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Synthesis of Zinc Oxide Activated Acor Montmorillonite and Its Performance on the Removal of Mercury Ions from Aqueous Media

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ABSTRACT

This paper investigated the synthesis of zinc oxide-activated ACOR montmorillonite composite and its performance in the removal of mercury ions in aqueous media. The ACOR montmorillonite was activated using Potassium Hydroxide solution. The activated ACOR montmorillonite was titrated with zinc nitrate to produce the zinc oxide-activated ACOR montmorillonite composite. The adsorption experiments were conducted using batch mode techniques, and under reducing condition at ambient temperature. The reaction mechanism indicated less than one proton coefficient, higher mass transfer rates than that of bare montmorillonite, and intraparticle diffusion containing intercept(c) equals 2.58, ≠ 0. In the presence of zinc oxide coating, the pH provided an adsorption efficiency of 85.55 % at pH=5 and 89.62 % at pH =7. Therefore, the zinc oxide—activated ACOR montmorillonite composite is a novel adsorbent with very high adsorption capacity. The zinc oxide- activated ACOR montmorillonite composite significantly enhanced the adsorption of mercury ions.

Keywords: *Activation; Adsorption Kinetics; Aging; Coatings; Zinc Oxide; Mercury; Montmorillonite*

INTRODUCTION

Mercury is known to be non-biodegradable and it accumulates in humans to cause series of health challenges. The major sources of mercury come from the amalgam of gold in the mining industry, production of chlorine, electrical appliances, preservatives, pharmaceuticals, electrodes, and reagents.

A modern method of the release of mercury into the aquatic environment is through the extractive industry. The recovery of heavy metals from ores is through hydrometallurgical leaching at low pH (i.e. pH=5). The World Health Organization has set the limits of inorganic mercury exposure to 10µg/L.

Above this limit, the effect of methylated inorganic mercury ranges from the late development of the child in the uterus to toxic effects on the nervous, digestive and immune systems of adult humans [1].Consequent on its effect, several methods have been adopted to remove mercury ions from the aquatic environment[2][3][4][5]. These methods include reverse osmosis, distillation, granular activated carbon filters, and lime softening. It is obvious that limited research exists in the use of activated clay minerals coated with oxides in the removal of mercury ions from the aquatic environment. Therefore, this research remains relevant in contemporary environmental science. The active removal of mercury ions at low concentrations using adsorption technique is dependent ona combination of factors namely the nature of the adsorbent and chemistry of the solution [6]. The adsorption technique is considered a simple technique for water treatment based on cost and simplicity of design. Furthermore, the removal of mercury ions using adsorption technique is related to the reaction mechanism and kinetics, and these characteristics are essentially dictated by time of reaction and the pH of the reacting solution. The other adsorption parameters include adsorbent dose, particle sizes, and chemistry of the of the adsorbent [7][8].The presence of aluminum on the surfaces of montmorillonite is known to reduce adsorption. An outer- sphere complexation is assigned to increase in mercury removal as adsorbent particle concentration was increased. However, the uptake of mercury as particle size and adsorbent dose increases are do not always exist.In addition, the uptake of mercury is controlled by the presence of surface area and surface-active sites. The reorganization of mineral surfaces in aqueous solution depends on the contact time or aging during reaction [9][10].

In some cases, an increase in metal concentration led to a quantitative decrease in adsorption and vice versa. There is evidence from kinetic studies that mercury removal undergoes a fast process of intraparticle diffusion and a slow process of outer- sphere complexation. Also, intraparticle diffusion, mass transfer rates, and coefficient protonation affect the removal of mercury from the aquatic environment. Here, the reaction mechanism and kinetics entailed in the removal of mercury by using zinc oxide-activated ACOR montmorillonite has received limited studies [11].

The previous studies were focused on the use of untreated montmorillonite in mercury removal. Furthermore, it has been reported that untreated montmorillonite possesses the capacity to absorb heavy metals using action exchange and inner-sphere complexes formation via the aluminol and silanol sites [12]. This study was aimed at determining the role of synthetic zinc oxide-activated ACOR montmorillonite composite in the treatment of mercury-contaminated water in relation to certain adsorption parameters that are linked to the reaction mechanism and kinetics of adsorption. The experiments were conducted using batch mode techniques over a range of adsorbent dose, mercury concentration and pH 4 to pH 8. The pH 5 has been discussed because hydro metallurgical waste is released into the aquatic environment at this pH. The synthesis of the adsorbent, the activation of the mineral system, and the testing of the zinc oxide-activated ACOR montmorillonite composite to remove mercury ions have been discussed.

