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## Adsorption and Desorption of Heavy Metals onto Natural Clay Material: Influence of Initial pH

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### ABSTRACT

The adsorptive capacity of natural clay materials towards adsorption of heavy metals as well as the heavy metals competitive adsorptive/desorptive selectivity sequences are greatly influenced by operating conditions. In this study, competitive adsorption of heavy metal ions (Cd, Cr, Cu, Pb and Zn) on natural clay was investigated in order to understand the influence of initial pH on the clay mineral adsorptive capacity and the heavy metals adsorption/desorption selectivity sequences. Batch adsorption and desorption experiments were performed at six different initial pH values (2, 4, 6, 8, 10 and 12). The amount of heavy metals removed at equilibrium in single and multi-component adsorption scenarios were analyzed and interpreted using distribution coefficients followed by selectivity sequence. The results indicated that the selectivity sequence of clay changed with pH for both Single Component (SC) and Multi-Component (MC) scenarios. The selectivity sequence of heavy metal ions on the adsorbent for the single component and multi-component scenarios were Cr>Pb>Cu>Cd>Zn and Cr>Cu>Pb>Cd>Zn, respectively while for multi-component desorption, the selectivity sequence was Cr<Cd<Cu<Pb<Zn. From the results, Pb ions became highest selective at pH 4 and 6 (SC scenario) but exchanged position with Cd ions in alkaline condition (pH 12). The initial pH plays a significant role in competitive adsorption and desorption of the heavy metals onto the clay mineral.

**Key words:** Competitive adsorption and desorption, pH effect, clay adsorptive capacity, heavy metals selectivity sequence, multi-component adsorption

### INTRODUCTION

Heavy metal ions in waters are toxic to human and aquatic animals even at low concentrations. They are usually stable and non-biodegradable within the ecosystem. As a result, they tend to bioaccumulate in living tissues thereby causing some serious health concerns.

According to the WHO (1984), some of the heavy metals of most immediate concern are lead (Pb), cadmium (Cd), copper (Cu), chromium (Cr) and zinc (Zn). Copper and zinc are essential dietary nutrients that our body need in trace amounts. However, intake of these trace elements beyond or below certain thresholds may cause health problem including gastrointestinal disturbance, liver and kidney failure, prostate cancer and bone anomalies (Han *et al.*, 2009; Leitzmann *et al.*, 2003). Saudi Arabian Standards Organization (SASO) limits the maximum level

of Cu and Zn in drinking water to 1 and 5 mg L<sup>-1</sup>, respectively (Alabdulaaly and Khan, 1999). Chromium is essential for several human metabolic processes, but affects human physiology, accumulates in the food chain and causes many ailments when present in larger concentrations (Bansal and Goyal, 2005). The Cr<sup>6+</sup> is more hazardous to health than Cr<sup>3+</sup> due to the former's high toxicity. Conversely, Pb and Cd have no essential function to plants and animals apart from causing different carcinogenic, mutagenic and chronic diseases in humans (Adie *et al.*, 2010; Futalan *et al.*, 2011; Ismail *et al.*, 2009; Oke *et al.*, 2011; Olarinoye *et al.*, 2011). SASO limits these trace elements in drinking water to a maximum of 50, 5 and 50 µg L<sup>-1</sup> for Pb, Cd and Cr, respectively (Alabdulaaly and Khan, 1999).

Various treatment techniques including adsorption, precipitation, ion exchange and reverse osmosis have been employed to eliminate or reduce these toxic heavy metal concentrations in water and wastewater. Adsorption on solid surfaces is the most common one and efforts are being made continuously to develop new, low cost and efficient adsorbents for removal of heavy metals.

For the removal of toxic heavy metals, recently, many efforts have been focused on adsorbents such as activated carbon, clay and sediments in riverbeds and in suspension. Over the years, the role played by adsorbents in water and wastewater treatment had been critically and elaborately investigated (Oke *et al.*, 2011).

