average diameter of the pores of bentonite, sepiolite and vermiculite are of at least 14 times higher than that of hydrated ionic radii of the corresponding metals.

The interactive behavior of the Pb–Cu system has shown that the studied clay samples removed greater

Table 5 Comparison of the adsorption capacities of metal ions in different mixtures

Metal	Mixture	Adsorbent	$q_{e\ \text{single}}$ (mg/g)	$q_{e\ \text{mixture}}$ (mg/g)	$q_{e\ \text{single}}/q_{e\ \text{mixture}}$
Lead	Pb–Cd	NC	29.11	27.65	0.95
		AC	50.94	46.5	0.91
	Pb–Cu	NC		15.83	0.54
		AC		36.4	0.71
	Pb–Zn	NC		21.07	0.72
		AC		39.03	0.77
	Pb–Cd–Cu	NC		14.65	0.50
		AC		24.17	0.47
	Pb–Cu–Zn	NC		12.26	0.42
		AC		16.36	0.32
	Pb–Zn–Cd	NC		16.43	0.56
		AC		29.39	0.58
	Cd–Cu–Pb–Zn	NC		6.92	0.24
		AC		11.19	0.22
Cadmium	Cd–Pb	NC	20.36	18.61	0.91
		AC	26.16	22.54	0.86
	Cd–Cu	NC		19.153	0.86
		AC		30.93	0.92
	Cd–Zn	NC		17.88	0.86
		AC		25.25	0.95
	Cd–Cu–Zn	NC		8.38	0.41
		AC		10.38	0.39
	Cd–Zn–PB	NC		13.00	0.64
		AC		15.42	0.59
	Cd–Cu–PB	NC		11.16	0.55
		AC		13.37	0.51
	Cd–Cu–Pb–Zn	NC		4.82	0.24
		AC		5.36	0.20
Copper	Cu–Pb	NC	22.30	11.98	0.54
		AC	33.66	21.64	0.64
	Cu–Zn	NC		10.5	0.50
		AC		16.33	0.62
	Cu–Cd	NC		19.153	0.86
		AC		30.93	0.92
	Cu–Pb–Zn	NC		9.45	0.42
		AC		13.84	0.41
	Cu–Pb–Cd	NC		8.55	0.38
		AC		12.14	0.36
	Cu–Cd–Zn	NC		11.45	0.51
		AC		17.92	0.53
	Cd–Cu–Pb–Zn	NC		6.91	0.31
		AC		9.90	0.29

Table 5 (continued)

Metal	Mixture	Adsorbent	$q_{e\ \mathrm{single}}$ (mg/g)	$q_{e\ \mathrm{mixture}}$ (mg/g)	$q_{e\ \mathrm{single}}/q_{e\ \mathrm{mixture}}$
Zinc	Zn–Pb	NC	20.86	13.82	0.66
		AC	26.44	20.79	0.79
	Zn–Cd	NC		17.88	0.86
		AC		25.25	0.95
	Zn–Cu	NC		10.5	0.50
		AC		16.33	0.62
	Zn–Pb–Cd	NC		11.28	0.54
		AC		16.96	0.64
	Zn–Pb–Cu	NC		4.88	0.23
		AC		6.64	0.25
	Zn–Cu–Cd	NC		9.00	0.43
		AC		13.51	0.51
	Cd–Cu–Pb–Zn	NC		3.87	0.18
		AC		4.41	0.17

amount of Pb^{2+} than Cu^{2+}, which proves their better affinity for lead (Usman 2008).

Cd^{2+} and Zn^{2+} showed similar adsorption behavior to the clay samples because of their close physicochemical properties (Mahamadi and Nharingo 2010). The highest affinity for lead and the lowest for cadmium further indicated the effects of the studied metal physicochemical properties on the removal mechanism; the extent of adsorption followed the affinity order (i.e., $Pb^{2+} > Cu^{2+} > Zn^{2+} > Cd^{2+}$). This is a clear dependence on physicochemical properties of the removed metal, especially electronegativity, atomic radius and relative binding strength (Pagnanelli et al. 2003). For clearer description of competitive adsorption in multi-solute systems, we defined a new parameter that reports the maximum adsorbed quantity in multi-solute system to that of mono-solute system. It can explain the effect of competitive adsorption as (1) synergism which can be observed when the amount adsorbed in the mixture is superior to that adsorbed alone in the reaction medium; (2) inhibition of adsorption and (3) absence of interaction between the adsorbates.

We note a net decrease in the amount of adsorbed metal ions on the studied clay materials for the multi-solute systems. This reduction is more accentuated in the case of quaternary mixture.