MATERIALS AND EXPERIMENTAL METHODS

Materials and Reagents

Here, analytical grade reagents were used. Acros Organics Company from Belgium provided the Montmorillonite nicknamed ACOR montmorillonite. Double distilled water was used to wash the ACOR montmorillonite. The mercury chloride used in preparing the stock solution was provided by Merck Company from Germany. The AAS stock solution of 1000 mgL^{-1}mercury chloride was prepared using a volumetric flask. As instructed by Merk guidelines, the content after filling up to mark was stored for use. The standard solutions of different concentrations were obtained by diluting the stock solutions. The zinc nitrate was used as the precursor, KOH purchased from Sigma-Aldrich Company in Belgium was used as the precipitating and activating agent to synthesize the zinc oxide nanoparticles.

Preparation of Anaerobic Suspensions

A reducing condition for all the solutions used in the experiments was created by bubbling purified nitrogen gas through de-aerated and deionized distilled water. The deionized water was obtained from a Millipore Milli-Q system (18.2 MΩ.cm at room temperature). The experimental content was bubbled through continuously for 24 hours and the content was securely sealed and stored in airtight containers in the anaerobic chamber in the dark before use [13].

Adsorbent Characterization

The x-ray diffraction (XRD) was used to verify the ACOR montmorillonite and the zinc oxide nanoparticles. The x-ray fluorescence was used to determine the elemental composition of the ACOR montmorillonite. The model 3340 Jenway ion meter was used to determine the pH of ACOR montmorillonite suspensions and reacting solutions. The cation exchange capacity (CEC) and specific surface area were determined using Na saturation method and standard volumetric Brunauer, Emmett, and Teller (BET) method respectively. Here, the latter was determined by measuring the adsorption of the N_2 gas on the mineral solid phase at the boiling point of liquid nitrogen. The particle sizes and spectral analysis were done using Coulter Laser and JEOLJSM 5900 LV Scanning Electron Microscopy (SEM) with Oxford INCA Energy Dispersive Spectroscopy (EDS) respectively [14]. The secondary electron images were acquired at low vacuum control pressureafter viewing the samples. The point of zero salt effect (PZSE) synonymous with the point of zero charges (pHzpc) of the adsorbent was determined using titrimetric method [15]. Potentiometric titration was conducted by equilibrating 1% (by mass) of activated ACOR montmorillonite suspensions. The pH range near the PZSE was used as a reference.

Activation of ACOR montmorillonite and synthesis of zinc oxide-ACOR montmorillonite composite

To produce the activated ACOR montmorillonite, the ACOR montmorillonite was charged with a 25% solution (by weight) of Potassium Hydroxide (KOH). This paste was dried at 400^0C. The dried ACOR montmorillonite was rinsed with distilled water and dried at 105^0C to produce the activated ACOR montmorillonite.In addition, a double distilled water was used to prepare the solution of zinc nitrate ($Zn(NO_3)_2$ of 0.2 M concentration and KOH of 0.4M concentration.

Here, 20 g of ACOR montmorillonite was mixed with 100 mL of the $Zn (NO_3)_2$ solution and 180 mL of the KOH solution [16]. The activated ACOR montmorillonite was dispersed into 150 mL of the $Zn(NO_3)_2$ solution. Subsequently, the KOH aqueous solution of three hundred micro liters was titrated slowly at the rate of 1 mL/h. The content was subjected to vigorous stirring under nitrogen flow condition at ambient temperature. The double distilled water was used to wash the precipitate. The precipitate was centrifuged and finally washed with absolute alcohol. This was done to free the content from NO_3^- ions. Thereafter, the solid was heated at 450^oC for 3 h in air to produce the zinc oxide-activated ACOR montmorillonite composite [17]

Batch Mode Adsorption Experiments

The detailed experimental set up involving bare ACOR montmorillonite has been provided in comparison papers [18][19]. Using a 1000 mg/L mercury stock solution, 10 mL, 15 mL, 20 mL, and 40 mL of themercury solutions were dispensed directly into a 100.0 mL volumetric flask to prepare the 10 mg/L, 15 mg/L, 20 mg/L, and 40 mg/L standards.