Several low cost adsorbents such as agricultural/industrial wastes and natural/synthetic clay minerals have been used as effective adsorbents for removal of heavy metals, organics and radionuclides (Ahmad, 1995; Covelo *et al.*, 2007a; Eloussaief *et al.*, 2009; Gier and Johns, 2000; Hizal and Apak, 2006; Ishii *et al.*, 2006; Jiang *et al.*, 2010; Liu, 2007; Liu and Zhang 2007; Vejsada *et al.*, 2005; Walker *et al.*, 1988; Wang *et al.*, 2011). Hence, in the past decades, clay minerals have been used as effective adsorbents for heavy metal removal in water treatment because of their strong ion-exchange and complex formation abilities with the heavy metals (Bekkouche *et al.*, 2012; Srivastava *et al.*, 2005). However, few investigations have been reported on natural clay application for simultaneous removal of multi-component heavy metal removal from water or wastewater. It is expected that, when several heavy metals exist in the water or wastewater stream, some will be more difficult to be removed than others and also competitive environment is created. For example, Cd ions are generally more difficult to be removed using adsorption compared to others such as Pb and Cu (Bekkouche *et al.*, 2012). In addition, to our best knowledge, local clay from Al-Hassa Oasis, Saudi Arabia has not been tested for feasibility of removal of heavy metals from water and wastewater streams. Knowing the sorption and desorption characteristics of the heavy metals on the clay minerals, will in no small measure, aid in modeling the behavior of the soil when contaminated by these heavy metals. It will also be useful in designing amendments and increasing fixation of the heavy metals on the soil in case of contamination by these species (Covelo *et al.*, 2007a). Prediction of the behavior of soils of arbitrary composition may also be achieved through studying sorption and desorption behavior of these clay minerals (Covelo *et al.*, 2007a). The clay buffer capacity and by extension, the initial pH play an importance role in the mobility of the heavy metals in the clay. Alkaline pH condition enhances the precipitation of the heavy metals thereby reducing their mobility. In this report, the adsorptive capacity of local Saudi Arabian clay from Al-Hassa Oasis was tested for single and multi-component heavy metals removal in simulated wastewater streams at different initial pH. The investigation focused on the competitive sorption and desorption behavior of 5 heavy metals (Cd, Cr, Cu, Pb, Zn) onto local clay.

## MATERIALS AND METHODS

**Reagents:** Throughout the study, analytical grade reagents were used. Standard solutions of the heavy metal ions which were prepared from their respective nitrate salts at concentration of 1000 mg L<sup>-1</sup> were used. Distilled water was used for stock solution preparation and dilution purposes. Solutions of single and multi-component metal ions were prepared at the same concentration (20 mg L<sup>-1</sup> each). pH adjustments to the desired values (2, 4, 6, 8, 10 and 12) were achieved using 0.1 N HCl or 0.01 M NaOH solution. All glassware were cleaned with dilute HNO<sub>3</sub> (10% v/v) and oven dried (Isotemp oven, Fisher Scientific) at 120°C before use.

**Characterization:** Clay used in this study is a local Saudi Arabian clay from Al-Hassa oasis. From the chemical analysis conducted by acid digestion of 5 g of clay sample using 20 mL of concentrated HNO<sub>3</sub> acid (analytical grade), it was found that heavy metals are present in the natural clay in trace amounts. Respectively, the clay pH, moisture content, soil organic matter (SOM) and electrical conductivity were determined according to the protocol outlined in ASTM D 4972, D 2216, D 2974 and D 1125 (ASTM, 2004). Surface area and pore volume were measured using the Brunauer-Emmet-Teller (BET) multipoint technique using nitrogen gas adsorption at -195.976°C.

The clay sample was also characterized using Scanning Electron Microscopy (SEM) and X-Ray Diffraction (XRD) using an FEI Nova Nano SEM 230 FE-SEM model and Rigaku Ultima IV MPD X-ray diffractometer fitted with a monochromator, respectively. Other standard geotechnical parameters of the clay such as specific gravity, liquid and plastic limits, sieve analysis and hydraulic conductivity were determined according to standard procedures set out by the American Society of Testing and Materials (ASTM, 2004).

**Adsorption and desorption experiments:** The clay mineral was powdered using a wooden pestle and sieved through mesh to obtain finer grains prior to its use in the adsorption and desorption studies. The resulting clay powder was acid washed and oven dried at 110°C. Exactly 5 g of the dried clay was mixed with 100 mL of metal ion solutions and the resulting suspension pH was adjusted to the desired value (2, 4, 6, 8, 10 or 12) using few drops of HCl or NaOH. Batch adsorption experiments were conducted at constant room temperature of 20°C for single metal adsorption (each component separately) and for multi-component (simultaneous presence of all the heavy metals). Different heavy metals in solutions with the clay in suspension were shaken on a horizontal rotary shaker (New Brunswick Scientific Co., Inc. USA) for 20 h. The suspension was filtered twice; first using a 0.45 µm, 150 mm Φ Whatman membrane and secondly, using suction filtration with a finer size membrane having pore size of 0.2 µm and 47 mm Φ.

For the desorption study, 1 g of the residue from the adsorption study was dried and 20 mL of 0.01 M NaNO<sub>3</sub> solution was added to the sample and stirred for 30 min. The suspension was then filtered and the filtrate was collected in vials for metal ions analysis. Method 200.2 guidelines prepared by the U.S. EPA for sample preparation procedure for spectro-chemical determination of heavy metals (Martin *et al.*, 1994) was strictly adhered to.

**Analytical method:** All filtrates from the adsorption and desorption studies were analyzed for the investigated heavy metals (i.e., Cd, Cr, Cu, Pb and Zn) using Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES, Spectro Ciros Vision model) owing to the expected high residual concentration of heavy metals in the analyte (Ortega, 2002). The standards used for initial

calibration verification and continuous calibration verification were from multi-element standards produced by CPI International (in 2% HNO<sub>3</sub>+tr HF). Five percent HNO<sub>3</sub> was used as the blank sample for calibration purpose. All tests were run in triplicates and the average of each of them was found.