The ratio $\mathrm{IE} = qe_{\mathrm{mixture}}/qe_{\mathrm{single}}$ allows to compare the competitive adsorption and non-competitive of each adsorbate studied. In fact, we have recorded a small decrease in the adsorption capacity of the lead on natural clay in the presence of cadmium with regard to the binary system Pb–Cu whose ratio goes from 0.780 to 0.537. This result further confirmed that this metal is not significantly influenced by the coexistence of cadmium in comparison with zinc and copper. For all the binary systems studied (i.e., Pb–Cu, Pb–Zn, Pb–Cd, Cd–Cu, Cd–Zn and Cu–Zn), IE was lower than the unit indicating potential competitive effects. The IE values were much lower in the case of ternary and quaternary mixtures (Table 5).

Comparative study

Based on current data and relevant publications, the amount of heavy metals removed (in mg:g) by several potentially low-cost adsorbents is highly variable (Table 6). In all cases, our results demonstrated superior heavy metals removal capabilities of both NC and AC samples. We noted the highest removal efficacy of lead by AC, exceeding 50 mg/g in some cases. This largely exceeded the findings of Minceva et al. (2008) and Mahamadi and Nharingo (2010) who studied the removal of several heavy metals in mixed systems by using zeolites and Eichhorina crassipes, respectively.

Conclusions

Adsorption of several metal cations in multi-element systems on natural and activated clay has been carried out to evaluate the efficiency of those abundant materials in wastewater treatment. It was found that both clay samples were mainly composed of silica, alumina and iron

Table 6 Comparison of the maximum adsorption capacity of heavy metals onto different adsorbents

Adsorbent	Cation	System	q_m (mg/g)	References
Eichhorina crassipes	Pb(II)	Pb	26.32	Mahamadi and Nharingo (2010)
		Pb–Cd	25.38	
		Pb–Zn	22.12	
	Cd(II)	Cd	12.59	
		Cd–Pb	4.05	
	Zn(II)	Zn	12.55	
		Zn–Pb	4.32	
Peat	Cd(II)	Cd	5.16	Liu et al. (2008)
		Cd–Cu	3.83	
		Cu	7.39	
	Cu(II)	Cu–Cd	6.18	
Zeolites	Cd(II)	Cd	5.16	Minceva et al. (2008)
		Cd–Pb	2.60	
		Cd–Zn	3.80	
	Zn(II)	Zn	3.92	
		Zn–Cd	2.02	
		Zn–Pb	0.88	
	Pb(II)	Pb	27.17	
		Pb–Cd	18.62	
		Pb–Zn	24.51	
Bagasse fly ash	Cd(II)	Cd	5.17	Srivastava et al. (2006)
		Cd–Zn	7.24	
Natural Clay	Cd(II)	Cd	21.93	This work
		Cd–Pb	18.61	
		Cd–Zn	19.26	
		Cd–Cu	15.55	
	Zn(II)	Zn	20.86	
		Zn–Cd	17.87	
		Zn–Pb	13.82	
		Zn–Cu	10.50	
	Pb(II)	Pb	29.11	
		Pb–Cd	27.64	
		Pb–Zn	21.07	
		Pb–Cu	15.83	
	Cu(II)	Cu	22.30	
		Cu–Cd	19.15	
		Cu–Zn	14.14	
		Cu–Pb	11.98	
Activated Clay	Cd(II)	Cd	26.74	This work
		Cd–Pb	15.55	
		Cd–Zn	24.99	
		Cd–Cu	17.37	
	Zn(II)	Zn	26.44	
		Zn–Cd	25.25	
		Zn–Pb	20.79	
		Zn–Cu	16.33	
	Pb(II)	Pb	50.94	
		Pb–Cd	46.51	
		Pb–Zn	39.03	
		Pb–Cu	36.40	
	Cu(II)	Cu	33.66	
		Cu–Cd	30.93	
		Cu–Zn	26.24	
		Cu–Pb	21.64	

oxide. They are smectitic samples with somewhat high specific area and enhanced textural properties. From the adsorption experiments, it appeared an affinity order of $Pb^{2+} > Cu^{2+} > Zn^{2+} > Cd^{2+}$. It was also found that mixed system adsorption capacity substantially decreased because of the competitive effect. In addition, natural and activated clay samples showed a greater affinity to lead than copper, zinc and cadmium because of its physicochemical properties (i.e., relative binding strength, hydrated radii, electronegativity and constants of hydrolysis). Among the models used to describe the adsorption data, extended Langmuir model best fitted the experimental results.

In conclusion, both NC and AC clay samples showed high efficiencies for the elimination of metal pollutants in single and multi-element systems; they can be used as effective adsorbents for removing toxic metals from wastewater. This is fundamentally important for an integrated and sustained environmental remediation strategy of contaminated effluents.

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