These standards were treated with 2 g/L, 4 g/L, 6 g/L, 8 g/L, and 10 g/L of the zinc oxide-activated ACOR montmorillonite composites and made onto 50 mL.A 0.45 µm pore size Whatman filter paper was used to filter the content and the filtrate was analyzed for mercury ions left in solution using a Hitachi Atomic Absorption Spectrophotometer (HG-AAS). The mercury concentration ranging between10mgL^{-1} to 40mgL^{-1} in the pH=4-8 range were treated with the zinc oxide-activated ACOR montmorillonite ranging from 2 gL^{-1} to 10 gL^{-1}. These solutions were equilibrated for 24h. These values were used to determine the parametric effects of solid concentration, pH, aging and reaction mechanisms. Here, the effect of initial mercury concentration was determined by making the suspension onto 50mL and thereafter equilibrated for 24h at pH=4-8. 1% each of zinc oxide-activated ACOR montmorillonite suspension was reacted with mercury solution (10 mgL^{-1} to 40 mgL^{-1}). This solution was made onto 50mL and equilibrated for 24h at pH=4-8. This content was used to determine the particle concentration effect (Cp). In addition, mercury concentrations (10mgL^{-1} to 40mgL^{-1}) was reacted with 1% zinc oxide-activated ACOR montmorillonite composite at pH=4-8. The solution made onto 50mL and aged from 24 - 720h. This content was used to determine the effect of aging. All experiments involving the adsorbent were done in triplicate under reducing condition, and at ambient temperature.

To predict the reaction mechanisms, the proton coefficient otherwise known as the proton exchange isotherm was derived from the pH versus LogKd plot. This plot was based on the Freundlich isotherm. The Freundlich isotherm was used to describe adsorption of mercury ions because the isotherm is suitable for heterogeneous surfaces over a wide range of solute concentrations [18][16]as given by equations (2, 3)

$$\alpha SOH \leftrightarrow SO^- + \alpha H^+ \qquad (1)$$

$$\log Kd \leftrightarrow \log(K_p\{SOH\}^\alpha) + \alpha pH \qquad (2)$$

Here, *SOH* equals the mineral surface-reactive site, *SO*$^-$ equals the surface-bound Hg^{2+}, log K_p equals the apparent equilibrium-binding constant and α equal the coefficient of protonation. This equals the number of protons displaced when one mole of Hg^{2+} binds to the mineral surface [20].

Again; a 1% zinc oxide-activated ACOR montmorillonite suspension was charged with Hg^{2+} ion solution of 10 mgL^{-1} regulated to between pH 4 and pH 8. This solution was made unto 50 mL and was used to determine the proton coefficient. In addition, the mass transfer rate and intraparticle diffusion were derived from equations (3,4,5):

$$Q_t = [C_0 - C_t]\, {}^{V}\!/_{m} \qquad (3)$$

Here, Co equals t the initial mercury concentration (mgL^{-1}) at time t=0; C_t equals the concentration (mgL^{-1}) at time t; V equals t the volume of the zinc oxide- activated ACOR montmorillonite composite suspension, and m is the weight of the adsorbent (g) [12]. The kinetics of Hg^{2+} ion adsorption to the mineral surface binding sites was controlled by the mass transfer constant constant K_f. Here, C_t/ C_o vs. time provided the slope of the curve derived from equation (4) [21]:

$$\left[\frac{d\left(C_t/C_0\right)}{dt}\right]_{t=0} \cong -K_f S_s \qquad (4)$$

