

## SIMULTANEOUS ADSORPTION OF LEAD (II), CADMIUM (II) AND MANGANESE (II) IONS FROM INDUSTRIAL WASTEWATER ONTO DIJAH-MONKIN NATURAL BENTONITE CLAY

\*Abdulsalam, S<sup>1</sup>., El-Nafaty, U. A<sup>1</sup>., Jock, A. A<sup>2</sup>. and Zaini, M. A. A<sup>3</sup>.

<sup>1</sup>Department of Chemical Engineering, Abubakar Tafawa Balewa University, Bauchi, Nigeria

<sup>2</sup>Chemical & Petroleum Option, Department of Science Laboratory Technology, University of Jos, Nigeria

<sup>3</sup>Centre of Lipids Engineering & Applied Research (CLEAR), Ibnu Sina Institute for Scientific & Industrial Research (ISI-SIR), Universiti Teknologi Malaysia, Johor Bahru, Malaysia.

\*Corresponding author: S. Abdulsalam, Ph.D., e-mail: surajudeen\_abdulsalam@yahoo.com

### ABSTRACT

Pollution posed by toxic heavy metals contamination as a result of industrial activities is at the increase and it has devastating effects on human and the environment at large. Activated carbon used as adsorbent has been successful in the treatments of toxic heavy metal ions from aqueous solutions although expensive. Therefore, the need for a safe, effective and low cost technology. As a result of the aforementioned, the potential of the Dijah-Monkin bentonite as adsorbent for the removals of Pb (II), Cd (II) and Mn (II) were investigated in a multi-component aqueous solution in batch mode. Characterization of the bentonite showed that the major components in the clay were silica (62.30 wt%) and alumina (21.00 wt%). In addition, the specific surface area and cation exchange capacity were 23.50 m<sup>2</sup>/g and 47.70 mEq/100g respectively. The surface morphology and the micro structure of clay showed the presence of pores that can allow favourable sorption to take place. The percentage removal of the metal ions were 58%, 27% and 15% for Pb (II), Cd (II) and Mn (II) respectively in the order: Pb (II) > Cd (II) > Mn (II). The equilibrium isotherm and kinetics studies of the data obtained revealed that the Langmuir model and the pseudo second order kinetics better described the adsorption process.

**Keywords:** Multicomponent; batch adsorption; heavy metals; wastewater; Dijah-Monkin bentonite; low cost.

### 1.0 INTRODUCTION

Environmental pollution has become a global concern and attracts much attention. Water bodies and soil are the most common natural resources that have been contaminated as a result of different human activities. One of the most important environmental problems related to water pollution throughout the world is the contamination of water bodies by heavy metal ions because of their toxic effects on the environment and human health (Saad *et al.*, 2015). Heavy metals in wastewater can have detrimental effects on all forms of life even at low concentrations when discharged directly into the environment (Mahdavi *et al.*, 2013). They are usually stable and non-biodegradable within the ecosystem. As a result, they tend to bioaccumulate in living tissues thereby causing health concerns (Lukman *et al.*, 2013). Every year at least five million people die from water-related diseases worldwide (Ghasemi *et al.*, 2015). Thus, it is very important to determine effective methods for remediating toxic heavy metal contamination.

Among heavy metals, lead, cadmium and manganese are the most widely used in western society for the manufacture of metal alloys and plating, batteries, fertilizer, oil, paint, electronic, glass, ceramics, etc. (Vieira *et al.*, 2010; Pawar *et al.*, 2016; Akpomie *et al.*, 2016). Lead is highly toxic to organisms, including humans, even at extremely low concentrations. Lead poisoning in humans causes severe damage to the kidneys, nervous system, reproductive system, liver, and

brain. Severe exposure to lead (II) is associated with various neurodevelopmental effects, cardiovascular diseases, mental retardation, sterility, abortion, stillbirth, and neonatal deaths (Pawar *et al.*, 2016). Cadmium is widely used and highly toxic in relatively low dosages, with cumulative effects causing kidney damage, renal disorder, high blood pressure, bone fracture and destruction of red blood Cells (Kumar *et al.*, 2010). Manganese is usually present in groundwater as a divalent ion and is considered a pollutant mainly because of its organoleptic properties (Akpomie *et al.*, 2016).

