

ADSORPTION OF LEAD ON A NATURAL CLAY FROM THE AGBOVILLE REGION (CÔTE D'IVOIRE) AND ACTIVATED CLAY WITH HYDROCHLORIC ACID. MODELING BY LINEAR ISOTHERMS OF LANGMUIR AND FREUNDLICH

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ABSTRACT

In this study, natural clay from Agboville (Ivory Coast) was modified with hydrochloric acid to increase its adsorption capacity towards metal ions. The adsorbents were characterized by XRD, SEM and NMR analysis. SEM of natural clay showed slips while that the acid-activated clay with hydrochloric acid (3M) at 65°C showed fibrous aggregates and slips. The XRD of the two adsorbents showed the presence of muscovite-3T, kaolinite and montmorillonite. MAS NMR spectra of ¹H and ²⁷Al show no noticeable difference. The ²⁹Si spectra show an absence of quartz peaks. The effects of adsorption time, pH, clay mass and initial ion concentration on Pb(II) ions adsorption were studied. The Adsorption process achieved equilibrium for around 60 minutes. The optimum pH was 5. The optimal mass of the adsorbents was 500 mg with a rate of about 70% for clay-activated and 54% for natural clay. The Langmuir linear model seems to be more suitable than the Freundlich model for fixing the Pb(II) ions on the two adsorbents studied. The linear model of Langmuir was better suited to describe the adsorption process of Pb(II) metal ions. It has been proven that chemically activated clay with hydrochloric acid has a higher adsorption capacity than natural clay.

Keywords: Clay, Adsorption, Acid-activated, Hydrochloric, Lead.

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INTRODUCTION

Several heavy metal ions are essential in diverse physiological functions and thus are essential for life. However, heavy metals become toxic to human beings when they exceed certainly allowed levels.¹ Water pollution is a major problem in the environmental system due to the release of toxic chemicals from various industrial wastes.² Lead and lead compounds are generally toxic pollutants (EPA safe limit is 0.015 mg/L³). Due to acute toxicity, lead along with mercury (Hg) and cadmium (Cd) forms “the big three” toxic metals with great hazards.⁴ Lead ions cause several disorders such as behavior and learning disabilities, vomiting, slow growth, neurotoxin⁵ and problems of the gastrointestinal and reproductive tract.⁶ Adsorption is one of the most effective and economical methods with high potential for the removal, recovery and recycling of metals from water. Adsorption has the additional advantages of applicability at very low concentrations, suitability for using batch⁷ and continuous processes, ease of operation, little sludge generation, the possibility of regeneration and reuse, and low capital cost.

Natural clays being low-cost adsorbents have been the focus of attention on the sorption of heavy metals from contaminated water.^{8,9} Clay minerals such as mesoporous silica¹⁰, montmorillonite clay and kaolinite are very effective, economical, versatile and simple in the removal of metal ions.^{7,10} Several studies on kaolinite clay used to remove heavy metals from an aqueous solution have been reported., S.S Gupta et al.¹¹ in their work used kaolinite clay to remove Pb(II), Cd(II) and Ni(II) in an aqueous medium. Similarly, kaolinite was used as an adsorbent to remove Fe(III), Co(II) and Ni(II) in medium aqueous solutions¹² and to remove Cu(II)¹³ and Pb(II).¹⁴

Kaolinite has a cation exchange capacity and a relatively small surface area.¹⁵ Thus, these clay minerals can be modified to increase their adsorbent properties. These modifications, of physicochemical type, are

essentially based on the ion exchange generally leading, to hydrophobic adsorbents or heterogeneous catalysts depending on the nature of the modification. Indeed, the acid activation of clay minerals with concentrated inorganic acids consists of replacing the exchangeable cations with H_3O^+ ions, partially removing Al and other cations from the tetrahedral and octahedral sites, while leaving the SiO_4 groups largely intact.¹⁶

In the present work, the parent kaolinite clay was treated with an inorganic acid (3M HCl) and the structural changes caused by this acidic treatment were followed by XRD, solid-state NMR, ^{27}Al and ^{29}Si . The adsorption capacities of natural kaolinite and acid-treated kaolinite concerning Pb(II) were evaluated through an adsorption study by varying various physicochemical parameters.

EXPERIMENTAL

Adsorbents Preparation

The extraction of the clay powder of fraction $\leq 2\ \mu\text{m}$ and its activation with hydrochloric acid (3M) is as follows: 100 g of clay of particle size $\leq 100\ \mu\text{m}$ are suspended in 500 ml of distilled water and stirred for 30 minutes. The mixture is aged for 4 hours at laboratory temperature and siphoned off. The siphon is then centrifuged for 16 minutes at 4500 rpm and the sludge obtained is dried in an oven at 100°C for 24 hours. The powder obtained is $\leq 2\ \mu\text{m}$.