Here, C_0 and C_t denote the initial concentrations of Hg^{2+} concentration at time t, Ss equals the exposed specific surface area of zinc oxide-activated ACOR montmorillonite, and K_f equals the coefficient of mass transfer. These models as reviewed previously and derived from the Freundlich isotherm were adopted to describe adsorption of Hg^{2+} ions. To investigate the role of intra-particle diffusion in the adsorption process, the Weber-Morris model was used [22] as given in equation (5):

$$Q_t = K_{i^{0.5}} + C \qquad (5)$$

Here, K_i equals the intraparticle diffusion constant (mg/g min) and the intercept (C) represents the effect of the layer boundary. Ki value is derived from the slope (K_i) of the plots of Q_t vs. $t0^{.5}$. A linear plot of Q_t versus $t^{0.5}$ indicated that diffusion of intraparticle was involved in the process of adsorption [16]. For these reaction mechanisms, a 1% zinc oxide-activated ACOR montmorillonite was charged with 10 mgL^{-1} Hg^{2+} ions solution adjusted to pH 5. The content was made onto 50 mL, and was used to determine the amount of Hg^{2+} ions remaining in solution after 2nd h, 4th h, 6th h, 8th h, 12th h, 18th h, and 24th h.

The percent of Hg^{2+} ions removed from solution was calculated from equation (6):

$$\text{Adsorption efficiency (\%)} = \frac{C_0 - C_e}{C_0} x\ 100 \qquad (6)$$

Where C_0 and C_e (mgL-1) are the initial and equilibrium concentrations of the Hg^{2+}in solution.

RESULTS AND DISCUSSION

Results

In this study, ACOR montmorillonite contained SiO_2 (54.00 %), Al_2O_3 (17.00 %), Fe_2O_3 (5.2 %), CaO (1.5 %), MgO (2.5 %), Na_2O (0.5 %), K_2O (1.50 %), 0.01-80.00µm, particle size range 0.53% colloid, 2.00 pH,10.00 surface area(m^2/g), and 56.00 cation exchange capacity(mmol/g). Therefore, the x-ray fluorescence (XRF) of the bare montmorillonite indicated the presence of quartz, alumina, iron oxide, magnesium oxide, calcium oxide, sodium oxide, and potassium oxide in the decreasing order. The Cation Exchange capacity was moderate and the colloidal fraction was low. The x-ray diffraction pattern (XRD) patterns of bare ACOR montmorillonite clay and copper oxide-montmorillonite composite indicated differing basal orders. The bare ACOR montmorillonite clay shows a peak of 3.38. The X-ray diffraction spectrum indicated smectite as the key constituent. The XRD for the zinc-oxide montmorillonite indicated a basal order of (101) reflections. The diffractions were due to the diffraction of random stacking of layers. The EDS spectrum and SEM morphology indicated the presence of montmorillonite.

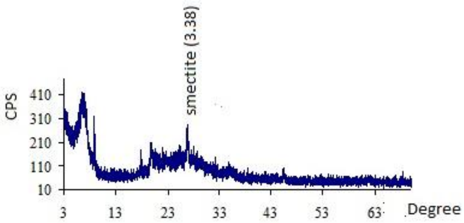

Fig1. *X-ray diffraction of ACOR montmorillonite*

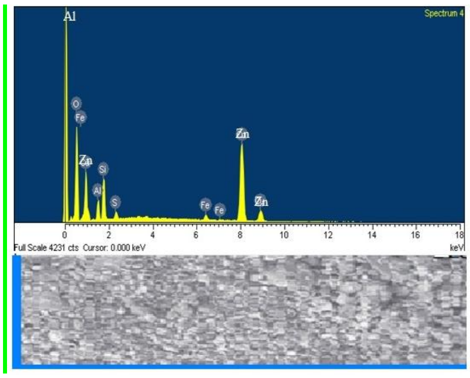

Fig2a. *EDS /SEM for zinc oxide-activated ACOR montmorillonite showing element peaks and particle sizes.*

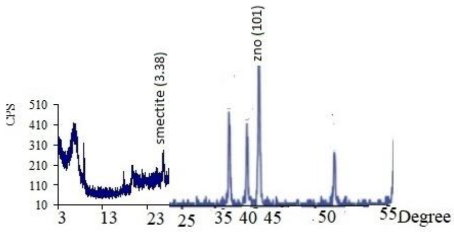

Fig2b. *X-ray diffraction of synthetic copper oxide - montmorillonite showing peaks*

