

Heavy Metal Adsorption Properties of the Basement Complex of Clay Deposit in Ire-Ekiti Southwestern Nigeria

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Abstract: Raw clay collected from Ire-Ekiti, Ekiti State, Nigeria, was used to adsorb some heavy metals (Pb^{2+} , Cr^{3+} , Ni^{2+} and Cu^{2+}) from aqueous solution of the metals. A laboratory batch adsorption study was performed to study the effect of concentration, pH, particle size, temperature and agitation time on adsorption characteristics of the adsorbates on the raw kaolinite clay. The experimental variables were found to have significant effect on metals sorption with an optimum pH of 5.0, 0.50g adsorbent dose, 200 μ m particle size and 50mL adsorbate solutions. Equilibrium sorption was obtained for Pb^{2+} , Cr^{3+} , Cu^{2+} and Ni^{2+} at 40, 60, 60, and 70 min respectively. The effect of temperature showed that the adsorption process was exothermic for Pb^{2+} while that of Cr^{3+} , Ni^{2+} and Cu^{2+} showed endothermic. The adsorption capacity of the clay for the metal ions is as follows: $Pb^{2+} > Cu^{2+} > Cr^{3+} > Ni^{2+}$ with percentage removal of 99.3, 80, 70.9 and 68.7 respectively. Efficiency of the raw clay showed possible suitability for removal of metals in their respective contaminated medium.

Keywords: adsorbate; adsorption; kaolinite; heavy metals; efficiency; equilibrium.

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I. Introduction

The direct discharge of effluents containing heavy metals like copper, lead, chromium etc., from industries like tanneries into bodies of water has become a growing environmental problem (Obaroh *et al.*, 2012). Globally, industries are growing permanently looking for new discoveries and technologies for removing heavy metals from effluents released into the environment as these metals are not eco-friendly and are hazardous to human health. Their toxicity typically affects multiple organ systems; severity of the health outcomes of toxic metals depends on the type and form of the element, route and duration of the exposure, and, to a greater extent, on a person's individual susceptibility (Ahmaruzzaman, 2011). It is important that metal contaminants are removed or reduced to the levels at which they can no longer pose any risk or danger to human health.

Precipitation, ion exchange, electrodialysis, chemical oxidation and sorption on activated carbon and other sorbents are conventional methods for the removal of heavy metal ions from aqueous solutions (Gomez-Serrano 1998; Chen and Chen, 2003; Hamdaoui, 2009; Fu and Wang, 2011). Membrane-filtration, reverse osmosis and electrodialysis are physical methods, which are usually based on very expensive materials, and cannot handle large volumes of waste-water. Due to high maintenance cost, these methods cannot be applied in the developing countries for heavy metal remediation.

The use of clays as adsorbent have advantages upon many other commercially available adsorbents in terms of low-cost, abundant availability, high specific surface area, excellent adsorption properties, non-toxic nature, and large potential for ion exchange (Crini, 2010). Recently, samples of clay materials from Morocco have been investigated for the removal of arsenic (V) from aqueous solution by Bentahar *et al.* (2016). Research by Rao and Kashifuddin (2012) showed that ball clay was found to exhibit an excellent adsorption capacity towards Cd (II) ions. Eloussaief and Benzina (2010) confirmed the applicability of Tunisian clay for the removal of lead from aqueous medium. Bourliva *et al.* (2004) also reported the removal of lead (II) and Zinc (II) from aqueous solutions by the raw vermiculite from Askos, Thessaloniki County, Greece, and Kent.

It has been reported that the naturally occurring and abundant Ire-Ekiti clay in Ekiti State, Nigeria could find application for remediation of non-metal. For instance, research by Asaolu and Awokunmi (2017) showed that Ire-Ekiti clay could find application in the de-fluoridation of waste water. Therefore, it is important to investigate the adsorption properties of naturally abundant Ire-Ekiti clay soil available in Nigeria for the remediation of heavy metals contamination in a polluted medium. This research is tailored towards investigating the heavy metals (Pb^{2+} , Cr^{3+} , Ni^{2+} and Cu^{2+}) adsorption properties of the basement complex of Ire-Ekiti clay deposit.

