

Examination of Adsorption Abilities of Natural and Acid Activated Bentonite for Heavy Metals Removal from Aqueous Solutions

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ABSTRACT

The effect of the initial concentration of Cr, Co, Cu, Ni, and Pb metal ions from multicomponent solutions on the sorption capacity of natural and acid activated bentonite was examined in this paper. The acid activation was performed by using hydrochloric and sulfuric acid at different concentrations. The results of adsorption research have shown that bentonite can be effectively used as an adsorbent for the removal of metal ions from multicomponent solutions. Acid activation of bentonite changes the structure and content of individual oxides, increases the porosity and the number of available spots for the adsorption process. For this reason, the bentonite removal efficiency increased after acid activation for all heavy metals tested. With increased acid concentration, the degree of bentonite adsorption increased, and sulfuric acid rather than chloric acid showed better results in removal efficiency.

Keywords-- Adsorption, Bentonite, Heavy Metals, Acid Activation

I. INTRODUCTION

Pollution of natural and wastewater is most often the result of the heavy metals discharge into the watercourses [1]. Heavy metals can be removed from aqueous solutions by various methods such as chemical precipitation, solvent extraction, membrane filtration, ion exchange, electrochemical removal, coagulation, etc. [2]. However, these techniques have disadvantages such as incomplete removal, high energy consumption, toxic sludge generation, low efficiency, sensitive operating conditions and high waste disposal costs [3,4]. To overcome such disadvantages, different approaches have been proposed, aimed at developing more inexpensive and more efficient methods for improving the quality of effluents [2]. Most are based on the application of the adsorption process, because adsorption has the greatest impact on the transport, toxicity and bioavailability of heavy metals (especially at low concentrations, in trace

amounts) in aqueous solution, in addition the process is inexpensive and easy to perform. [5,6].

Considering the fact that bentonite is a natural material, the mechanical milling method can produce inexpensive adsorbents, and the activating adsorbents method is also environmentally friendly.

Aluminum oxides and clay minerals such as bentonite, kaolin and pyrophyllite are relatively widespread minerals in the earth's crust, which are known to be good adsorbents of various metal ions. Bentonite belongs to the smectite family and is classified as a natural clay of layered phyllosilicates composed of alternating octahedrons and tetrahedrons in a 2:1 ratio. The structure, chemical composition, exchangeable ionic type and small size of the crystals contribute to the unique properties of these clays, including a large chemically active surface, high cation exchange ability and high porosity. The degree of adsorption efficiency of heavy metals depends on a number of factors such as: pH value influence, temperature influence, adsorbent dose influence, initial concentration influence, contact time influence, etc. Bentonite has been shown to be effective adsorbent for heavy metals removal from waste water. However, despite the very good adsorption properties they possess naturally, there is increasing emphasis on the modification of natural clays in order to improve the general physicochemical properties. Activation methods with chemical agents or temperature are most commonly used to improve these properties. Acidic activation of clay achieves an increase in specific surface area and porosity [7]. The alteration degree of the active surface and the clay structure porosity caused by the action of acids depends on the type of clay minerals, i.e. chemical composition of clays, the type of interlayer cations, the acid applied and its concentration, temperature and time of action [8]. Acid-activated clays in industry are most commonly used as adsorbents, bleaches and catalysts [9].

The aims of the paper are as follows:

- To examine the possibility of using natural and modified bentonite as an inexpensive adsorption material

for the removal of heavy metal ions.

- To examine the adsorption capacity of heavy metals (Pb, Cr, Cu, Co and Ni) from multi component solutions using natural and modified bentonite.

- To determine the effect of acid activation (with hydrochloric and sulfuric acid) on the sorption removal properties of heavy metals.

II. EXPERIMENTAL PART

The bentonite sorption property for Pb, Cr, Cu, Co, and Ni ions was examined for its natural and modified form. The modified form of bentonite was obtained by acid activation with hydrochloric (HCl, 36%) and sulfuric acid (H₂SO₄ 96%). Based on the previous calculation, 0,4; 0,5; 0,6 M HCl and 0,4; 0,5; 0,6 M H₂SO₄ were prepared by adding known concentrations of pure acid into a 500 ml volumetric flask. After the required acids were prepared, 400 ml of 0.4 M HCl were weighed using a measuring cylinder and carefully transferred into a 500 ml laboratory beaker.