Acid activation at 3 M HCl was done according to the protocol described by Allahdin *et al.*¹⁷

10 g of this powder $\leq 2\ \mu\text{m}$ are suspended in 200 ml of HCl solution (3 M) and stirred vigorously for 6 hours at a temperature of 65°C , then centrifuged and washed with distilled water until pH = 7 and then dried in the oven for 24 hours.

Characterization

The X-ray diffraction (XRD) patterns of the adsorbents were obtained using a powder Bruker D8 PASSEUR diffraction instrument with filtered $\text{CuK}\alpha$ radiation ($n=1.54060\ \text{\AA}$) operated at 40 kV and 40 mA. The XRD pattern was recorded at a temperature of 25°C from 5 to $65^\circ 2\theta$ with a scanning speed of $0.02^\circ (2\theta)$ per second.

A scanning electron microscope was used to visualize the morphology of adsorbents. The two samples were covered with gold under vacuum in argon atmosphere (Fig.-1).

The specific surface area was evaluated by the Brunauer-Emmet-Teller (BET) method. The volume and the pore size distribution were calculated by the Berrett Joyner Halenda (BJH) method.

^1H and ^{27}Al MAS NMR experiments were recorded at 400 MHz on 9.4 Bruker Avance III spectrometer equipped with a standard probe 4 mm HXY of three-channel used in dual mode and operating at frequencies respective 400.115 MHz and 104.257 MHz at 400 MHz.

One-D NMR MAS spectra of ^{27}Al were measured with a delay of $2\ \mu\text{s}$, an acquisition time of 10 ms, a pulse length of $1\ \mu\text{s}$ ($\pi/2$ flip angle) corresponding to a pulse power of 4 dB, 1024 transients. The chemical shift scale was referenced to the peak of $\text{Al}(\text{Al}(\text{H}_2\text{O})_6)^{3+}$. ^1H MAS NMR analyses were performed with a pulse length of $2.5\ \mu\text{s}$ ($\pi/2$ flip angle) which corresponds to a pulse power of 2.80 dB, an acquisition time of 10 ms, 16 transients, a delay of $2\ \mu\text{s}$ and the chemical shift scale was referenced to the peak of adamantane.

The solid-state NMR MAS spectra of the ^{29}Si Udefit-CpAp sequence were obtained on 9.4 T Bruker Avance III spectrometer at a spinning frequency of 10 kHz and operating at 79.492 MHz using a 4 mm probe. These spectra were recorded with pulse length of $3.67\ \mu\text{s}$ ($\pi/2$ flip angle), an FID duration of 10 ms, a dwell time of $10\ \mu\text{s}$ and 512 transients. Recycle times of 60 s and 120 s were used and were sufficient for complete relaxation. The chemical shift scale was referenced to the peak of tetramethylsilane (TMS) at 0.0 ppm.

Adsorption study

The method consists first of all in preparing a stock solution of $1000\ \text{mg.L}^{-1}$ of Pb^{2+} from lead nitrate salt ($\text{Pb}(\text{NO}_3)_2$) with a molar mass $331.21\ \text{g.mol}^{-1}$. The distilled water used in our tests is characterized by a pH between 5.3 and 6.6.

10 ml of a single metal solution and a pre-weighed amount of adsorbent were poured into vials and placed on a MULTISTIRRER 6 shaker for 24 hours and the pH was adjusted with HCl (0.1N) and NaOH (0.1N). The samples of the solutions are filtered using a $0.45\ \mu\text{m}$ membrane of porosity. The final concentration of each metal was determined by atomic absorption spectroscopy (AAS).

The operating parameters studied for the study of the adsorption of Pb (II) ions were: the contact time, the pH of the suspension, the mass of adsorbent and the metal concentration.

RESULTS AND DISCUSSION

Characterization of Adsorbents

Based on SEM images of the two samples, it can be seen the plates and the distance between these plates is nm level. The SEM image of natural clay formed by sheets and every sheet clinged closely to each other. The SEM image of clay activated with hydrochloric acid is formed by sheets and fibrous aggregates. The natural clay has a smaller surface area and leads to low adsorption of metal ions.