**Adsorptive capacities:** The amount of heavy metals removed (adsorbed) at equilibrium in single and multi-component adsorption studies were analyzed and interpreted using adsorptive capacity,  $q$ , percentage adsorbed onto the clay soil,  $R_a$  and distribution coefficient,  $K_d$  which were computed using Eq. 1-3. Desorption results were analyzed by computing the percentage desorbed,  $R_d$ , according to Eq. 4, after 30 min of stirring:

$$q = \frac{(C_0 - C_e)}{M} V \quad (1)$$

$$R_a = \frac{C_0 - C_e}{C_0} 100 \quad (2)$$

$$K_d = \frac{C_s}{C_e} \quad (3)$$

$$R_d = \frac{C_t}{C_e} 100 \quad (4)$$

where,  $C_0$  is initial liquid-phase concentration of sorbate ( $\text{mg L}^{-1}$ );  $C_a$  is equilibrium solid-phase adsorbed concentration of sorbate onto the adsorbent;  $C_e$  is equilibrium liquid-phase concentration of sorbate;  $C_t$  is experimental concentration in the solution at time  $t$  ( $\text{mg L}^{-1}$ );  $M$  is adsorbent mass (g);  $V$  is volume of solution (mL);  $R_a$  is per cent pollutant adsorbed (%);  $R_d$  is per cent pollutant desorbed (%);  $K_d$  is distribution coefficient of the sorbate ( $\text{L kg}^{-1}$ ).

Using the calculated the distribution coefficients for the heavy metals, selectivity sequence for each pH value was arrived at.

## RESULTS AND DISCUSSION

Findings of this study will be presented and discussed under the following headings: characteristics of the clay soil, single and competitive adsorption studies, selectivity sequence and statistical comparison and desorption study.

**Characteristics of the clay soil:** Table 1 summarizes the physico-chemical properties of the clay sample obtained from the numerous analyses carried out as outlined above.

The pH value of the investigated clay is naturally alkaline (9.53) which promotes heavy metals precipitation and adsorption onto the clay surface. Soil organic matter (4.3%) plays an importance role in the adsorption of heavy metal ions even in soils where its value is very low (Sparks, 2003). This is because, SOM possesses very high specific surface area that may reach up to  $800\text{-}900 \text{ m}^2 \text{ g}^{-1}$  and a Cation Exchange Capacity (CEC) which may range between 150 and 300  $\text{cmol kg}^{-1}$  (Stevenson, 1982). Stevenson (1982) posited that the majority of a

Table 1: Physical and chemical properties of the clay

Property	Value
pH (ASTM D 4972)	9.53
Moisture content (%) (ASTM D 2216)	3.91
Soil organic matter (%) (ASTM D 2974)	4.30
Hydraulic conductivity (cm sec <sup>-1</sup> ) (ASTM D 5084)	6.91081×10 <sup>-09</sup>
Electrical conductivity (mS cm <sup>-1</sup> ) (ASTM D 1125)	56.17
Average pore width (by BET <sup>r</sup> ), Å	75.64
BET Specific surface area (m <sup>2</sup> g <sup>-1</sup> ) (UOP964)	42.13
Pore volume (cm <sup>3</sup> g <sup>-1</sup> ) (UOP964)	0.08
Specific gravity (ASTM D 854)	2.77
Liquid limit (ASTM D 4318)	44.71
Plastic limit (ASTM D 4318)	25.95
Plasticity index	18.76
USCS classification (ASTM D 2487)	CL <sub>s</sub> (Clay)
<b>Particle size distribution (ASTM D 422)</b>	
Clay (%)	78
Silt (%)	6
Very fine sand (%)	10
Fine sand (%)	5
Medium sand (%)	1

BET: Branaur-Emmett-Teller

surface soil's CEC is in fact attributable to its SOM. Soil Electrical Conductivity (EC) varies with the amount of moisture held by soil particles. Hence, sands have a low EC, followed by silts while clays have the highest EC. It has strong correlation to soil particle size and texture (Grisso *et al.*, 2009). Soil EC as defined by Grisso *et al.* (2009) 'is the ability of a material to transmit (conduct) an electrical current'. Electrical conductivity of clay typically lies between 10 and 1000 milli siemens per meter. The EC of the clay sample is 5617 milli Siemens per meter which implies that it has an excess of dissolved salts (Grisso *et al.*, 2009; Sparks, 2003). The clay surface area (42 m<sup>2</sup> g<sup>-1</sup>) will give it ability to adsorb heavy metals on its surface.

Reddi and Inyang (2000) posited that the water contents at which clay soil transit from one state to the other represent its entire physico-chemical behavior. Plastic limit gives a measure of the water content at which transition from semi-solid to plastic state occurs while liquid limit represents the water content needed for the clay soil to begin exhibiting flow characteristics similar to liquids. For the clay soil used in this study, its plastic and liquid limits are 25.95 and 44.71, respectively (Table 1).