Several techniques have been developed for heavy metal removal from aqueous solution such as chemical precipitation, electrochemical treatment, evaporation, ion-exchange, filtration, oxidation/reduction, solvent extraction, membrane technologies and adsorption (Akpomie *et al.*, 2015). Among the various removal technologies available for the treatment of heavy metals-containing wastewater, adsorption has been proven to be an effective and affordable method, due to the low initial cost, flexibility and simplicity of design as well as ease of operation (Gao *et al.*, 2016).

Owing to the low cost of natural clay minerals, their abundance in most continents of the world, and high sorption properties, they have been used for sorption or elimination of heavy metals present in effluents (Gao *et al.*, 2016). The cost of clays is relatively low as compared to other alternative adsorbents, including

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activated carbon, natural and synthetic zeolites, ion-exchange resins, and other adsorbent materials (Zhu *et al.*, 2016). Clay minerals such as montmorillonite, vermiculite, illite, kaolinite and bentonite are among the natural materials that have been investigated as heavy metal adsorbents (Vieira *et al.*, 2010). Other advantages in using clays as adsorbents are their intrinsic properties, such as large specific surface area, excellent physical and chemical stabilities, and a number of other structural and surface properties (Zhu *et al.*, 2016).

In this study, bentonite clay from Dijah-Monkin occurrence in Taraba State, Nigeria was investigated for simultaneous adsorption of lead (II), cadmium (II) and manganese (II) in a mixed aqueous solution. The adsorption data were interpreted using the isotherm and kinetic models. The choice of this clay material was based on its low cost and availability in Nigeria while heavy metals chosen were due to their health risk and wide areas of application.

### 2.0 MATERIALS AND METHODS

#### 2.1 Sample collection and preparation

The raw bentonite clay sample was collected from a typical site at Dijah-Monkin town in Zing L.G.A, Taraba state of Nigeria. Ten kilograms (10 kg) of the clay was crushed to fine powder and soaked in water for 24 h. The clay-water mixture was blunged (stirred) for 3 h at 25°C and was allowed to age for four days for the quartz impurities to settle to the bottom leaving colloidal solution of clay and suspended particles at the top. At each day of sedimentation, decantation of the overflow was done and replaced with fresh tap water to the fourth day when the overflow has become less milky and free from suspended particles. The colloid clay sample was then collected and separated from the quartz sediments and sieved through a 230 mesh Tyler sieve (63 µm sieve opening) to further remove coarse impurities and organic particles present in the clay. The thick slurry clay was put in a filter cloth and pressed under heavy mass of 10 kg to squeeze out the water. The resulting cake was sun dried and also oven dried at 110°C to a constant weight. The dried clay was milled and sieved with a 125 µm mesh. The sieved clay was then stored in large polyethylene bag for analysis and subsequent experiments were carried out according to procedure described by Nwafulugo *et al.* (2014).

#### 2.2 Characteristic of the Bentonite Clay

The bentonite clay was characterized for chemical composition using analysis X- ray fluorescence (model Mini PAC4 EDXRF, Rigaku, Japan). The morphological structure of the bentonite clay was determined by a field emission scanning electron microscope (model SU8020, Hitachi, Japan) coupled with energy dispersive spectrophotometer (EDS) of Oxford Instrument while the specific surface area was determined using the adsorption and desorption nitrogen isotherms, at liquid nitrogen temperature of -196°C on Surfer Thermo Scientific (Thermo Scientific, USA). The FTIR spectra

were recorded with a FTIR spectrophotometer (model Spectrum One, PerkinElmer, USA) using KBr pressed disk technique and the cationic exchange capacity of the clay was estimated using the ammonium acetate NH<sub>4</sub>OAc method (Burt, 2004). The thermogravimetric (TGA) curves were obtained using a Q500 equipment (TA Instruments, USA). All the analyses were carried out at the Central laboratory, Universiti Teknologi Malaysia.