The resulting mixture was stirred on a magnetic stirrer for eight hours at 200 rpm. Upon completion of the mixing process, the suspension was filtered through fine filter paper on a pre-set apparatus. During the filtration, the bentonite on the filter paper was washed with distilled water until a negative reaction to Cl⁻ ions, which was checked with silver nitrate (AgNO₃ 5%).

The bentonite filter paper was dried in a drying oven at 105 ° C for four hours. The dried bentonite was then ground in a porcelain mill and sieved through a 75 micrometer sieve. In this way, bentonite was acid activated with 0,4; 0,5; 0,6 M HCl. The same procedure was repeated for 0,4; 0,5; 0,6 M H₂SO₄, except that the bentonite on the filter paper was washed by distilled water until negative reaction to SO₄²⁻ ions, which was checked by BaSO₄ solution.

2.1. Materials

Bentonite from a deposit in Šipovo, Bosnia and Herzegovina, was used for experimental research. Experimental research was performed in the accredited laboratory of the Institute for Quality, Standardization and Ecology. The laboratory is licensed for wastewater testing and is accredited to BAS ISO 17025: 2006, which implies that certified reference materials and chemicals of proven traceability and purity are used.

Standard solutions of Cr, Co, Cu, Ni and Pb prepared from certified reference materials in different concentration ranges were used.

After preparation of all materials, a batch adsorption process of the tested heavy metals ions from aqueous solutions was carried out using the following:

1. Natural (crude) bentonite
2. Acid-activated bentonite with 0,4; 0,5; 0,6 M HCl
3. Acid-activated bentonite with 0,4; 0,5; 0,6 M H₂SO₄

The following standard method was used to determine the content of Cr, Co, Cu, Ni, Pb heavy metals:

BAS ISO 8288: 2002 Method A Water quality (Flame atomic absorption spectrometry method). A 240 Series Agilent Technology atomic absorption spectrophotometer was used to determine the content of heavy metals. All experiments were performed at room temperature.

The contact time between the adsorbent and the multipart solution was 2 hours and did not change during the analyses.

The X-Ray method was used to determine the chemical composition of bentonite, and the pH value of the biosorbent was determined by the zero-charge method.

III. RESULTS AND DISCUSSION

The obtained chemical analysis values for SiO₂, Al₂O₃, Fe₂O₃ (48.28%, 23.04%, 4.52%) show a similar trend in the results obtained by researchers Abdullahi and Audu, 2017: who tested two bentonite samples in parallel, and those were: (48.16% and 49.87% for SiO₂, 14.86 and 14.98% for Al₂O₃ and Fe₂O₃, respectively: 4.80% and 5.12%).

The results also obtained for SiO₂ are similar to the values reported by other authors (45 wt. %); and (48.35 wt. %) [11,12]. However, when it comes to Fe₂O₃ content, the results obtained are lower than those (11.10 wt. %) (8.26 wt. %) but higher than (3.82 wt. %) [11,12,13].

Since these are clays of smectite origin, the presence of Ca, Mg, Na and K is expected. Considering that the adsorption of heavy metal ions on clays depends on a large number of parameters, and that the pH value is one of the most significant, the optimal pH value at which the process is guided was determined before following the sorption processes of heavy metal removal.

The figure 1 presents a review of the change in pH values, concluding that the zero charge point for bentonite is 8.27. Above these values the removal of positively charged ions will be more efficient. Comparing the results for natural clay 7.8 can be concluded that a slightly lower value than our [14].

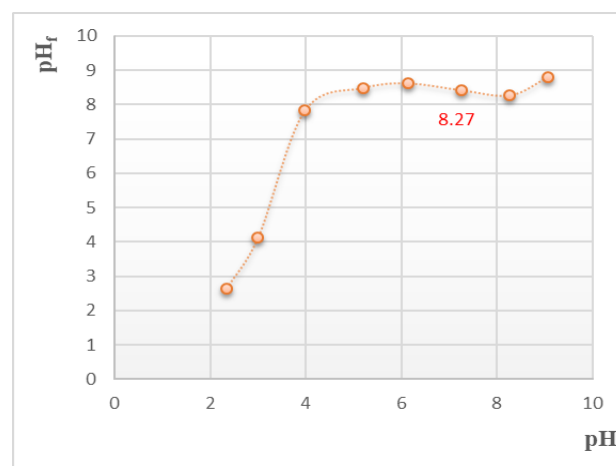


Figure 1: Zero charge point for bentonite

The effect of different metal concentrations in solution on the removal efficiency was examined, as well as the different types of acid activation carried out using HCl and H₂SO₄ in different concentration ranges.