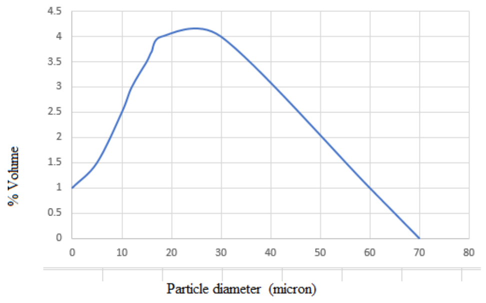

Fig3. *Particle size distribution of ACOR montmorillonite at suspension pH*

The point zero charge pHzpc also was known as the point of zero salt effect. The value was 7.14. This value determines the positive and negative charge divide on the mineral surface. The specific surface area of the adsorbent controls the quantity of exposed mineral surface available for reaction. Subsequently, the specific surface area of the zinc oxide activated ACOR montmorillonite was 400.52 m^2/g.

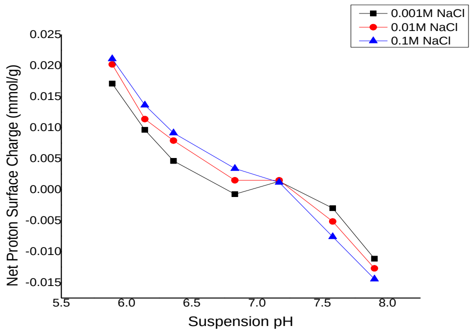

Fig4. *Plot of net proton charge versus suspension pH for ACOR montmorillonite [10 mg/L Hg concentration,2 g/*L adsorbent *concentration*

The proton coefficient ((α)) was based on a theoretical framework given by equations (1, 2), predicted and derived from the plot (Fig. 5), (Supplementary Table 1).

The value of the proton coefficientwas 0.36. The Log Kd-pH plot had a maximum distribution coefficient (Kd) of 2.90 mgg-1. The intraparticle diffusion was based on a theoretical framework given by equation (5), predicted and derived from the plot (Fig. 6), (Supplementary Table 2). The intraparticle diffusion constant derived from the slope was 0.35(mg-1) min0.5 and the intercept C was 2.58, $\neq 0$. This plot consisted of three linear parts, with the first part representing the external mass transfer. The second and third parts represented the intraparticle diffusion and adsorption inside the adsorbent surface.

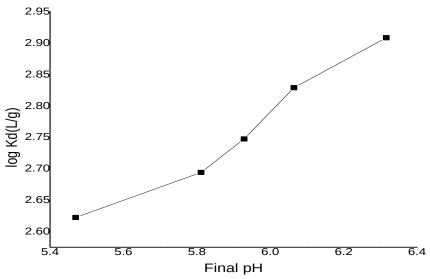

Fig5. *Plot of Log Kd (Distribution coefficient) versus final pH for proton coefficient*

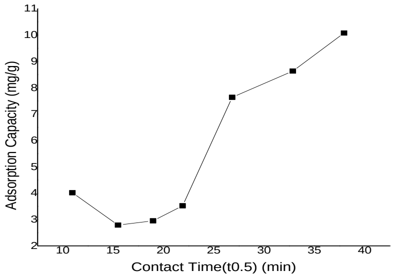

Fig6. *Plot of Adsorption capacity versus time for intraparticle diffusion*

The mass transfer constants (K_f) predicted from equations (3, 4) and derived. From Fig. 7 are given (Supplementary Tables 3). Also, this consisted of three linear parts. The second linear part started after the 4th h and the third linear part started after the 8th h. The Supplementary Fig. 1 in Supplementary material had an increase in capacity of adsorption as Hg^{2+} initial concentration was increased. The adsorption capacity of the zinc oxide-activated ACOR montmorillonite increased with an increase in residence time (Supplementary Fig. 2). The adsorption of mercury ions over the range of contact time investigateddemonstrateda complex pattern. This adsorption pattern increased onto the plunging aftr the 576th h and plunged thereafter. The maximum adsorption capacity was 9.95 mgg-1 at the 720th h.

The adsorption efficiency predicted from equation (6) generally increased with an increase in pH (Supplementary Fig.3). In the absence of zinc oxide coating the pH provided an adsorption efficiency of 90.1% at pH=5, and 90.7 % at pH =7. In the presence of zinc oxide coating, the pH provided an adsorption efficiency of 93.6% at pH=5 and 94.55 % at pH =7 when 10 mgL^{-1} of mercury concentrations and 2 g/L of the adsorbent were used.