The results from the SEM which show the clay morphological and elemental composition are provided in Fig. 1, 2 and Table 2. The elemental composition in Table 2 indicated that the dominant elements in the clay are O and Si whose percentage compositions are 53 and 18% respectively. Other elements present in lesser quantities are Ca, Al, Fe, Na, Cl, K and Mg. The clay surface area will enhance the contact area and facilitate adsorption of positively charged ions. It will also make it possible for the clay soil to accommodate heavy metals on its active sites through ion exchange and complexation. The mineralogical composition using XRD revealed that the clay is mainly composed of montmorillonite; quartz and calcite are also present in lesser quantities. Montmorillonite has been described by Reddi and Inyang (2000) to possess a 2:1 layer structure, with extensive isomorphous substitution of iron and magnesium for aluminum

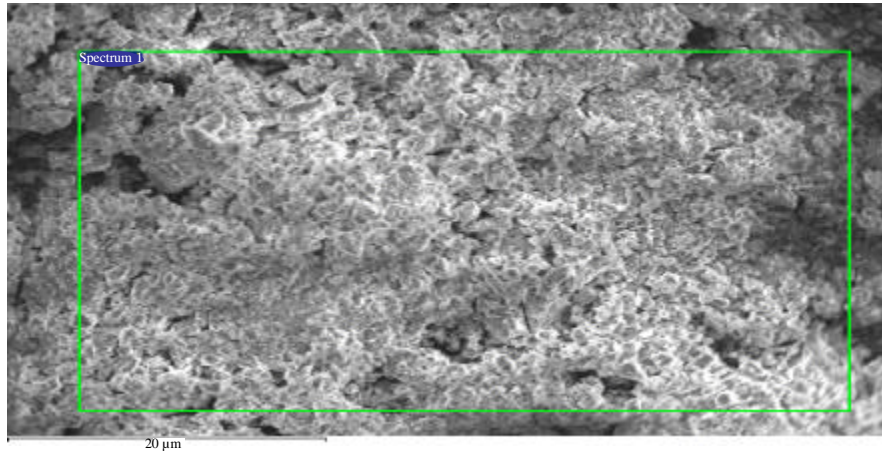


Fig. 1: Scanning electron micrograph of clay at 40,000 magnification

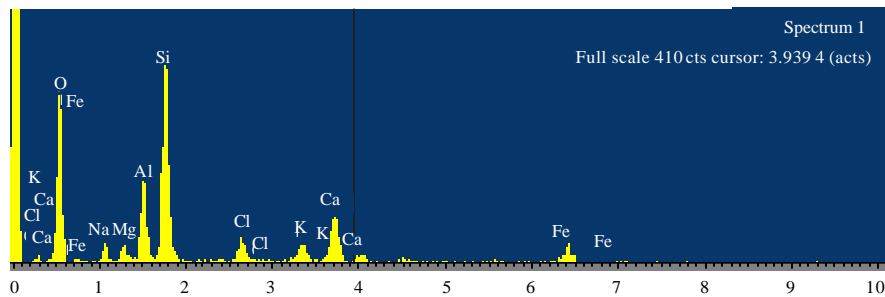


Fig. 2: Elemental composition of the clay mineral

in the octahedral sheets, the layer of which are separated by several sheets of water molecules. Belonging to the secondary minerals, montmorillonite has the highest specific surface area, plastic and liquid limits, hence serves as good adsorbent (Reddi and Inyang, 2000). In acidic environment, calcite may be leached away or decomposed to yield carbon dioxide, thereby creating more pores in the solid matrix. It may also help raise the buffer capacity of the clay soil due to the presence of carbonate.

### Single and competitive adsorption studies

**Cadmium ions:** Due to different ionic forms of the heavy metals and ionization state of the surface functional groups, pH plays the most significant role in adsorption studies (Bekkouche *et al.*, 2012). The first systematic studies of Cd ions adsorption from aqueous solutions using Activated Carbons (ACs) were reported by Haung and Ostovic (1978). From Fig. 3, single component adsorption of Cd ions increases with an increase in pH of the solution. The amount of Cd ions adsorbed was smallest at pH values less than 4, but increases at higher pH values. In the same vein, the lowest percentage removal from solution was observed to be 90.2% (at pH = 2) as shown in Fig. 4, but remained more or less constant at pH values greater than 10. Similar trend was observed by Ferro-Garcia *et al.* (1988) and Huang and Ostovic (1978) using different ACs as adsorbents. At lower pH, hydrogen ions are adsorbed onto the clay surface, thus, suppressing Cd

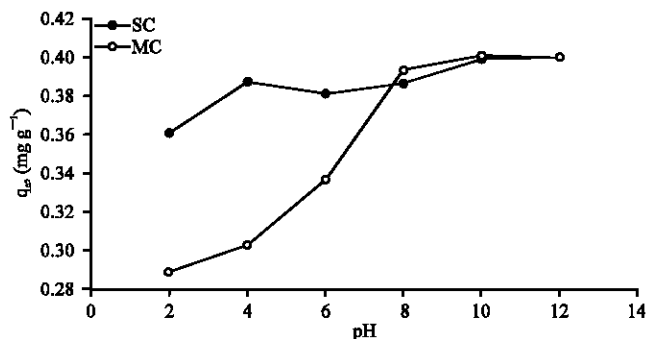


Fig. 3: Effect of pH on the adsorptive capacity of clay for cadmium for both single component and multi-component adsorption scenarios