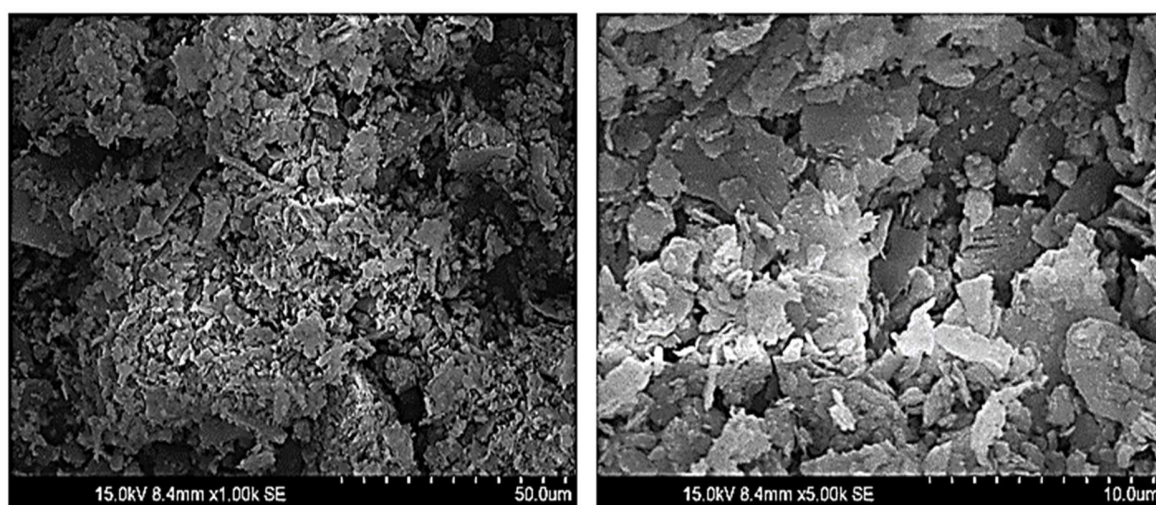


Fig.-1: SEM Images of Natural Clay

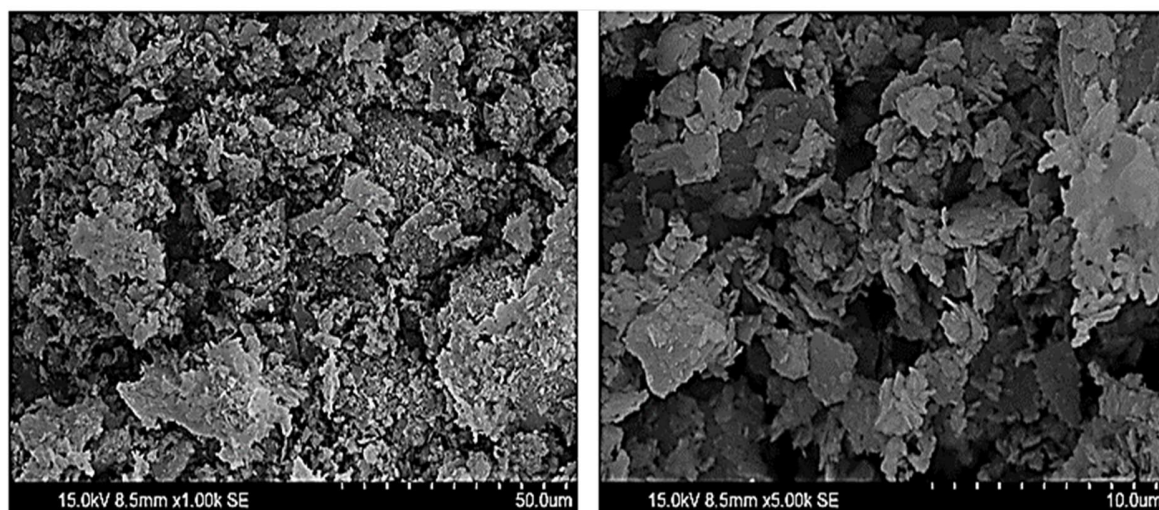


Fig.-2: SEM Images of Activated Clay with Hydrochloric Acid (3M at 65°C)

The diffractograms of the powders of the raw clay fraction $\leq 2\mu\text{m}$ and the clay activated with hydrochloric acid (3M) at 65°C do not contain mineralogical impurities (or are not seen on the XRD diagrams) but only phyllic phases dominated by muscovite-3T and kaolinite. The characteristic peaks of kaolinite-1Ad appear at 12.333 °, 24.853 ° and 37.652 ° (2 θ). The corresponding basal spacings are 7.188, 3.580 and 2.386 Å

with respective intensities of 753, 999 and 197. The characteristic peaks of muscovite-3T occur at: 8.862° , 17.760° , 26.742° , 35.907° and 45.330° (2θ) with respective basal spacings of 9.970, 4.990, 3.331, 2.499 and 1.999 Å. The intensities of these lines are respectively 100, 56, 11, 100, 13 and 45.