### 2.3 Batch Adsorption

#### 2.3.1 Preparation of stock solution

Heavy metals solutions were prepared using Pb(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O, Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O and MnO<sub>2</sub> for lead (II), cadmium (II) and manganese (II), respectively. Distilled water was used for solution preparation and dilution to desired concentrations of 10, 20, 30, 40 and 50 mg/L for each metal ion. All the reagents used in this study were of high grade quality.

#### 2.3.2 Equilibrium experiments

Fifty milligrams (50 mg) of the oven dried powdered clay (bentonite) was mixed with 50 mL of metal solution prepared at different concentrations. Batch adsorption was carried out on heavy metal ions (lead (II), cadmium (II) and manganese (II)) in aqueous solution (the three metal ions present simultaneously). The mixtures were shaken on orbital shaker (SASTEC™) at 25°C and speed of 110 rpm for 72 h (Plate I). The contact period is presumably sufficient for the adsorption of heavy metals to attain the equilibrium (Hajahmadi *et al.*, 2015). Then, the suspension was filtered using a 0.45 µm syringe filter. The residual metal ions concentration was measured using ICP-OES. The removal of Pb (II), Mn (II) and Cd (II) ions from aqueous solution was calculated using mass balance equation,

$$q_e = \frac{C_o - C_e}{m} V \quad (1)$$

where,  $q_e$  (mmol/g) is the adsorption capacity,  $C_o$  and  $C_e$  (mM) are the initial and equilibrium concentrations, respectively,  $V$  (L) is the solution volume and  $m$  (g) is the mass of adsorbent.



Plate I: Experimental setup for batch adsorption process

#### 2.3.3 Kinetic experiments

Batch adsorption kinetic experiments were conducted on the mixed metals solution (10, 30 and 50 mg/L) by varying agitation (contact) time. Zero point five grams (0.05 g) of clay was brought into contact with a series of 50 mL multicomponent heavy metals solution of known concentration in 250 mL Erlenmeyer flasks. The mixtures were shaken on orbital shaker (SASTEC™) at a speed of 110 rpm, and 25°C. The contact time was varied from 0 to 720 min. At predetermined time intervals (0-720 min), the suspension was withdrawn and filtered using a 0.45 µm syringe for concentration measurement using ICP-OES.

### 3.0 RESULTS AND DISCUSSION

#### 3.1 Characterization of bentonite clay

Table 1 Characteristics of bentonite samples

Sample	Chemical composition (wt.%)						Specific area, $S_{BET}$ (m <sup>2</sup> /g)	CEC (meq/100 g)
	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	K <sub>2</sub> O	TiO <sub>2</sub>		
NB	62.3	21.0	8.20	1.17	4.59	1.22	23.5	47.70

Figure 1 shows the EDX spectra of bentonite samples consisting mainly of silicon (Si) and aluminium (Al). Other elements present include calcium (Ca), magnesium (Mg), potassium (K), iron (Fe) and titanium (Ti). The result of the EDX is in agreement with the chemical analysis obtained from XRF (Table 1) and the major components in the clay sample were Si and Al, which are the basic elements for smectite clay group (Araujo *et al.*, 2013).