II. Materials And Methods

2.1. Sample collection and preparation

Clay soil was collected from Ire-Ekiti, Ekiti State, Southwestern Nigeria. An adequate amount for use was crushed and dispersed in deionized water, then floating debris from plants were removed by hand picking and also by decantation. The suspension was thoroughly stirred to allow none clay materials to be separated from the clay. The clay soil was recovered from water by centrifuging the suspension at 3000rpm. The recovered clay soil was oven dried at 110°C for 12 hours and cooled in a desiccator. After cooling, the dried clay sample was crushed in a ceramic mortar and sieved using sieves of different sizes ranging from 200 - 500µm. The sieved clay soil was stored in a black polyethylene bag prior to analysis.

2.1.1. Preparation of metal solution

The reagents used to prepare solutions of metal ions were all extra pure analytical grades. The stock solutions (1000mgL⁻¹) of the metals ions (Ni²⁺, Pb²⁺, Cu²⁺ and Cr³⁺) were prepared by dissolving weighed quantities of metal salts (potassium chromate, lead nitrate, copper nitrate and hydrated nickel sulphate) in de-ionised water and serially diluted to prepare solutions of varying initial concentration for experimental works. The concentrations of metal ions were determined using a Flame Atomic Adsorption Spectrophotometer (Agilent AAS 55AA).

2.2. Physico-chemical properties of the clay sample

The soil pH was determined by weighing 10g of the clay sample into a 250ml beaker and 100mL deionized water was added to the clay soil sample and stirred for 15min and the mixture was allowed to settle down for 10 min (Ramachandra *et al.*, 2012). The pH was determined by an already calibrated (Buffer 7) Jenway pH meter. Cation exchange capacity of the clay soil samples was determined by methods described by Thorpe (1973). The particle size distribution was determined by hydrometer method as described by Bouyoucos (1962), while the soil organic matter was determined by method of lost on ignition (LOI); the modified method of Heiri (2001).

2.3. Chemical characterization

The functional group elucidation of the soil sample was carried out by Fourier Transformed Infrared Spectrophotometer (FTIR). Scanning Electron Microscope (SEM) was used to show morphology of the clay soil sample. Metals concentration was determined by Flame Atomic Absorption Spectrophotometry (FAAS). The chemical composition of the clay soil sample was determined using X-ray Fluorescence (XRF), while the elemental make-up was determined by Particle Induced X-ray Emission technique (PIXE).

2.4. Batch adsorption experiments

Adsorption experiments were carried out by adding 50mL adsorbate solution of 10mg/L into conical flasks containing 0.50g of the adsorbent. The adsorbent and adsorbate mixtures were then equilibrated at pH value of 5.0 by shaking at 200rpm in a temperature (298K) using a rotary orbital shaker until equilibrium; where necessary during the experiments, the pH of the working solutions was adjusted by adding drops of either HCl or NaOH. After equilibration, the mixtures were centrifuged for 10min at 3000rpm after which the supernatants were collected and analysed for equilibrium concentrations of the Cu, Ni, Pb and Cr using Flame Atomic Absorption Spectrophotometer. Effect of pH on adsorption processes was studied at pH values of 3, 4, 5, 7 and 8 with equilibration time of 90 min. Effect of agitation time was investigated at time varied from 10 to 80 min at pH value of 5. The rate of Cu, Ni, Pb and Cr removal were evaluated as a function of adsorbent particle size at pH of 5 using different particle sizes of 500, 425, 355, 250, and 200µm with equilibration time 90 min. The adsorption of Cu, Ni, Pb and Cr unto the clay soil was optimized at different concentrations of 20, 40, 60, 80 and 100ppm with equilibration time of 90 min at pH value of 5 in order to study the effect of adsorbate concentration on the adsorption processes. Effect of temperature on the metals removal was carried out at different temperatures of 300, 315, 330, 340 and 350K with agitation time of 90 min at pH value of 5.

2.4.1. Data treatment

The per cent metal removal was calculated according to Equation (I)

$$\% \text{ Metal removal} = \frac{C_0 - C_e}{C_0} \times 100 \quad \text{..... (I)}$$

Where C_0 (mg/L) and C_e (mg/L) are the initial and equilibrium concentrations of adsorbate solution respectively.

III. Results and discussion

The mean values of the physico-chemical properties of the clay sample are presented in Table 1. The soil pH has a mean value of 6.17 ± 0.01 . This showed that the soil is slightly acidic.