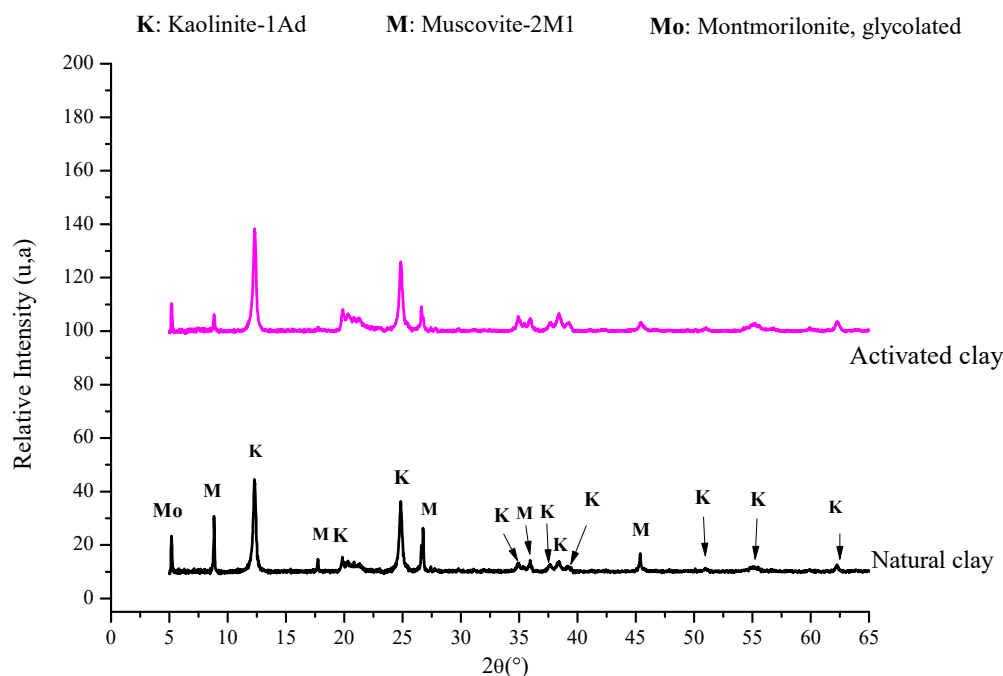


Fig.-3: XDR Diagrams of Raw Clay and Clay Activated with Hydrochloric Acid (3M at 65°C)

The specific surfaces area of the original clay and activated-clay with hydrochloric acid (3M) at 65°C are respectively 22.20 and $44.22\text{ m}^2/\text{g}$. In Table-1 are illustrated the values of the specific surfaces area and the pore volumes of the original clay and the activated-clay with hydrochloric acid (3M) at 65°C . The specific surface area increases with acid treatment. Indeed, the acid treatment opens up the edges of the platelets and, as a consequence, both the specific surface area and the pore diameter increase^{18,19}.

Table-1: Specific Surface Area and Pore Volumes of the Adsorbents Studied

Sample	Température of Treatment	SBET (m^2/g)	Vpore (cm^3/g)	Average Pore Diameter (nm)
Original clay	-	22.19	0.097	15.793
Activated-clay	$65^\circ\text{C}/4\text{h}$	44.22	0.198	15.373

The ^1H MAS NMR spectrum of natural clay and the activated clay with hydrochloric acid (3M) at the temperature of 65°C (Fig.-3) show two peak signals at 1.7 and 3.1 ppm and are assigned respectively to the hydroxyls of the aluminol groups (Al-OH) and hydroxyls of the silanol groups (Si-OH).¹⁷

The ^{27}Al MAS NMR spectrum of natural clay (Fig.-3) and the activated clay with hydrochloric acid (3M) at the temperature of 65°C shows a single peak with the isotropic chemical shift at 7.6 ppm, a quadrupolar constant coupling (C_Q) of 3.3 MHz and an asymmetry parameter (η_Q) of 0.6. This chemical shift at 7.6 ppm can be attributed to the octahedral aluminum found in the kaolinite sheets.

The ^{29}Si MAS NMR ^{29}Si spectrum of natural clay (Fig.-5) shows three peaks at chemical shift values of -91.7 ppm, -92.9 ppm and -107.7 ppm. The resonance at -91.7 ppm and the shoulder at -92.9 ppm are attributed to the Q^3 silica present in the tetrahedral layer of kaolinite. The presence of these two signals in kaolinite has been observed in several studies.²⁰⁻²³

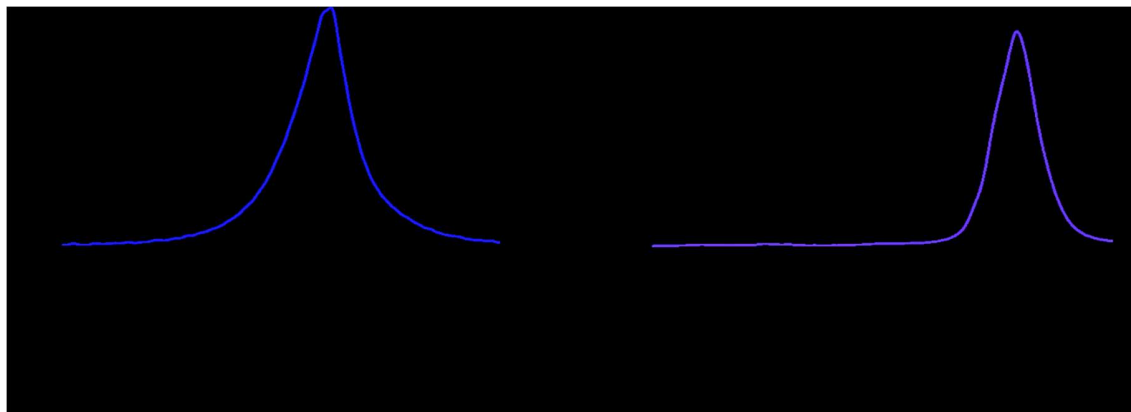


Fig.-4: ^1H , ^{27}Al MAS NMR Spectra of Raw Clay and Activated Clay with Hydrochloric Acid (3M at 65°C) at 9.4T

These two signals are due to two silicon populations of the tetrahedral layer that interact differently with the adjacent octahedral layer. The signal at -107.7 ppm is assigned to quartz in Q^4 units. The ^{29}Si MAS NMR ^{29}Si spectrum of activated clay with hydrochloric acid (Fig.-5) shows two peaks at chemical shift values of -91.30 ppm and -91.97 ppm. These two resonances are assigned to Q^3 silica present in the tetrahedral layer of kaolinite.