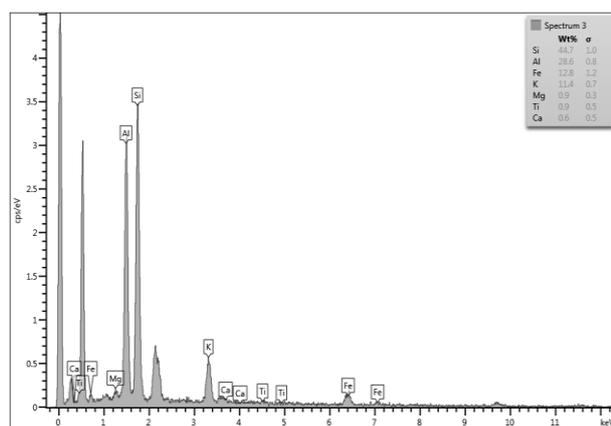


Figure 1: EDX spectra of natural bentonite

Similarly, the clay sample can be designated as polycationic bentonite due to the presence of Ca<sup>2+</sup> and Mg<sup>2+</sup> cations, which are suitable for adsorption process (Bertagnolli *et al.*, 2011).

The specific area of the bentonite clay in Table 1, is adequate for adsorption to occur and according to IUPAC definition, the clay is predominantly

The result of chemical analysis (wt%) in Table 1 shows that the clay consists mainly of silica and alumina, with metallic oxides such Fe<sub>2</sub>O<sub>3</sub>, K<sub>2</sub>O, CaO and TiO<sub>2</sub> present in minute quantities. The brownish colour observed in the clay may be due to the relatively high concentration of Fe<sub>2</sub>O<sub>3</sub> (8.20 wt.%). The presence of CaO in the clay and the absent of Na<sub>2</sub>O (Table 1), suggests that the predominant clay mineral is the Ca-rich type (Nweke *et al.*, 2015). In Table 1, the chemical composition was obtained from XRF while the ICPOES was used to measure the concentration of the cations for CEC determination and the specific area was obtained using BET method.

mesoporous materials with average pore diameter in a range of 2-50 nm (Budsareechai *et al.*, 2012).

The cation exchange capacity described the ability of a clay to exchange cations in aqueous solution. From Table 1 and Figure 1, the major cations in bentonite sample were Ca<sup>2+</sup> and Mg<sup>2+</sup>. The clay exchange sites contain mostly calcium, and a higher CEC value allows a higher capacity to trap trace elements, which is also beneficial in the adsorption of positively-charged pollutants (Zhansheng *et al.*, 2006). The cation exchange capacity of calcium montmorillonite ranges from 40 to 70 mEq/100 g, while that of sodium montmorillonite is between 80 and 150 mEq/100 g (Murray, 2007). Therefore, the bentonite sample with a cation exchange capacity of 47.7 mEq/100 g (Table 1) has the tendency of exchanging its cation with heavy metals in solution.

The surface morphology and the micro structure of adsorbent materials play a vital role in knowing the surface heterogeneity and presence of pores that can allow sorption to take place. The SEM image and morphology of bentonite clay is shown in Plate II.

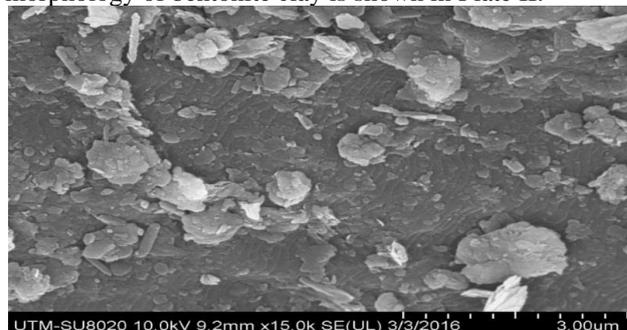


Plate II: SEM images of natural bentonite (magnification: x 15, 000)

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Bentonite clay (montmorillonite) generally exhibits ultrafine, thin, leaf-like crystals forming a dense aggregates, or open honeycomb texture (Zuzana *et al.*, 2012). The micrograph of the clay in Plate II shows that the bentonite grains are aggregated mass of irregularly shape particles that appeared to have been formed by several flaky particles stacked together in the form of agglomerates.