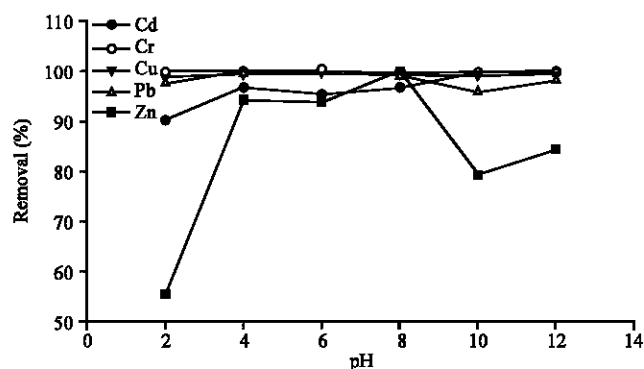


Fig. 4: Percentage of heavy metals removed against pH for single component adsorption scenario

ions adsorption. Further increase in the hydrogen ions concentration (decreasing pH) will only lower the adsorptive capacity of Cd ions (Ismail *et al.*, 2009). As the pH increases, hydrogen ions concentration decreases, providing more space for Cd ions to be adsorbed onto the clay surface. Although Ferro-Garcia *et al.* (1988) have reported extremely low percentage adsorption (<5%) of Cd ions onto different ACs (olive stone, peach stone and Almond shell), the present study found high percentage adsorption (90.2%) of Cd ions onto clay even at low pH values. This observed difference may arise due to the fact that clay soil is negatively charged even at low pH, thus having higher capacity for the adsorption of positive ions, whereas carbon surface is positively charged at low pH which enables the electrostatic repulsive interactions between the cations and the positively charge carbon surface to prevail (Ferro-Garcia *et al.*, 1988). From the aqueous speciation of Cd ions, it remains mainly as Cd<sup>2+</sup> up to about pH = 8 (Srivastava *et al.*, 2005).

In the presence of competitive ions (Cr, Cu, Pb and Zn), Cd ions adsorption was found to be suppressed as depicted in Fig. 3, but exhibited similar trend as in single component adsorption that is, percentage removal increases with an increase in pH as shown in Fig. 5. The effect of competitive adsorption has reduced the percentage removal from 90.2% (in single component adsorption) to 72.24% (in multi-component adsorption) which gives a percentage decrease of about 20%. At pH values greater than 10, complete removal was achieved (Fig. 4, 5). This is because more ions are competing for a limited number of adsorption sites on the clay surface. Cd ions were found to be the least adsorbed during competitive adsorption. This finding is in agreement with earlier studies on competitive adsorption of Cd ions onto clay soil as corroborated by Srivastava *et al.*



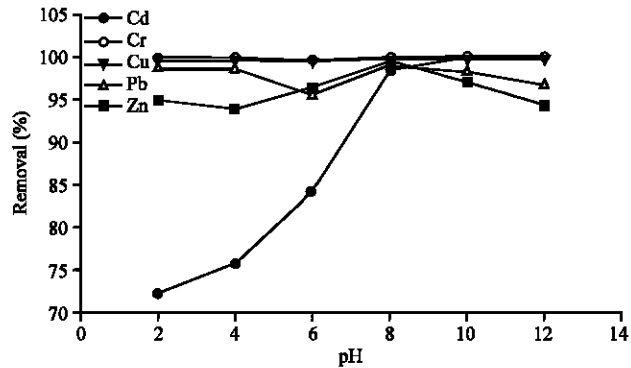


Fig. 5: Percentage of heavy metals removed against pH for multi-component adsorption scenario

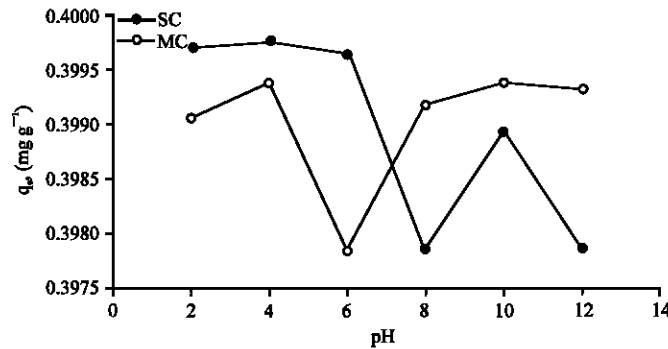


Fig. 6: Effect of pH on the adsorptive capacity of clay for chromium for both single and multi-component adsorption scenarios

(2005), Benjamin and Leckie (1981) and Biddappa *et al.* (1981). Low adsorption of Cd ions in the presence of other competing heavy metal ions may not be unconnected with its relatively low electronegativity value. Futalan *et al.* (2011) suggested that adsorptive capacities of metal ions are influenced by their electronegativity values. Beyond pH = 8, Cd ions removal was not affected by the presence of other metals (Fig. 3). Regardless of the presence of other metals in solution, Cd ions removal increased with increasing solution pH (Fig. 5).