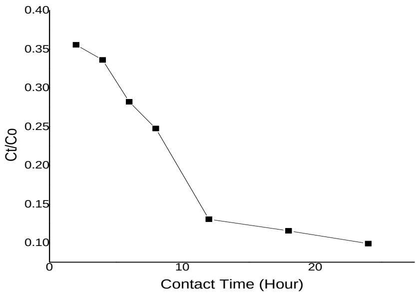

Fig7. *Plot of Ct/Co versus contact time for mass transfer rates*

DISCUSSION

Reaction Mechanism

The reaction mechanism is discussed based on the proton coefficient, intraparticle diffusion, and mass transfer rates. In previous studies with bare montmorillonite, proton coefficient was greater than one [23]. Here, α for zinc oxide-activated ACOR montmorillonite was less than one. This suggested that strongly acidic sites in the compositesystem-controlled protonation. There is an indication that protonation was lowered in the presence of zinc oxide coating. The reactive sites of acidity on the edges and planar surfaces have been masked by the presence of a coated medium. The results indicated that intraparticle diffusion was involved in the adsorption process. However, this characteristic was not a rate-limiting reaction.

Furthermore, there was an indication of boundary layer control when compared with previous studies [24].The slope and intercept for the bare montmorillonite were higher than those of the composite. It could be suggested that the presence of zinc oxide coating enhanced intraparticle diffusion. Again, when compared with previous studies, the mass transfer rates for the composite were higher than those of the bare montmorillonite.

Reaction Kinetics

The adsorption of mercury by the composite was dependent on a time attribute. The dependent on a time attribute of mercury removal was assessed from 24h to 720h at ambient temperature. This was at initial mercury concentration of 10 mgL^{-1} at pH 5.

The adsorption rate was initially fast, increased over time, and plunged after the 576th h. The initial speedy adsorption of mercury ions in the first step may be ascribed to larger numbers of active adsorption sites [25]. The plunging of adsorption may indicate a gradual saturation of reactive sites.

The investigation of different metal concentrations is relevant in adsorption because most contaminated aquatic systems provide different concentrations of metal ions. The increase in adsorption capacity as metal concentration was increased indicated that the active and reactive sites of the composite were not yet saturated. This characteristic was different from the report of [7] for Cu-Oxide coated kaolinite, where the quantity of adsorption decreased with an increase in metal concentration. It could be suggested that a concentration gradient controlled the mass transfer of metal ions between the solid-solution phase.

The Effect of Ph on the Adsorption of Mercury

The pH regulates the degree of protonation and hydroxylation of a mineral surface. Consequently, pH investigation is relevant to this paper. As the pH was increased, there was a decrease or loss in protonation and increased or enhancement in hydroxylation.

This characteristic favored the adsorption of mercury. The adsorption of mercury ions was low at low pH since enormous amount of quantities of protons competed with the mercury ions for reactive and active sites on the composite. There was a decrease in the number of available protonation sites as the pH was increased, thus giving rise to increased hydroxylation and negative charges on the adsorbent surfaces.

CONCLUSIONS

The synthesis of zinc oxide- activated ACOR montmorillonite composite was done. The adsorbent was analyzed for spectral and chemical characteristics using x-ray diffractometer and x-ray fluorescence techniques respectively. The batch mode technique was used to test the removal of Hg^{2+} by the zinc oxide -activated ACOR montmorillonite composite. The mechanism of reaction tested included proton coefficient that was lower than one, intraparticle diffusion that was controlled by boundary layer, and mass transfer rates that were higher than those of bare ACOR montmorillonite. There was an increase in adsorption capacity as mercury concentration was increased, thus indicating that the active and reactive sites of the composite were not yet saturated.

The adsorption of Hg^{2+} was increased by the aging process. The adsorption pattern was essentially controlled by hydrolysis, increased reorganization of reactive sites, and the reactive support of zinc oxide coating. Based on the pH deprotonation and hydroxylation of zinc oxide-activated ACOR montmorillonite composite controlled the adsorption process. As the pH was increased, there was a decrease in protonation and enhancement in hydroxylation, thus leading to an increase in the adsorption of Hg^{2+}ions.The presence of zinc oxide coating enhanced the reorganization of active sites for mercury adsorption.