Figure 2 shows the nitrogen adsorption-desorption isotherms of bentonite clay sample. It can be seen that it shows type IV isotherm according to IUPAC classification (Budsaereechai *et al.*, 2012). The volume of adsorbed gas decreases in relation with the relative pressure.

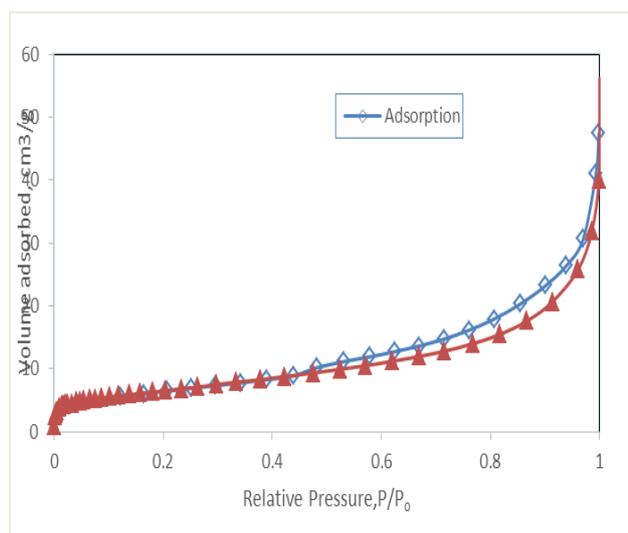


Figure 2: Adsorption and desorption isotherms of bentonite clay sample

The FTIR spectrum serves not only as a fingerprint for mineral identification, but also gives unique information about the mineral structure, including the family of minerals to which the specimen belongs, the degree of regularity within the structure, nature of isomorphous substituents, the distinction of molecular water from constitutional hydroxyl, and the presence of both crystalline and non-crystalline impurities (Djomgoue and Njopwouo, 2013).

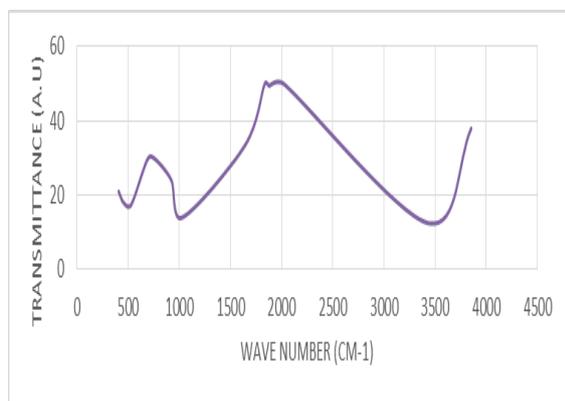


Figure 3: FTIR spectra of bentonite clay material

Figure 3 shows the spectra of bentonite clay sample in the wave number range of 4000-400  $\text{cm}^{-1}$ . The bands corresponding to the water molecules in the interlayers, and the structural hydroxyl groups in the clay layers are in the region between 3750 and 3500  $\text{cm}^{-1}$ , and the characteristic silicate bands are found between 1200 and 700  $\text{cm}^{-1}$ . The bands at 600-400  $\text{cm}^{-1}$  could be originated from Si-O bending and Al-O stretching vibration (Tomul and Balci, 2007). Water molecules basically exhibit three types of vibration: symmetric and asymmetric stretching and angular deformation of H-O-H group.