**Chromium ions:** For the single component adsorption study of Cr ions, Figure 6 shows that Cr ions adsorption was highest at pH = 4. This is similar to the results obtained when lignite coal and bituminous coal were used as adsorbents as reported by Kannan and Vanangamudi (1991). The percentage removal remained fairly constant and maximum up to pH = 6, then, declined at higher pH values (Fig. 4). Also Huang and Wu (1975) observed similar trend for Cr ions adsorption on calcined charcoal and Fitrasorb-400 activated carbons. This observation was attributed to reduction which occurs in acidic solutions of  $\text{Cr}^{6+}$  to  $\text{Cr}^{3+}$  and adsorption of  $\text{Cr}^{6+}$  was much larger than that of  $\text{Cr}^{3+}$  as investigated by Huang and Wu (1977, 1975). Overall, Cr ions adsorption onto clay minerals was found to be extremely good irrespective of the pH value, in all cases, exceeding 99% as shown in Fig. 4.

The competitive effect of adsorption on Cr ions lead to reduction in their adsorptive capacities up to pH = 6 in the multi-component adsorption scenario. But, beyond pH = 7, the

adsorptive capacities of Cr ions are higher than their single component adsorptive capacities (Fig. 6). This was as a result of the reduction in the adsorptive capacities of Cu, Pb and Zn ions. The highest difference in SC and MC adsorptive capacities of Cr ions was observed to be at pH = 6. Also, in the MC adsorption of Cr ions, their percentage removals at all pH values were greater than 99% as shown in Fig. 5. It is worth noting that Cr ions have the highest adsorptive capacities, hence, highest percentage adsorption onto the clay minerals for both SC and MC adsorption scenarios. Similar conclusions were drawn by Covelo *et al.* (2007a) where they found the sorption selectivity of Cd, Cr, Cu, Ni, Pb and Zn on kaolinite clay to follow the following order at pH = 4.5: Cr>Pb>Zn>Cd>Ni>Cu.

**Copper ions:** Adsorption of Cu ions in SC scenario (Fig. 7) was observed to be highest between pH values 4 and 6. Bekkouche *et al.* (2012) also found out that the optimum pH for Cu ions removal from a single component solution using titanium dioxide to be 6. In another related studies, (Bansal and Goyal, 2005) reported Cu ions removal using powdered activated carbon at different pH values was considerable at pH values less than 7. In addition, Khan and Khattak (1990, 1992) found the optimum pH range for Cu ions removal to be 4.2-5.1. Similar findings were corroborated by Goyal *et al.* (2001). The low adsorption within the pH range 2-4 may be attributed to high solubility and ionization of copper salt in the acidic medium. The maximum adsorption in the pH range 4-6 might be due to partial hydrolysis of  $\text{Cu}^{2+}$  which results in the formation of  $\text{Cu}(\text{OH})^+$  and  $\text{Cu}(\text{OH})_2$  whose adsorption capacities are higher than that of  $\text{Cu}^{2+}$  (Khan and Khattak, 1992). Beyond pH = 6, lower adsorption of Cu may be attributed to the precipitation of Cu ions as  $\text{Cu}(\text{OH})_2$  which in turn, lowers the availability of the clay surface due to occupation or blockage or a large portion of the clay surface. The percentage removals have been extremely high for each pH value investigated, with pH = 2 having the least percentage removal of 98.65% (Fig. 4) thereby rendering Cu ions to have the second largest adsorptive capacity in the single component scenario after Cr ions.

Figure 7 depicts higher adsorptive capacity for Cu ions in the multi-component scenario, with the percentage removals ranging from 99.37-99.76% (Fig. 5). Srivastava *et al.* (2005) have shown that greater proportions of the hydroxyl species  $\text{CuOH}^+$ ,  $\text{Cu}(\text{OH})_2^-$  and  $\text{Cu}(\text{OH})_{2(\text{aq})}^-$  (with higher adsorptive capacities than  $\text{Cu}^{2+}$ ) were formed in the multi-component scenario, as compare to the single component scenario. As such, adsorption was higher in the MC scenario.