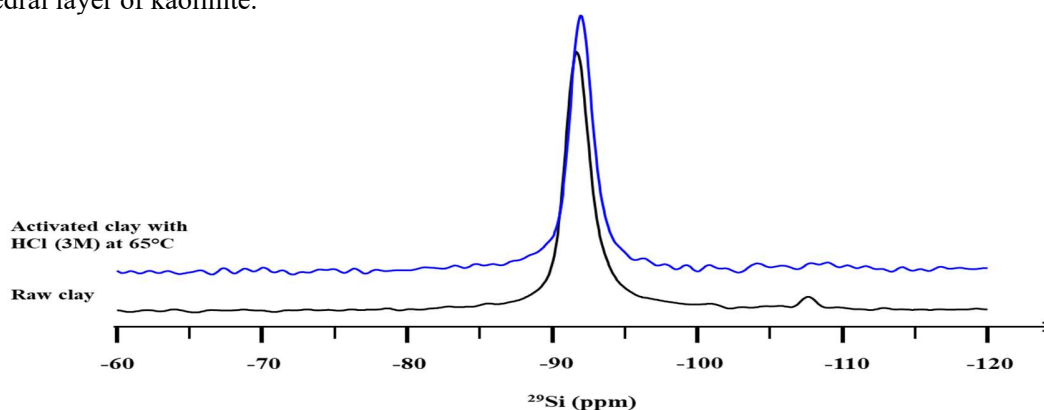


Fig.-5: ^{29}Si MAS NMR Spectra of Natural Clay and Activated Clay with Hydrochloric Acid (3M) at 65°C at 9.4T

Table-2: ^1H MAS NMR Data of Natural Clay and Activated Clay with Hydrochloric Acid (3M) at 65°C at 9.4T

9.4T				
Sample	δ_{iso} (ppm)	Width (ppm)	G/L	% Integral
Raw clay $\leq 2\mu\text{m}$	1.75	3.99	0.4	82.16
	3.08	5.76	0.98	17.84
9.4T				
Activated clay with HCl(3M)	1.73	2.5	0.50	65.94
	3.12	6.12	0.8	34.06

Table-3 : ^{29}Si MAS NMR Data of Natural Clay and Activated Clay with Hydrochloric Acid (3M) at 65°C at 9.4T

9.4T				
Sample	δ_{iso} (ppm)	Width (ppm)	G/L	% Integral
Raw clay	-91.65	1.81	0.6	82.16
	-92.94	3.78	0.00	17.84
	-107.63	1.49	1.00	
9.4T				
Activated clay with HCl(3M)	-91.30	1.0	0.00	1.20
	-91.97	1.7	0.5	98.80

Effect of Contact Time

The effect of contact time on the adsorption of Pb(II) was investigated at different time intervals in the range of 10–30 min. After they were filtered, the supernatant solutions were taken for metal ion analysis using AAS²⁴. As mentioned in the Fig.-6, the adsorption equilibrium is established rapidly after 40 minutes. Commonly, the adsorption capacity increased rapidly, and then slower adsorption follows because the available sorption sites are slowly decreased.²⁵ This behavior could be assigned to the quick employment of available sorption sites of the natural clay and activated clay for adsorption during the initial stage. Once equilibrium is reached, the remaining unoccupied surface sites are difficult to be occupied due to repulsive forces between Pb(II) ions on the surface of the natural clay and activated clay.²⁶ In this study, 54% of Pb (II) ions were adsorbed on natural clay and 69% on activated hydrochloric acid clay when equilibrium was reached at 40 min. Based on these results, it can be seen that these adsorbents can be used to remove these metal ions. The contact time of 1 hour was optimized and selected for the rest of the study.