In addition, the 1600 to 1700  $\text{cm}^{-1}$  range corresponds to angular deformation of H-O-H, while the 3100 to 3700  $\text{cm}^{-1}$  range corresponds to the O-H stretching (Bertagnolli *et al.*, 2011). The peaks at 3433 and 3439  $\text{cm}^{-1}$  are assigned to OH stretching, and are within the range of 3420-3450  $\text{cm}^{-1}$  for water in montmorillonite that gives a broad band (Zuzana *et al.*, 2012). The peaks at 1030, 1045 and 1049  $\text{cm}^{-1}$  are assigned to stretching vibration of Si-O, and the band observed at 922  $\text{cm}^{-1}$  corresponds to Al-Al-OH (Er-ramly and Ider, 2014). Various bands at 733, 750 and 752  $\text{cm}^{-1}$  are assigned to Al-O-Si, while peak at 685  $\text{cm}^{-1}$  indicates OH deformation (Davarcioğlu and Ciftci, 2010). The functional groups in bentonite clay include Al-OH, Al-O, Si-O, Si-OH, Al-Al-OH, Al-Mg-OH (Araujo *et al.*, 2013; Yu *et al.*, 2016). The main surface functional groups in clay that generate loads for possible adsorption are the pH dependent Si-OH and Al-OH groups (Araujo *et al.*, 2013).

### 3.2 Equilibrium studies of heavy metals adsorption

Adsorption at equilibrium indicates the uptake capacity of adsorbent at which the rate of adsorption is equal to the rate of desorption. The metal uptake for all the three metals increased from low concentrations to a saturation points, where their uptakes remain almost constant even when their concentrations were increased as shown in Figure 3.

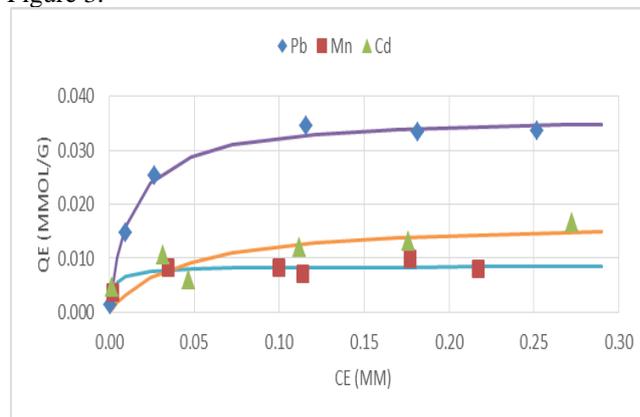


Figure 4: Equilibrium adsorption of lead (II), cadmium (II) and manganese (II) ions onto natural bentonite

Figure 4 shows the equilibrium adsorption of heavy metals in multicomponent system. The adsorption of Pb (II), Mn (II) and Cd (II) onto the bentonite sample could be prompted by the surface area in addition to the surface functional groups via ion-exchange mechanism between the metal ions and the surface active sites of bentonite (Vhanangwele and Muger, 2015).

The difference in adsorption capacities between metals are commonly explained using hydration energy, hydrolysis constant, electro-negativity, and hydroxide solubility product of the metals (Nguyen *et al.*, 2015). From Figure 5, Pb (II) ions were favourably adsorbed over Mn (II) and Cd (II) ions.

The Langmuir and Freundlich models both incorporated three parameters into an empirical isotherm were employed to test for the fitness of the experimental data. The models were solved through non-linear regression using *Solver* for the least sum of squared error and optimum correlation of determination ( $R^2$ ). The respective constants are summarized in Tables 2. The data for the adsorption of all the metals from the mixed metals solution satisfactorily fitted to the Langmuir model. This suggests that the adsorption sites were homogeneous with monolayer adsorption (Nguyen *et al.* 2015). The values of maximum uptake ( $Q_m$ ) predicted by the Langmuir model were in accordance with the experimental data (Figure 4).