Table 1: Mean Physico-chemical analysis of the raw clay

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pH	CEC (meq/100g)	OM (%)	PSD (%)
6.17 ± 0.01	8.5 ± 0.05	10.28 ± 0.08	Clay = 58.1
			Sand = 32.4
			Silt = 9.50

The result of the particle size distribution (PSD) showed that the soil sample is composed of clay, sand, silt and gravel, having the values of 58.1%, 32.4%, 8.6% and 0.9% respectively. This showed that the soil is majorly composed of clay. The results obtained in this study showed that the mean organic matter is 10.28 ± 0.08%. The mean cation exchange capacity (CEC) is 8.5 ± 0.05 meq/100g. This indicates that the clay soil has a low CEC which is a typical characteristic of kaolinite clay (Adebowale *et al.*, 2003).

Figure 1 shows SEM image of the raw Ire-Ekiti clay soil. The photograph of the natural clay presents a uniform laminar structure as if particles tend to pile on one another. The inter-aggregate pores in this structure are small in size as the particles are stacked on one another in consistent order resulting in the highly dense arrangement.

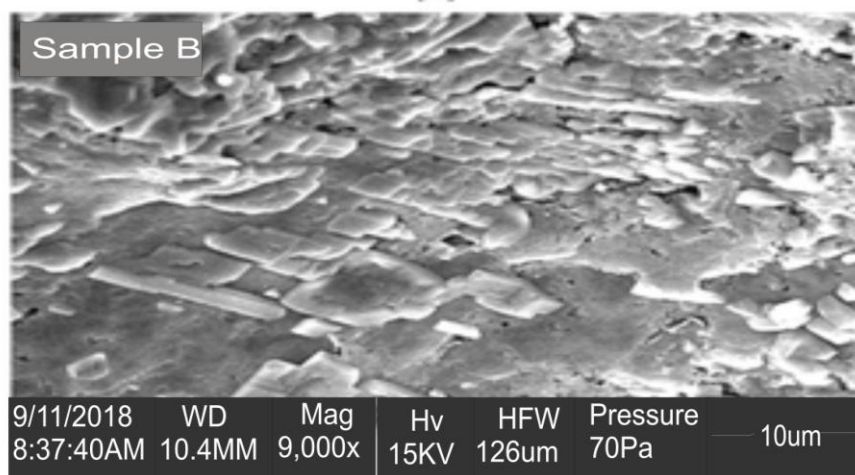


Fig. 1: Scanning microscope photographs of raw clay sample

The small pore size may hinder the permeability of the adsorbate, result to low diffusion and reduced adsorption. The particle size of the clay sample (10µm) is above those of nanomaterial, hence, cannot be classified as a nanomaterial.

The result from the Proton Induced X-ray Emission technique showed that Al³⁺ and Si⁴⁺ are the major elemental composition having the highest concentration of the clay soil matrix as presented in Table 2.

Table 2: Elemental composition and concentration of raw Ire-Ekiti clay soil

Atomic no.	Symbol	Conc (ppm)
11	Na	28810
12	Mg	153101
13	Al	242444
14	Si	558138
15	P	329
17	Cl	281
19	K	3101
20	Ca	2723
22	Ti	2097
24	Cr	261
25	Mn	312
26	Fe	41320
29	Cu	381
30	Zn	138
37	Rb	35.8
40	Zr	562
46	Pd	20.5
47	Ag	217
48	Cd	91.6

50	Sn	217.8
82	Pb	13.8

The chemical composition showed that silica and alumina are the major constituents of the clay with per cent composition of 55.8 and 24.28 respectively.

Table 3: Chemical composition of raw Ire-Ekiti clay

Oxide	Composition (%)
SiO ₂	55.8
Al ₂ O ₃	24.28
Fe ₂ O ₃	4.16
Na ₂ O	2.91
K ₂ O	0.32
MgO	1.54
CaO	0.27
TiO ₂	0.2
ZrO ₂	0.06
MnO	0.03
LOI	10.3
Total	99.87

The result of the chemical composition as shown in Table 3 agrees with the result obtained from the PIXE. The results obtained from the PIXE and XRF analysis, showed that the clay soil is an Alumino-silicate (kaolinite) (Emamet *et al.*, 2016; Awokunmi and Asaolu, 2017). A study by Akinola *et al.* (2014) also showed that Ire-Ekiti clay soil is kaolinite.