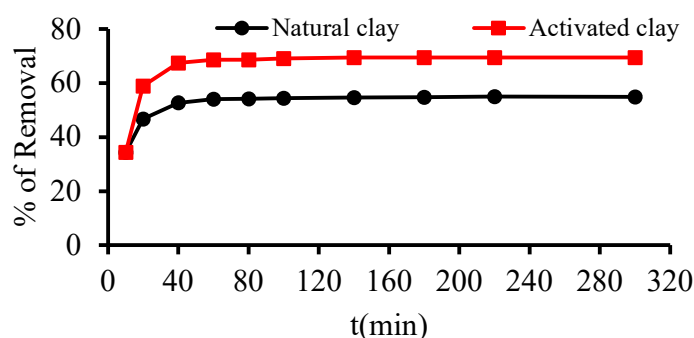


Fig.-6: Influence of Contact Time on the Adsorption of Pb(II) Metal Ions by Natural Clay and Activated Clay with HCl (3M) at 65°C, pH = 5, Initial Concentration of the Metal 25 mg.L⁻¹, Mass of the Adsorbent 500 mg

Effects of Initial Metal Ion Concentration

The adsorption capacity of the adsorbed Pb (II) ions per unit mass (Q_e) of the two adsorbents increases with the increase of the metal concentration, while the adsorption rate (%) decreases with the increase of the charge in metal ions. By varying the initial Pb (II) ion concentration from 10 to 100 mg/L, the adsorption (Q_e) capacities increase from 0.064 mg/g to 0.433 mg/g for natural clay and from 0.057 mg/g at 0.53 mg/g for activated clay with hydrochloric acid (3M) at 65°C. At the same time, the adsorption rates vary from 64.68% to 20.30% for natural clay and from 71.11% to 26.3% for activated clay with hydrochloric acid (3M) at 65 °C. When the initial concentration of metal ions is low, the ratio between the number of metal ions and the number of available adsorption sites is small and, therefore, the adsorption is independent of the initial concentration. However, as the concentration of metal ions increases, the situation changes and competition becomes fierce for adsorption sites.²⁷ At high metal concentrations, a portion of the adsorbent is exposed to a greater number of metal ions and this results in an increase in the adsorption capacity of metal ions with the progressive filling of the appropriate binding sites. As a result, Q_e increases and the rate of elimination decreases. Similar results have already been reported for the adsorption of metal ions on different adsorbents (eg Cd(II) on activated-carbon from coconut coir pith²⁸, Cu(II) on maple sawdust²⁹, Ni(II) and Cd(II).) on bagasse fly ash, etc.).³⁰

Effect of pH

The pH of the solution is one of the important parameters verifying the adsorption processes.³¹ It modifies the surface charge of the adsorbent, the extent of ionization of the various contaminants.³² In this study, the effect of the pH of the solution on the absorption of Pb (II) using natural clay and activated-acid clay at 65°C was studied in the pH range between 1 and 9 and the results are shown in Fig.-8. About 55% and 70% Pb (II) can be removed at a pH of 5 in the order of original clay and activated-clay with hydrochloric acid (3M) at 65°C. At very low pH, the concentration of H₃O⁺ ions was high. This led to the development of a positive charge on the active sites of adsorbents and also a competition between Pb(II) ions and H₃O⁺. So,

there were a minimum binding of Pb(II) ions at low pH. However, as pH increases, there is less competition of Pb(II) ions with H_3O^+ ions. This improves the adsorption of positively charged metal ions through the electrostatic attraction force.³³ Thus, the adsorption of Pb(II), the adsorbed amount was increased to pH 5.0, after which it decreased. So, it was concluded that optimum pH for adsorption of Pb(II) ion on original clay and activated-clay was 5.

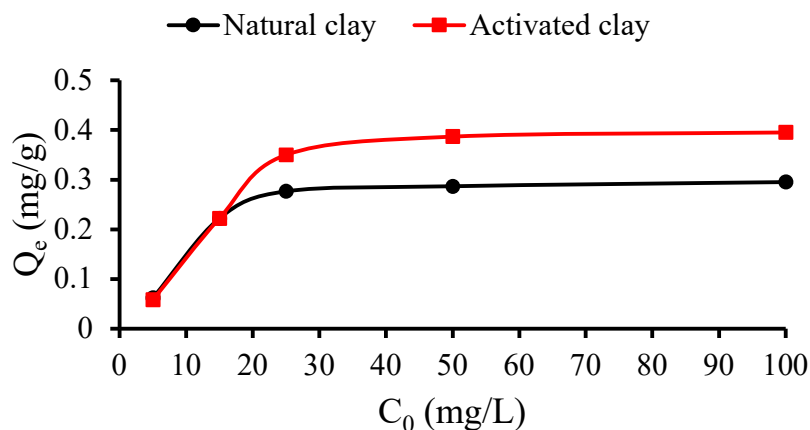


Fig.-7: Isotherm Plots for Adsorption of Pb(II) on Natural Clay and Activated Clay with Hydrochloric Acid, pH of Metal Solution Mass of the Adsorbent 500 mg., Initial Metal Ion Concentration 5, 15, 25, 50, 100 mg/L.