By varying the concentration of individual ions from 5 to 30 mg/dm³ in multicomponent solution, the effect of this parameter on the adsorption of Cr, Co, Cu, Ni, and Pb ions on natural bentonite and bentonite activated with HCl and H₂SO₄ in a different concentration range was investigated. The individual results of removal efficiency, E (%) and adsorption capacity q_i (mg/L) for the indicated ions are shown in the figures 2. - 8.

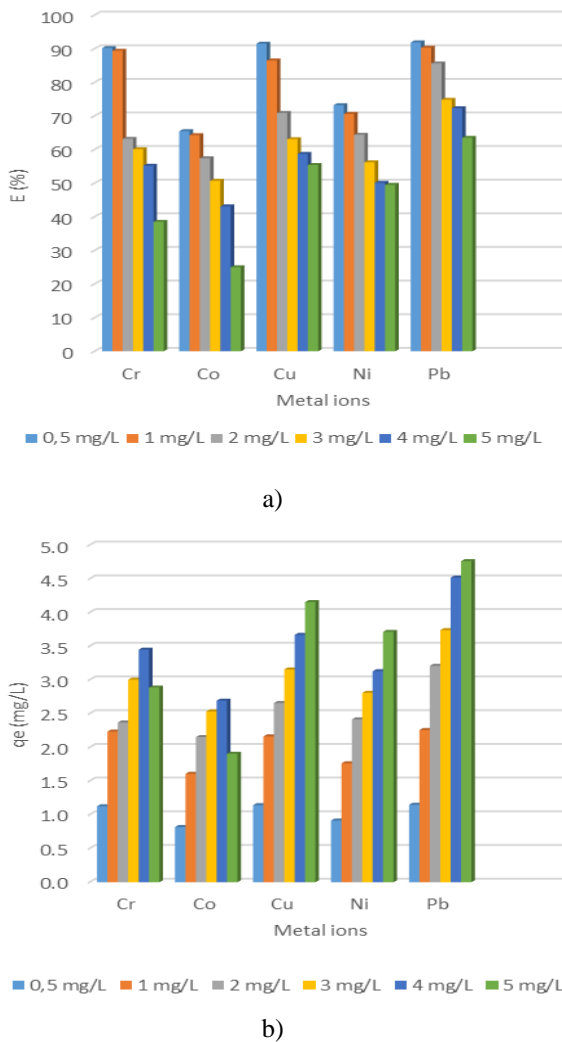


Figure 2: Effect of initial concentration of multicomponent heavy metal solution C_i (mg/dm³) on removal efficiency a) E (%), and b) equilibrium adsorption capacity q_e (mg/L) of crude bentonite