The results of the FTIR analysis are shown in Figure 3. Results from the FTIR study showed adsorption bands at 3697, 3620, 3421 and 3263 cm⁻¹ are due to the hydroxyl group of the inner surface of the clay (Djebbaret *et al.*, 2014). The bands at 1099 and 1006 cm⁻¹ correspond to Si-O-Si group. The band at 694 cm⁻¹ is due to the bending mode of the same group.

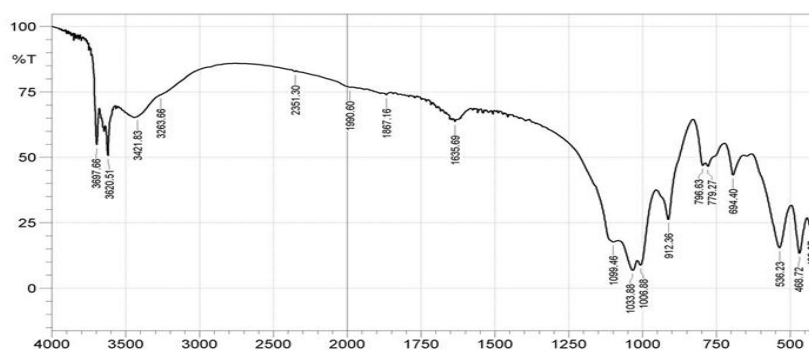


Fig. 3: Fourier Transform Infrared Spectra of the raw clay soil

The bands at 1633 and 1402 cm⁻¹ are due to the presence of C=O and C=C of the organic components of the clay soil. The band at 536 cm⁻¹ is due to the presence of Si-O-Al group (Van der Marel & Beutelspacher, 1976; Petit & Decarreau, 1990; Wilson, 1994; Saikia *et al.*, 2003). The presence of metallic oxide in the clay soil is indicated by the intensity bands at 468 and 432 cm⁻¹.

3.1. Effect of agitation time

The effect of adsorption time on the removal rate of Ni²⁺, Pb²⁺, Cu²⁺ and Cr³⁺ is shown in Figure 4. The removal rate of Pb²⁺ in solution was optimized (98.75%) within a short period (40 min) and tended to be stable for 80 min. The rapid adsorption during the initial stages might be due to the presence of abundant active sites on the surface of the kaolinite clay, which becomes saturated with time (Akpomie *et al.*, 2016). Fast rate of lead adsorption by kaolinite clay was also observed in the research conducted by (Juan *et al.*, 2018). The optimum removal of copper was observed to be at 60 min then reduced after 60 min which shows saturation and reduction in the available active sites as sorption operation or adsorption equilibrium is achieved (Bedouiet *et al.*, 2008), while chromium and nickel adsorption increased significantly with increase in time. A good adsorbent must not only have a high adsorption capacity but also a fast rate of removal.

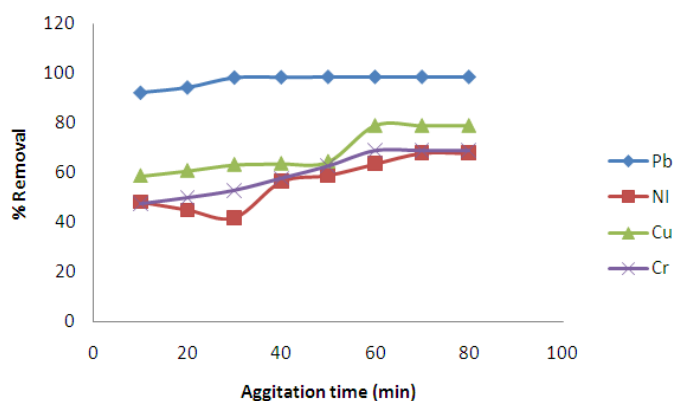


Fig. 4: Adsorption trend with increase agitation time for the metals

The fast adsorption of Ni^{2+} , Pb^{2+} , Cu^{2+} and Cr^{3+} on raw Ire-Ekiti clay indicated the applicability of the adsorbent in industrial processes.

3.2. Effect of pH

The effect of pH on the metal ions (Ni^{2+} , Pb^{2+} , Cu^{2+} and Cr^{3+}) removal rate was investigated at 298 K for 90 min as shown in Figure 5. The removal rate for all metal ions was observed to be optimum at pH 4 and 5.