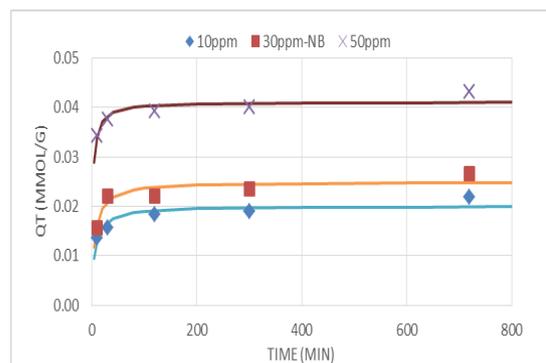
**Table 2: Isotherm constants for multicomponent adsorption of Pb (II), Cd (II) and Mn (II) onto bentonite clay**

Heavy Metal	Langmuir				Freundlich			
	$Q_m$ (mmol/g)	$K_L$ (L/mmol)	SSE	$R^2$	$K_F$ (mmol/g) (L/mmol) <sup>1/n</sup>	1/n	SSE	$R^2$
Pb (II)	0.0363	79.6	$5.9 \times 10^{-6}$	0.993	0.0534	0.261	$8.6 \times 10^{-5}$	0.910
Mn (II)	0.0085	391.0	$4.3 \times 10^{-6}$	0.802	0.0113	0.152	$6.2 \times 10^{-6}$	0.714
Cd (II)	0.0170	25.0	$3.9 \times 10^{-5}$	0.743	0.0233	0.283	$1.8 \times 10^{-5}$	0.819

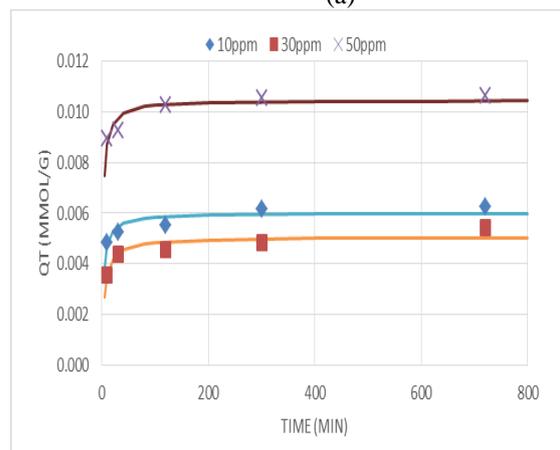
The maximum uptakes (% removal) for the metal ions were 0.036 mmol/g (58.1%) for Pb (II), 0.017 mmol/g (27.4%) Cd (II) and 0.009 mmol/g (14.5%) Mn (II). It indicates that lead (II) uptake was predominant as compared to those for cadmium (II) and manganese (II). The sorption capacities of metal ions was in the following order: Pb (II) > Cd (II) > Mn (II). This trend is in agreement with the increasing order of hydrated ionic radii of metal ions of 0.401, 0.426 and 0.438 nm for Pb (II), Cd (II) and Mn (II) ions respectively (Wang *et al.*, 2011). The smallest cations should ideally be adsorbed faster and in larger quantities compared to the larger cations, since the smaller cations can pass through the micropores and channels of the bentonite structure with ease (Afordita and Mirjana, 2014).

### 3.3 Kinetics of Multicomponent Adsorption

Simultaneous adsorption of lead (II), cadmium (II) and manganese (II) was measured at different time intervals and concentrations. The results shown in Figures 5a, b and c are the effects of contact time on the adsorption of lead (II), cadmium (II) and manganese (II), respectively. The uptakes at equilibrium remained constant even with increasing initial concentrations. Lead (II) ions were favourably adsorbed at all concentrations used over Mn (II) and Cd (II) ions. This was also similar with the decreased order of hydrated ionic radii of metal ions earlier discussed.

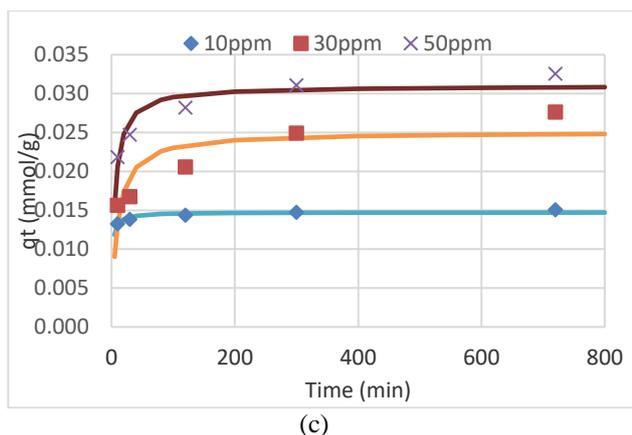


(a)