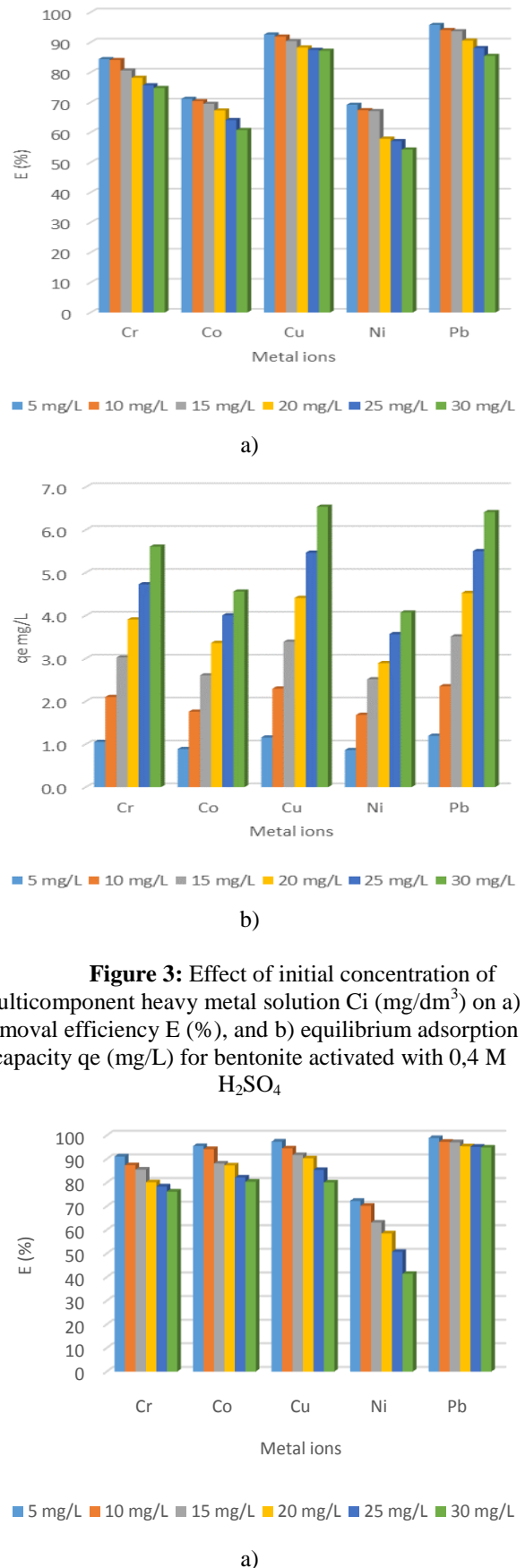
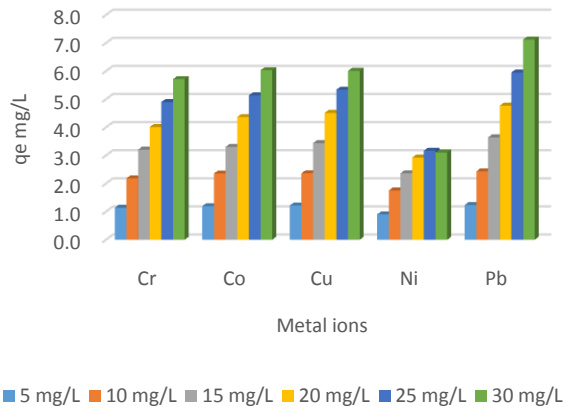
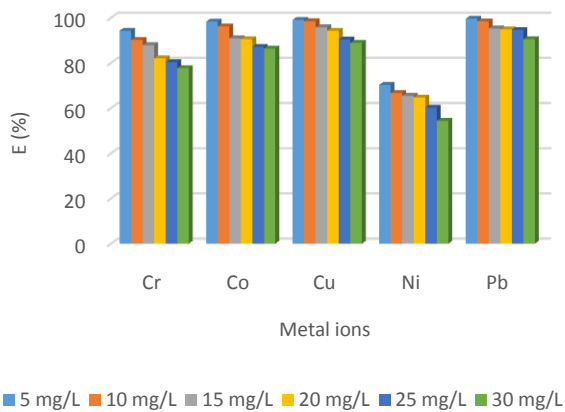


Figure 3: Effect of initial concentration of multicomponent heavy metal solution C_i (mg/dm³) on a) removal efficiency E (%), and b) equilibrium adsorption capacity q_e (mg/L) for bentonite activated with 0.4 M H₂SO₄

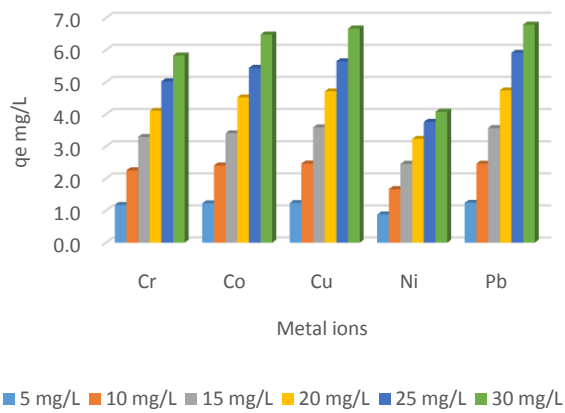


b)

Figure 4: Effect of initial concentration of multicomponent heavy metal solution C_i (mg/dm^3) on a) removal efficiency E (%), and b) equilibrium adsorption capacity q_e (mg/L) for bentonite activated with 0,4 M HCl