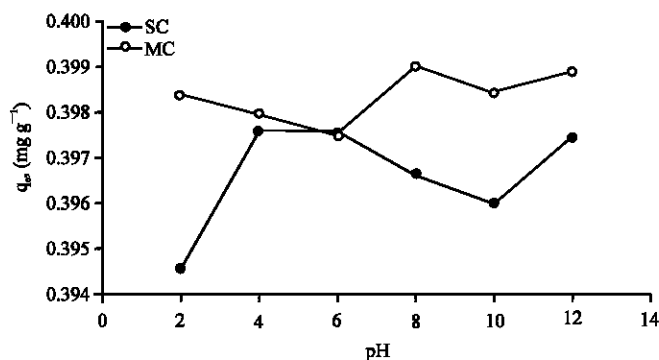


Fig. 7: Effect of pH on the adsorptive capacity of clay for copper for both single component and multi-component adsorption scenarios

**Lead ions:** Removal of Pb ions was attributed to adsorption and precipitation onto the clay surface and within the pores. In SC scenario, adsorptive capacity of Pb ions increased with increasing pH of the solution up to pH = 6, beyond which it started declining (Fig. 8). Increase in Pb ions adsorption with pH was also noticed and reported by Corapcioglu Huang (1987) and Reed *et al.* (1996). Formation of  $Pb(OH)_2$  at higher pH values greater than 10, lead to the removal of Pb ions via adsorption and precipitation. Complete removals (100%) were noted at pH values of 4 and 6 (Fig. 4).

Apparently, the competitive adsorption of other heavy metals ions onto the clay minerals has lowered Pb ions adsorptive capacity up to pH = 8, as compared with the SC scenario (Fig. 8). Thereafter, Pb ions became more adsorbed onto the clay minerals (pH = 10). For all the pH values investigated, more than 95% of Pb ions were adsorbed onto the adsorbent in MC scenario (Fig. 5).

**Zinc ions:** Adsorption of Zn ions was observed to be increased with increasing pH up to pH = 8, where all Zn ions were removed in SC scenario (Fig. 4, 9). Lower adsorptive capacity was noticed below pH = 4 as corroborated by Ferro-Garcia *et al.* (1988). Zn ions were the least adsorbed in the SC scenario, having the lowest percentage removal of 55.56% (Fig. 4).

Adsorptive capacity increased in the MC scenario, moving a step forward, from the least adsorbed in the SC scenario to the second least adsorbed after Cd ions (Fig. 5). Similar selectivity of Zn ions over Cd ions during adsorption was reported by Srivastava *et al.* (2005) and

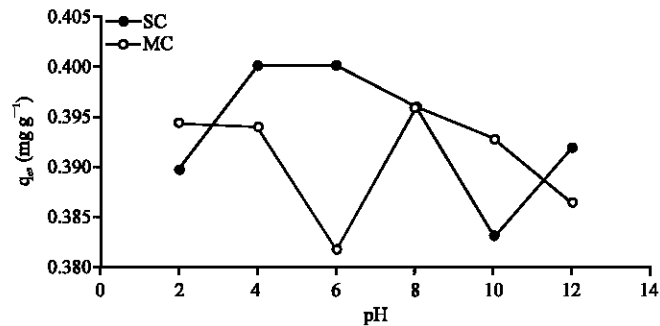


Fig. 8: Effect of pH on the adsorptive capacity of clay for lead for both single component and multi-component adsorption scenarios

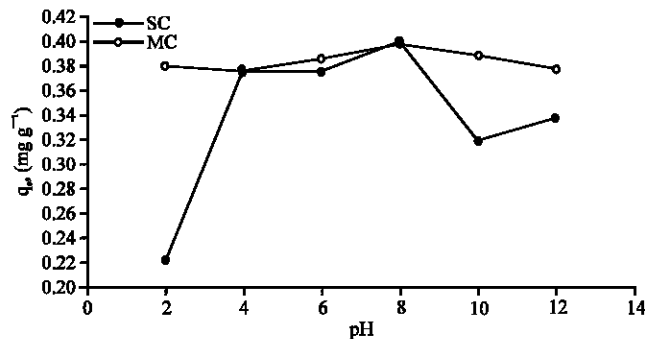


Fig. 9: Effect of pH on the adsorptive capacity of clay for zinc for both single component and multi-component adsorption scenarios

Table 2: Distribution coefficients and selectivity sequences for various pH values

Single component distribution coefficients, $K_d$ (L kg <sup>-1</sup> )						
pH	Cd	Cr	Cu	Pb	Zn	Selectivity sequence
2	184.08	26646.67	1456.01	756.70	24.99	Cr>Cu>Pb>Cd>Zn
4	603.05	33313.33	3285.79	*	321.88	Pb>Cr>Cu>Cd>Zn
6	402.83	22202.22	3258.69	*	300.00	Pb>Cr>Cu>Cd>Zn
8	564.80	3718.32	2360.95	1940.78	*	Zn>Cr>Cu>Pb>Cd
10	6133.85	7527.17	1980.00	451.70	77.56	Cr>Cd>Cu>Pb>Zn
12	*	3753.58	3105.00	967.65	107.80	Cd>Cr>Cu>Pb>Zn
Average	-	16193.55	2574.41	-	-	Cr>Pb>Cu>Cd>Zn
Multi-component distribution coefficients, $K_d$ (L kg <sup>-1</sup> )						
pH	Cd	Cr	Cu	Pb	Zn	Selectivity sequence
2	52.07	8490.64	4918.27	1393.43	368.73	Cr>Cu>Pb>Zn>Cd
4	62.30	12883.23	3901.57	1291.48	302.58	Cr>Cu>Pb>Zn>Cd
6	106.18	3683.70	3154.60	417.64	516.91	Cr>Cu>Pb>Zn>Cd
8	1174.03	9736.10	8143.27	1857.93	2837.14	Cr>Cu>Zn>Pb>Cd
10	*	12883.23	5043.29	1078.90	656.82	Cr>Cd>Cu>Pb>Zn
12	*	11744.71	7252.73	564.80	322.76	Cd>Cr>Cu>Pb>Zn
Average	-	9903.60	5402.29	1100.70	834.16	Cr>Cu>Pb>Cd>Zn