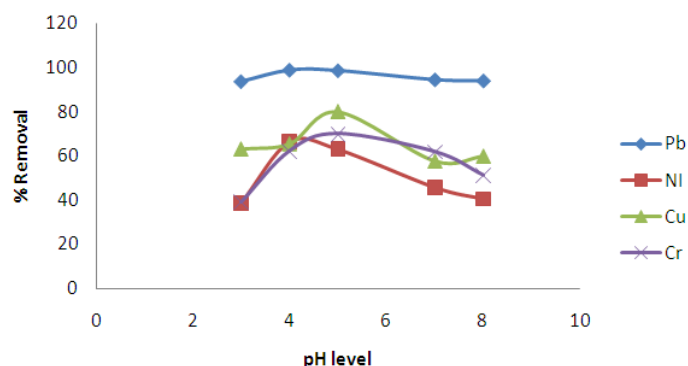


Fig. 5: Adsorption trend with increase pH for the metals

Among the adsorption conditions, the pH of the aqueous solution is an important variable for the adsorption of metals onto adsorbents (Deng *et al.*, 2017). In this study, the adsorption efficiency was significantly low at pH below 4.0. At a low pH, the number of H^+ ions exceed that of Ni^{2+} , Pb^{2+} , Cu^{2+} and Cr^{3+} ions several times and the surface of the clay is most likely covered with H^+ ions, which account for less Ni^{2+} , Pb^{2+} , Cu^{2+} and Cr^{3+} adsorbed (Krishna and Susmita, 2006). As the pH increases, more and more H^+ ions leave the clay surface, creating more available sites for the metal ions to bind through a mechanism similar to that of exchange interactions (Jiang *et al.*, 2009) thereby, resulting in increased adsorption. This increase in adsorption occurs steadily with pH until optimum pH when further adsorption is not possible (Olu-Owolabiet *et al.*, 2016). When the solution pH is greater than 6.0, the metal solution tends to form a metal hydroxide precipitate and the solution system become relatively complex (Juan *et al.*, 2018). The equilibration pH of this research which is below 6.0 indicates the suitability of the raw Ire-Ekiti clay for removal of Ni^{2+} , Pb^{2+} , Cu^{2+} and Cr^{3+} ions from waste water under an acidic condition. This is in accordance with the results obtained by Jiang and Akpomiet *et al.*, 2017).

3.3. Effect of adsorbate concentration

The effect of initial metal ion concentration on adsorption onto the raw clay is shown in Figure 6. Results from this study showed that the adsorption capacities of adsorbent increased with the increase in equilibrium metal ion concentration, for Ni^{2+} , Pb^{2+} , Cu^{2+} and Cr^{3+} from 20mg/L to 100mg/L. A higher concentration of adsorbate solution implies a higher concentration of metal ion to be fixed on the surface of the adsorbent (Krishna *et al.*, 2006).

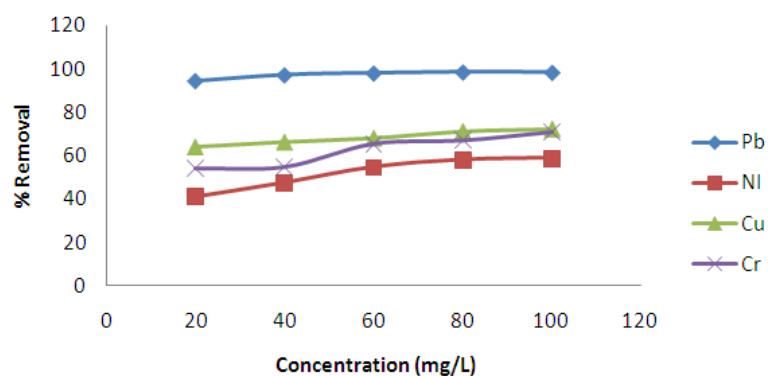


Fig. 6: Adsorption trend with increase concentration for Ni²⁺, Pb²⁺, Cu²⁺ and Cr³⁺

When pore diffusion limits the adsorption process, the relationship between the initial solute concentration and the rate of adsorption will not be linear (Knocke and Hemphill, 1981). Linearity in Figure 4 showed that pore diffusion does not limit the adsorption process (Emamaet *al.*, 2016). Similar results were reported by Eba (2010); Mbaye *et al.* (2014); Zourai (2016).