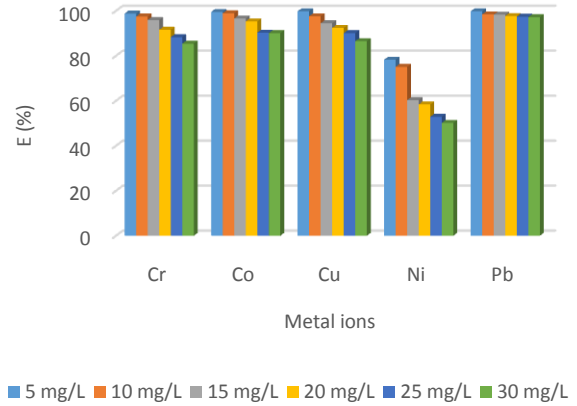
a)



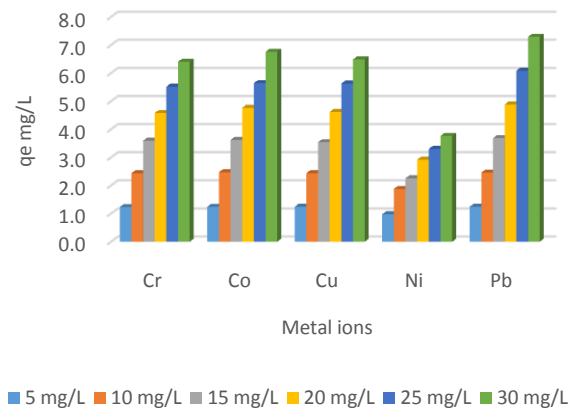
b)

Figure 5: Effect of initial concentration of multicomponent heavy metal solution C_i (mg/dm^3) on a)

removal efficiency E (%), and b) equilibrium adsorption capacity q_e (mg/L) for bentonite activated with 0,5 M H_2SO_4

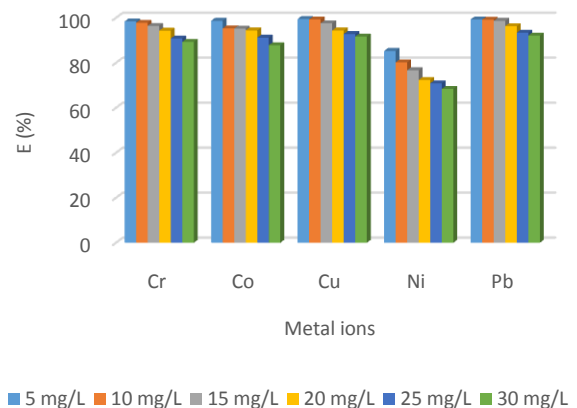


a)

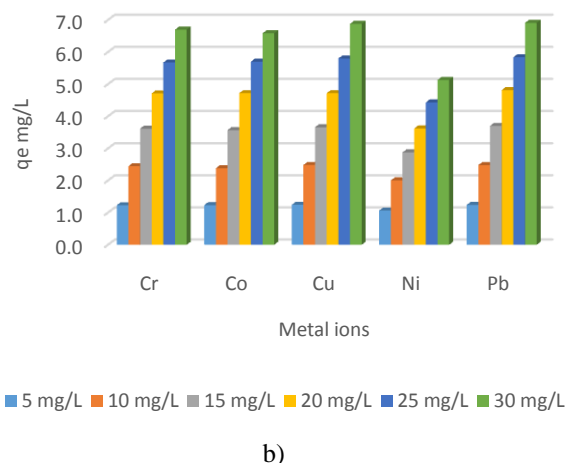


b)

Figure 6: Effect of initial concentration of multicomponent heavy metal solution C_i (mg/dm^3) on a) removal efficiency E (%), and b) equilibrium adsorption capacity q_e (mg/L) for bentonite activated with 0,5 M HCl

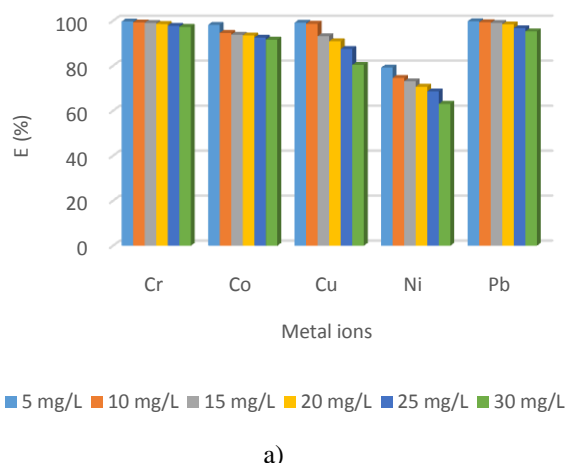


a)