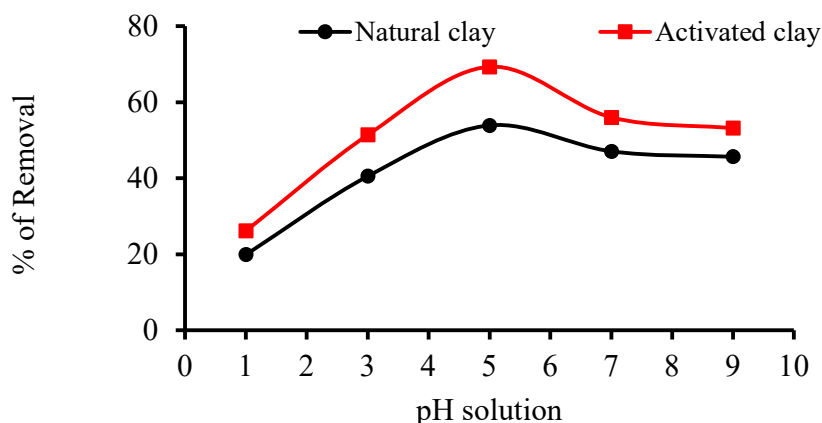


Fig.-8: Influence of pH on the Adsorption of Pb(II) Ions by Natural Clay and Activated Clay with HCl (3M) at 65°C. Contact Time 24 hours, Initial Concentration of Metal 25 mg.L⁻¹, the Mass of Adsorbents 500 mg

Effect of Amount of Adsorbents

The effect of the amount of adsorbents was studied at room temperature by fixing the pH of solutions containing 25 mg.L⁻¹ of Pb(II) at 5 and varying the amount of adsorbents from 0.1g to 1.1g. The results obtained are shown in the Fig.-9. The adsorption of Pb(II) ions on both adsorbents increased as the amount of adsorbents increased. This is not unexpected since, for a fixed initial solute concentration, an increasing amount of adsorbent provides a greater surface area and a correspondingly greater number of adsorption sites.³⁴ For subsequent tests of the experiment, 500 mg of the quantity of adsorbents was applied as optimum.

Adsorption Isotherm

The adsorption equilibrium is usually described by an isotherm equation whose parameters express the surface properties and affinity of the adsorbent. Several isotherm models are available to describe the equilibrium sorption distribution in which two models are used to fit the experimental data: Langmuir and

Freundlich models. The Langmuir model assumes that uptake of metal ions occurs on a homogenous surface by monolayer adsorption without any interaction between adsorbed ions.

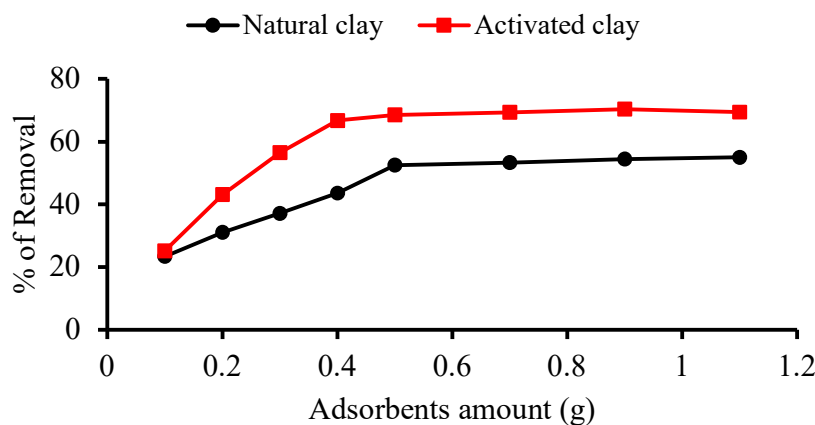


Fig.-9: Effect of the Amount of Adsorbent on Adsorption of Pb(II). Contact Time 24 hours, pH of Solution 5; Initial Concentration of Metal 25 mg.L⁻¹

The exploitation of the results according to Langmuir and Freundlich laws is carried out considering a fixed the amount of the adsorbent optimum (0.5g) and variable concentrations of Pb(II) solutions: 5, 15, 25, 50 and 100 mg/L. The Langmuir equation may be written as:

$$\frac{C_e}{q_e} = \frac{1}{K_L Q_m} + \frac{C_e}{Q_m}$$

Where,

Q_e : quantity of adsorbed Pb(II) ions per unit mass of the adsorbent (mg/g),

C_e : concentration of Pb(II) in solution (mg/L) at equilibrium,

Q_m : monolayer adsorption capacity of Pb(II) ions (mg/g),

K_L : Langmuir adsorption constant (L/mg).

We also used the separation factor R_L (dimensionless) to show the favorable nature of our adsorption system. The adsorption process is favorable when $0 < R_L < 1$. The separation factor is defined as follows:

$$R_L = \frac{1}{1 + C_o K_L}$$

Where, C_o is the initial concentration of Pb(II) in the solution (mg.L⁻¹).

The Freundlich linear model is an empirical equation based on adsorption on a heterogeneous surface. The equation is commonly represented as:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e$$

Where,

C_e : concentration of the adsorbate at equilibrium (mg.L⁻¹).

q_e : quantity of adsorbate fixed at equilibrium (mg.g⁻¹)

K_F : Freundlich adsorption constant (mg¹⁻ⁿ Lng⁻¹)

The parameters of Langmuir are summarized in Tables-3. Isotherm-fitting yields good results with Langmuir equation and this indicated that the adsorption sites were non-uniform and nonspecific. It conformed with the existence of different types of possible adsorption sites on adsorbents surface with considerable difference in energy if the site was on an edge or was located in a defect position.

