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ADSORPTIVE CAPACITY OF MONTMORILLONITIC CLAYS

Arial 11

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Arial 10

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The present study has been carried out to evaluate the applicability of natural clays in the removal of several metal ions including Pb(II), Cd(II), Cu(II) and Zn(II) from aqueous solutions by batch adsorption process. Environmental pollutants of these heavy metals have to be removed from wastewaters before being discharged in the receiving ecosystems. Therefore the use of natural clays for the removal of heavy metals was a significant target of this study. Moreover, the advantages of Tunisian clay were demonstrated with this regards. The effects of contact time and initial metal concentration were studied in detail. The effects of the removal of impurities on the adsorption of heavy metals were also emphasized. The adsorption isotherms including Langmuir, Freundlich and Dubinin Radushkevich (D-R) isotherm were applied to the equilibrium data for describing the main interactive mechanisms involved in the removal processes. Kinetic parameters were also calculated from the pseudo-first-order and pseudo-second-order models for better description of adsorption mechanism.

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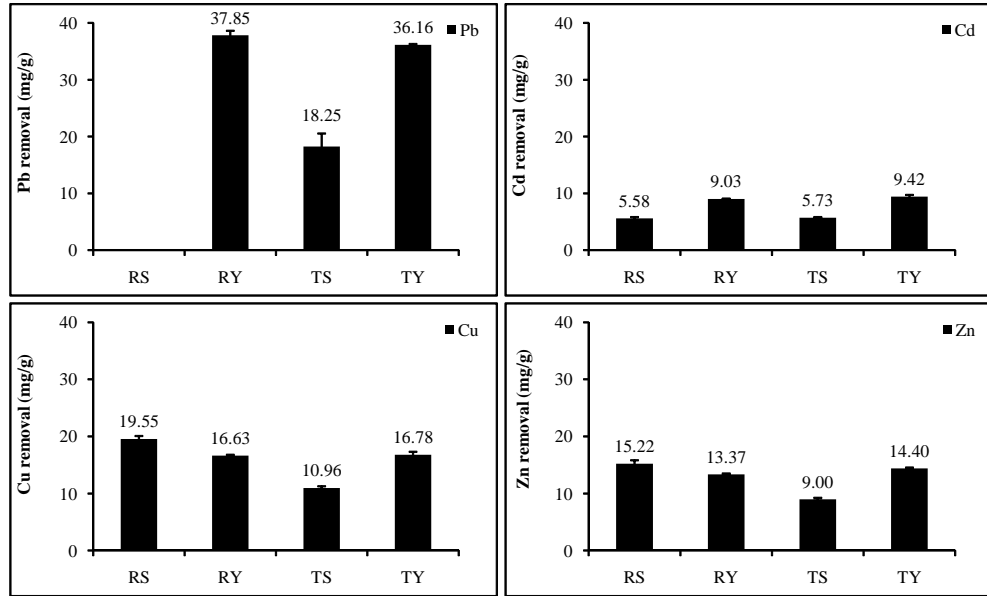
Two natural clay samples were collected from of Gabes (Y sample) and Gafsa (S sample) areas, south of Tunisia. Further preparation of the samples from natural clays was done to remove carbonate minerals and organic matter. Then, both original and treated clay samples were saturated with 1M NaCl solution. Na⁺ homoionic clay samples thus obtained were dried at 105 °C for 24 h and crushed to collect the desired particle size of < 210 μm. For batch experiments, a polypropylene tube containing 1 g/L of clay samples (RS, RY, TS and TY, where R and T refer to raw and treated clay samples, respectively), and metal ion solution of known concentration and pH was shaken at 200 rpm for 60 min to reach equilibrium. The adsorption experiments were carried out with concentrations of Cd(II) 10 mg/L, Zn(II) 20 mg/L, Cu(II) 40mg/L, and Pb(II) 60 mg/L under the operating pH of 6, and agitation speed of 200 rpm within the equilibrium time of 60 min at 25°C. The suspension was then centrifuged, and 10 mL of supernatant were withdrawn, filtered with 0.45 μm syringe driven filter (Millex-LH, PTFE, Millipore Corp., Ireland), and stored at 4°C till the measurement of each metal concentration using an ICP-AES Instruments (Optima 7300 DV series, PerkinElmer Inc., Tokyo). All experiments were run in triplicate.