3.4. Effect of adsorbent particle size

Findings from this research work as shown in Figure 7 depicts that adsorption increased with decreased particle size of the raw clay adsorbent for all targeted metal ions. It could be concluded that adsorption of metals tends to decrease with increased particle size and *vice versa*.

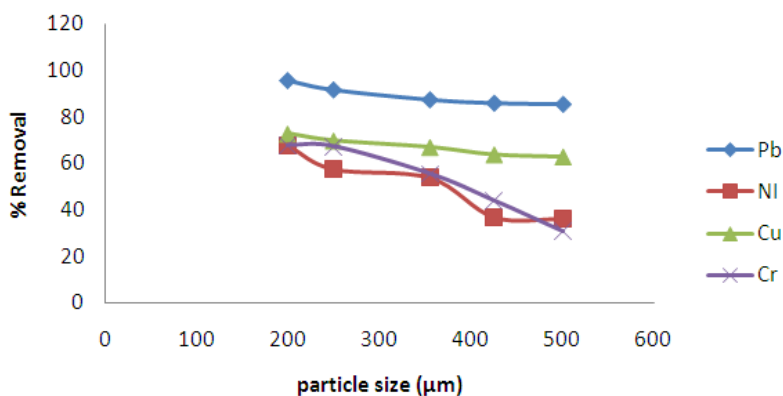


Fig. 7: Adsorption trend with increase particle size for the metals

The decrease is attributed to decrease in surface area of the adsorbent with increase in particle size while decrease in particle size would yield larger surface areas and availability of more active sites for adsorption (Karaa *et al.*, 2007).

3.5. Effect of temperature

The adsorption phenomenon is usually affected by many parameters, particularly temperature. In fact, the temperature affects two major aspects of adsorption: the equilibrium position in relation with exothermicity and endothermicity of the process and the swelling capacity of the adsorbent (Rattanaphani *et al.*, 2007; Natalia *et al.*, 2015). Thus, adjustment of temperature may be required in the adsorption process. As observed in Figure 8, the uptake capacity of Pb by the clay material decreases with increasing temperature. This is possibly due to the exothermic effect of the surroundings during the adsorption process (El-Sayed *et al.*, 2011). The enhanced sorption of copper, chromium and nickel by the clay adsorbent with temperature increase is attributed to endothermicity of the adsorption process (Akpomie *et al.*, 2016).

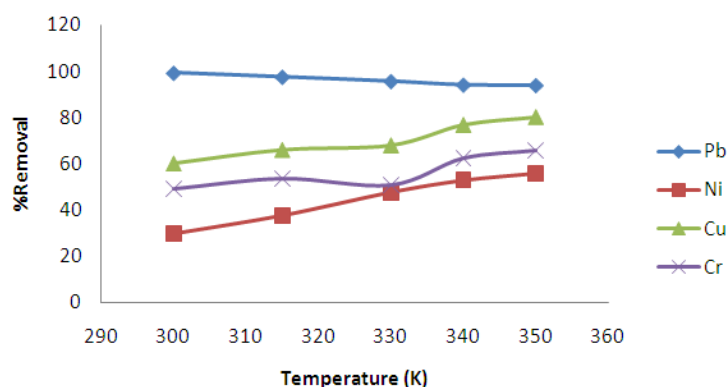


Fig. 8: Adsorption trend with increase temperature for the metals

This showed the ability of copper, chromium and nickel ions to overcome resistance to mass transfer with increase in kinetic energy to undergo an interaction with the active sites of the adsorbents (Gonzalez *et al.*, 2005). Similar results have been reported (Rattanaphani *et al.*, 2007; Zourabiet *et al.*, 2016).

IV. Conclusion

Ire-Ekiti clay in its raw form, showed a considerable ability to remove Ni^{2+} , Pb^{2+} , Cu^{2+} and Cr^{3+} from their aqueous solutions. The clay best removed lead ion. The excellent lead and Copper removal reached the value of 99.3% and 80% respectively. Efficiency of the raw clay showed its suitability for removal of the metals in their respective contaminated medium.

Competing interests

The authors declare that there are no competing interests.

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