(b)

**Simultaneous Adsorption Of Lead (II), Cadmium (II) And Manganese (II) Ions From Industrial Wastewater Onto Dijah-Monkin Natural Bentonite Clay**



**Figure 5: Effect of contact time on (a) lead (II), (b) cadmium (II) and (c) manganese (II) adsorption**

The kinetics data were evaluated using the pseudo first and pseudo second order kinetics. These models revealed the nature and mechanism of adsorption process. The constants were also determined using Solver and the values summarized in Tables 3. Comparing the regression coefficient ( $R^2$ ) values, the pseudo second order model fitted better the adsorption kinetics than the pseudo first order model. The better fit of the pseudo second order model suggests that chemical process may be the rate-limiting step in the adsorption (Nguyen *et al.*, 2015).

**Table 3 Rate constants of pseudo-kinetics models for multicomponent heavy metals adsorption**

Heavy metal	Initial conc. (mg/L)	$q_{e,exp}$ (mmol/g)	Pseudo-first order kinetic				Pseudo-second-order kinetic			
			$q_{e,cal}$ (mmol/g)	$K_1$ ( $min^{-1}$ )	SSE	$R^2$	$q_{e,cal}$ (mmol/g)	$K_2$ (mmol/g.min)	SSE	$R^2$
Pb(II)	10	0.022	0.019	0.110	$1.6 \times 10^{-5}$	0.604	0.020	8.77	$7.1 \times 10^{-6}$	0.825
	30	0.027	0.024	0.103	$1.1 \times 10^{-5}$	0.823	0.025	7.14	$8.6 \times 10^{-6}$	0.865
	50	0.043	0.040	0.192	$1.7 \times 10^{-5}$	0.614	0.041	11.4	$7.9 \times 10^{-6}$	0.815
Cd(II)	10	0.006	0.006	1.00	$1.4 \times 10^{-6}$	0.533	0.006	58.7	$2.9 \times 10^{-7}$	0.802
	30	0.005	0.005	1.00	$1.9 \times 10^{-6}$	0.652	0.005	45.1	$3.0 \times 10^{-7}$	0.840
	50	0.011	0.010	1.00	$2.4 \times 10^{-6}$	0.525	0.010	47.7	$3.8 \times 10^{-7}$	0.843
Mn(II)	10	0.015	0.014	1.00	$2.1 \times 10^{-6}$	0.581	0.015	55.4	$3.2 \times 10^{-7}$	0.845
	30	0.028	0.024	0.079	$5.7 \times 10^{-5}$	0.506	0.025	4.48	$2.9 \times 10^{-5}$	0.736
	50	0.033	0.030	0.121	$3.1 \times 10^{-5}$	0.617	0.031	6.40	$1.1 \times 10^{-5}$	0.866

**4. CONCLUSIONS**

The potentials of Dijah-Monkin bentonite for simultaneous adsorption of lead (II), cadmium (II) and manganese (II) ions in aqueous solution in a batch were investigated and from the results obtained, the following conclusions were drawn:

- (i) Adsorption of each metal ion increases with increased in initial concentration until equilibrium was attained and the order of selectivity of metal ions was Pb (II) > Cd (II) > Mn (II).
- (ii) The adsorption efficiencies were 58, 27 and 15% for Pb (II), Cd (II), Mn (II) respectively.
- (iii) The Langmuir isotherm model yields a better fit to the experimental data.
- (iv) The pseudo second order model appeared to fit the data satisfactorily.

The overall result of the study shows that Dijah-Monkin bentonite clay is a promising low-cost adsorbent for effective removal of mixed heavy metals ions from aqueous solution.

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