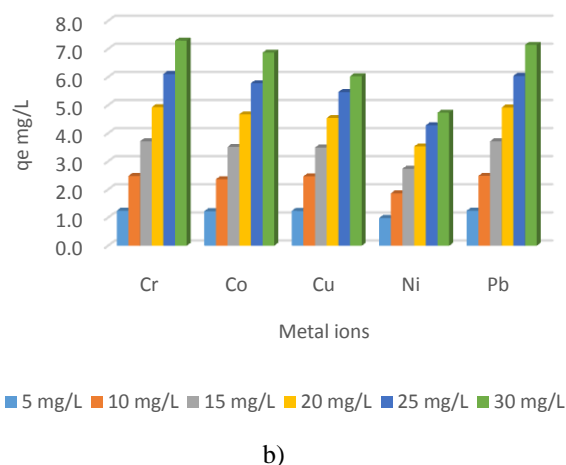


b)

Figure 7. Effect of initial concentration of multicomponent heavy metal solution C_i (mg/dm^3) on a) removal efficiency E (%), and b) equilibrium adsorption capacity q_e (mg/L) for bentonite activated with 0,6 M H_2SO_4



a)



b)

Figure 8. Effect of initial concentration of multicomponent heavy metal solution C_i (mg/dm^3) on a)

removal efficiency E (%), and b) equilibrium adsorption capacity q_e (mg/L) for bentonite activated with 0,6 M HCl

The initial concentration of the metal has a significant effect on the adsorption process. The removal efficiency of Cr, Co, Cu, Ni, and Pb using natural and treated bentonite is decreased when increasing the initial concentration of heavy metal ions in aqueous solutions. The reason for the decrease lies in the fact that as the concentration increases, the contact surface of the adsorbent decreases in such a way that the number of adsorption spots is reduced. In contrast, the change in the equilibrium adsorption capacities, q_i , shows the opposite process, that is, the increasing trend of changes relative to the change in the removal efficiency of heavy metal ions; the increase in q_i with increasing initial concentration of solution of heavy metal ions is a result of stronger attractive forces between the active spots of bentonite and metal ions.

Using natural bentonite, it was concluded that heavy metals were removed from aqueous solutions in the following sequence: Pb (63.5-91.9%) > Cu (55.4 - 91.5%) > Ni (49.5-73.2 %) > Co (25.4–65.5%) > Cr (38.5–90.2%). The use of acid-treated bentonite showed an increase in ion removal efficiency, and the series of adsorbed heavy metals remained the same as in natural bentonite.

Many authors have tried to explain in their works the influence of certain physicochemical properties of metal ions on different removal adsorption.

The affinity of the adsorbent for a given metal ion is correlated with the physicochemical properties (ionic radius, electronegativity, electronic configuration, molar mass, oxidation state, etc.).

In order to determine the efficiency of the process of bentonite acid activation, the influence of different starting concentrations of HCl and H_2SO_4 on the adsorption removal capacity was observed. The results obtained show that with increasing acid concentration, the removal efficiency of all tested heavy metals increases, as expected, the surface areas increased after acid treatment, which is a likely consequence of the cations removal from the clay structure, thereby promoting porosity. Following acid activation of bentonite, it was noticed that higher removal efficiency of heavy metals was given by H_2SO_4 compared to HCl acid. From the obtained values it can be concluded that 0.6M H_2SO_4 gives the best results. Similar results were obtained by many other authors for different metal ions.

IV. CONCLUSION

Adsorption results have shown that bentonite can be used as an effective adsorbent for the simultaneous removal of Cr, Co, Cu, Ni and Pb ions from aqueous solutions when the pH value is adjusted to about 8.2. The improvement in the adsorption properties of acid-treated

bentonite is the result of structural alterations, which have led to an increase in the number of spots available for adsorption. Sulfuric and hydrochloric acid can be used to increase the sorption properties of bentonite, since sulfuric acid obtains better results.

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