The pH provided an adsorption efficiency of 93.6 % at pH= 5 and 94.55 % at pH= 7 when 10 mg/L of mercury concentration and 2 g/L of the adsorbent were used. These results supported the need to source for different nano-sized coatings to treat toxic materials in the environment.

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CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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SUPPLEMENTARY MATERIALS

Table1. *Statistical presentation of proton coefficient derived from Fig. 5*

Equation	**Y=a+b*x**		
Proton coefficient α	0.36		
Residual Sum of Squares	0.01		
Pearson's r	0.92		
Adj. R-Square	0.81		
		Value	Standard Error
Log Kd(L/kg)	Intercept	0.60	4.04^{-5}
	Slope	0.36	0.36

Table2. *Statistical presentation of intraparticle diffusion data derived from linear fit of Fig. 6*

Equation	**Y=a+b*x**		
F-Value	19.28		
Prob >F	0.00		
Pearson's r	0.89		
Adj. R-Square	0.75		
		Value	Standard Error
Q_t(mgkg^{-1}) min$^{0.5}$	Intercept	2.58	1.10^{-4}
	Slope	0.35	4.37^{-6}

Table3. *Mass transfer rates for Hg(II) adsorbed on zinc oxide-montmorillonite composite derived from Fig. 7*

Slope I(hr^{-1})	**SlopeII(hr^{-1})**	**Exposed Surface Area (cm^{-1})**	**K_{fI} (cmhr^{-1})**	**K_{fII} (cmhr^{-1})**
0.015	0.004	1000	1.5^{-5}	4^{-6}

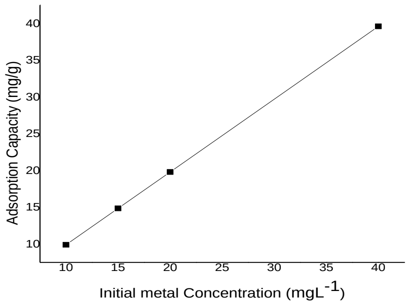

Fig1. *Plot of adsorption capacity versus initial metal concentration [pH=5, 2 g/L adsorbent]*

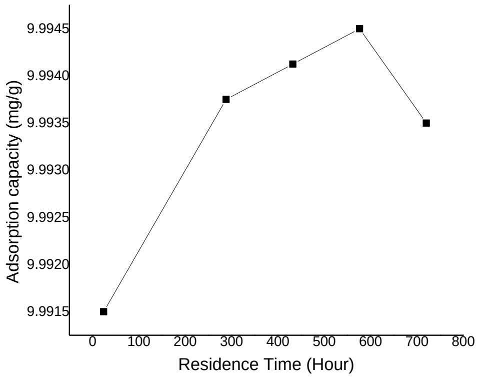

Fig2. *Plot of adsorption capacity versus residence time –ageing for mineral systems [pH=5, 10mgL-1 metal concentration, 2 g/L adsorbent]*

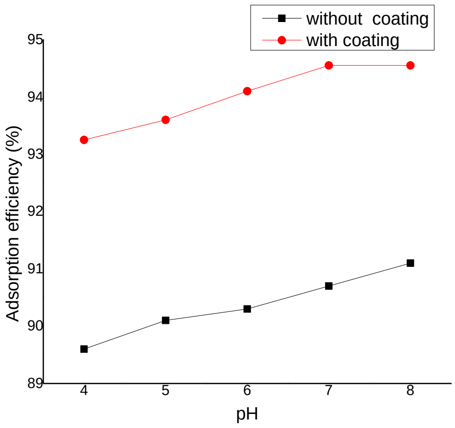

Fig3. *Plot of adsorption efficiency versus initial pH [10mgL-1 metal concentration, adsorbent 2 g/L]*

Citation: *Davidson. E. Egirani et al. "Synthesis of Zinc Oxide Activated Acor Montmorillonite and Its Performance on the Removal of Mercury Ions from Aqueous Media". Open Access Journal of Chemistry, 2(4), pp.36-44*