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Chemical analysis showed that the main constituents of natural (RS and RY) and treated (TS and TY) clays were silica, aluminum and iron oxides. The results indicated that RS clay, collected from Gafsa area, contained high amount of calcium and its chemical composition was significantly affected by acetic acid treatment. The data indicated that the percentage of silica of S sample increased from 40.096% to 57.144%, with a significant increase in the mass fraction of aluminum and iron oxides. The data also indicated that TS showed a reduction in the fraction of CaO and MgO after acid treatment, decreasing from 26.667 to 2.372% and from 4.667 to 2.751%, respectively. The occurrence of magnesium oxide in both samples may bear witness to the presence of smectite and also small amount of dolomite in the carbonate rich clay (RS). It should be emphasized that SiO₂, Al₂O₃, and Fe₂O₃ contents were obviously higher in RY than RS clay, but this difference disappear after the removal of calcium and other impurities. The removal of carbonate and organic matter enhanced the percentage of silica and aluminum in the treated clays, but that of both the exchangeable and the octahedral cations has clearly decreased.

High removal efficiency of Pb(II) was achieved by RS due to the precipitation as lead carbonate, but the removal capacity decreased to 18.25 mg/g Pb(II) for TS due to the removal of carbonate minerals. The same behaviour was observed with Cu(II) and Zn(II) by S sample (both RS and TS) with a decrease from 19.55 mg/g to 10.96 mg/g and from 15.22 mg/g to 9 mg/g for Cu(II) and Zn(II) removal, respectively, but not for Cd(II). The amount of Cd(II) removal was 5.58 mg/g, 5.73 mg/g, 9.03 mg/g and 9.42 mg/g by RS, TS, RY and TY, respectively (Fig. 1). This indicate that both original and treated carbonate free samples removed similar amounts of Cd(II).

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Fig. 1 Removal of heavy metals by natural clays in single element system (figure's legend must be written under the figure)

Based on previous relevant studies, the amount of heavy metals removed by various clay materials is highly variable (Table 1). In the current study, natural clay samples demonstrated a substantial removal of metals when compared with treated forms. It was clear from the study data that the removal efficiency was dependent upon the physicochemical characteristics of the clay and the metal removed; The calculated Langmuir capacities were 131.58 mg/g, 51.28 mg/g, 32.89 mg/g and 50.76 mg/g for lead, and 27.40 mg/g, 17.89 mg/g, 12.97 mg/g and 17.10 mg/g for copper removal by RS, RY, TS and TY samples, respectively. The lowest removal occurred for cadmium and zinc. Generally, the removal remained roughly constant in the case of RY and TY; and decreased somewhat for the TS sample with regards to RS because of carbonate removal. All these results indicate much higher removal efficiency for the present clay samples than was shown other author, who reviewed the removal of metals like lead, cadmium, copper and zinc by various kinds of clay (table 1). We found that the clay collected from southern Tunisia exhibited greater removal efficiency than those reported in literature. Therefore, its plausible to confirm that the coniacian-early Campanian clays of southern Tunisia are suitable for the removal Pb(II), Cd(II), Cu(II) and Zn(II) from aqueous solutions.

Table 1 Comparison of adsorption capacity with those of previous removal studies with natural clays (table's legend must be written on the top of the table)

Metal	Sorbent	$q_{max}(mg/g)$	$k_L(L/mg)$
Lead	RS	131.579	2.054
	RY	51.282	0.436
	TS	32.895	0.533
	TY	50.761	0.552
	Kaolinite clay	31.75	0.049
	Smectitic clay	25	0.99
	Illitic clay	25.44	0.041

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