\*100% removal from solution

Covelo *et al.* (2007a). From Table 2, the selectivity sequence for the adsorption of the investigated heavy metals onto the tested clay minerals in SC and MC scenarios are Cr>Pb>Cu>Cd>Zn and Cr>Cu>Pb>Cd>Zn, respectively. Forbes *et al.* (1976) and Srivastava *et al.* (2005) have reported similar selectivity sequence (MC scenario). It is to be noted that selectivity of Cd ions was the most affected in the presence of other metals ions, followed by Pb.

**Selectivity sequence for single and multi-components scenarios:** Selectivity sequences for pH 2, 4, 6, 8, 10 and 12 for SC and MC scenarios are presented in Table 2 together with the associated overall selectivity sequence for each scenario. These sequences were arrived at, based on the distribution coefficient of the heavy metals as presented in the Table 2. For both scenarios, two ions that lie on opposite extreme ends are Cr and Zn. This is because, the former have the overall highest distribution coefficient while the latter have the lowest. It can be seen how Pb ions became highest selective at pH 4 and 6 (SC scenario) but became substituted by Cd ions in alkaline condition. It is to be noted that, the selectivity of Cd ions increases with increase in pH for both scenarios. As presented in Table 2, the values of the distribution coefficients generally increases with increasing selectivity of clay for the heavy metals and vice versa. For instance, Cd ions were completely adsorbed onto the clay minerals at pH 12 in SC scenario, giving their aqueous concentration to be zero and distribution coefficient to be infinite. Pb and Zn ions also experienced complete removal at pH values 4-6 and 8, respectively.

**Desorption study:** Multi-component desorption study undertaken revealed that Cr ions were the least desorbed (Fig. 10), having percentage desorption of 0.18%, followed by Cd and Cu ions. Zn and Pb ions were desorbed most, as indicated by their percentage desorption values of 6.55 and 3.49, respectively. Selectivity sequence during desorption may be written as

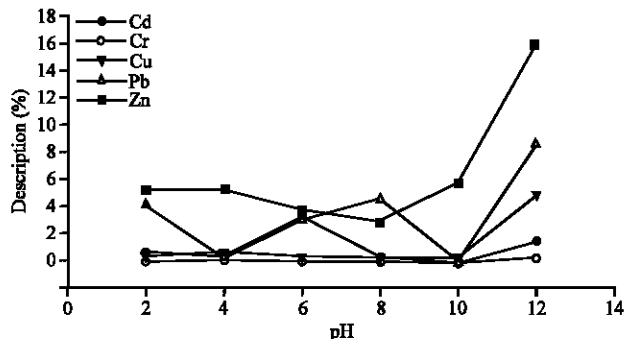


Fig. 10: Percentage desorption of heavy metals against pH for multi-component adsorption scenario

Cr<Cd<Cu<Pb<Zn. Different selectivity sequences for different soil components were reported by Covelo *et al.* (2007a, b) from which they found the selectivity sequences to be highly dependent on clay material used.

## CONCLUSION

The adsorption and desorption behaviors of Cd, Cr, Cu, Pb and Zn ions onto natural clay minerals were investigated in single and multi-component scenarios. The adsorption selectivity sequences for the SC and MC scenarios were found to mainly follow the order Cr>Pb>Cu>Cd>Zn and Cr>Cu>Pb>Cd>Zn, respectively. Adsorptive capacities of Cu and Zn ions were observed to be higher in the MC adsorption scenario than in the SC scenario. The Pb ions possessed the highest selective for adsorption which occurred at pH 4 and 6 (SC scenario) though exchanging position with Cd ions under alkaline condition (pH 12). Remarkable removals (between 55-100%) of the heavy metals were observed at all the pH values, though the pH slightly affected the adsorptive capacities of all investigated heavy metals in both the SC and MC scenarios. The MC desorption study revealed a selectivity sequence in the order Cr<Cd<Cu<Pb<Zn with the highest percentage desorption occurring at pH = 12 (15.98% desorption) associated with Zn ions. The initial pH plays a significant role in competitive adsorption and desorption of the investigated heavy metals onto clay minerals and the local clay used in this study has proved to be a candidate adsorbent for heavy metal removal in wastewater streams. The knowledge derived herein, may be brought to the fore when remediating a clay soil contaminated by these metals.

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