The adsorption coefficients agreed well with the conditions supporting favorable adsorption. The Langmuir monolayer capacity was large in conformity with its capacity to take up more of the metal ions. The R_L values of Langmuir isotherm are respectively 0.9932 and 0.9961 for natural and activated clay. These values between 0 and 1 suggest that the adsorption process is favorable.³⁵

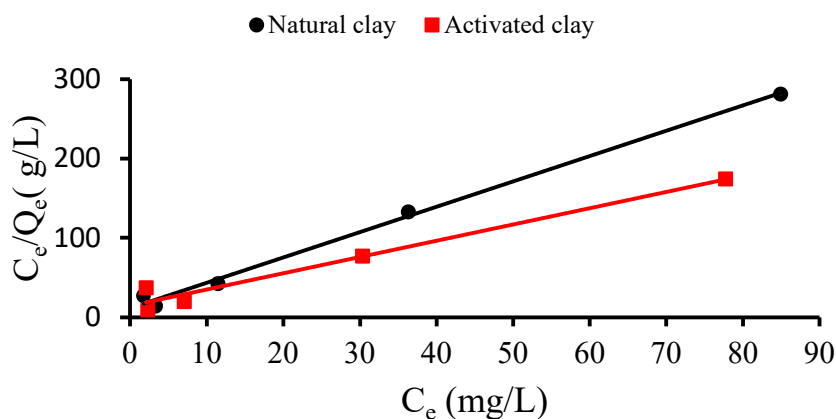


Fig.-10: Langmuir Adsorption Isotherms of Pb(II) Ion on Natural Clay and Activated Clay with Hydrochloric Acid (3M) at 65°C, pH 5 at Room Temperature

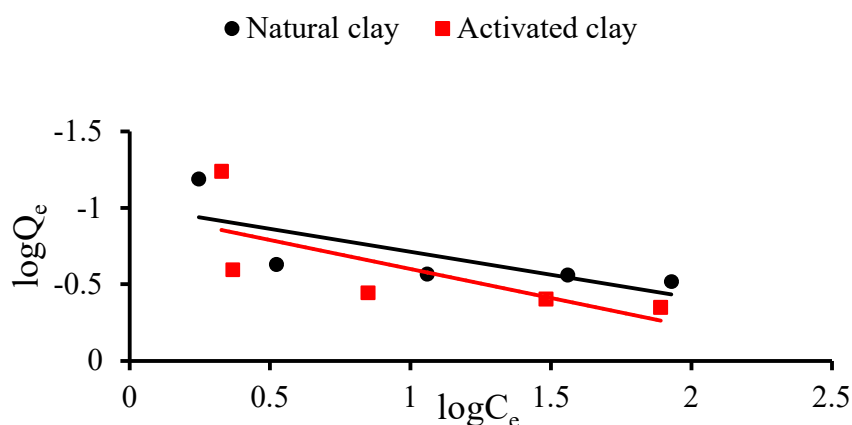


Fig.-11: Freundlich Adsorption Isotherm of Pb(II) Ion on Natural Clay and Activated Clay with HCl (3M) at pH 5

Table-4 : Langmuir Adsorption Parameters of Pb(II) Over Natural Clay and Activated Clay with Hydrochloric Acid (3M) at 65°C

Natural Clay			
Q_m	K_L	R_L	R^2
0.3135	0.2733	0.9932	0.9954
Activated Clay with HCl (3M) at 65°C			
Q_m	K_L	R_L	R^2
0.4876	0.1552	0.9961	0.9713

The linear plots of the Freundlich isotherm give ($R^2 = 0.5619$ for the adsorption of Pb(II) ions on the natural clay and $R^2 = 0.5119$ for the adsorption of Pb(II) on the activated clay at 3M of hydrochloric acid at 65°C (Fig.-11) and the values of the coefficients n (all values > 1.0) and K_F (0.0970 for natural clay and 0.1045 for clay activated with 3 M hydrochloric acid at 65°C) indicate that adsorbents have good potential to be used as adsorbents of Pb(II) metal ions. It should be noted that the Freundlich isotherm applies to adsorption on nonspecific and heterogeneous sites on solid surfaces, but no precise mechanism could be achieved. The K_F value of activated clay with 3M hydrochloric acid at 65°C is greater than that of the natural clay. The Freundlich data are given in Table-5.

Table-5 : Freundlich Adsorption Data of Pb(II) Over Natural Clay and Activated with HCl(3M) at 65°C

Natural Clay			Activated Clay with HCl(3M) at 65°C		
n	K_F	R^2	n	K_F	R^2
3.3356	0.0970	0.5619	2.6350	0.1045	0.5119

CONCLUSION

Natural clay and acid-activated clays are capable of removing metal ions such as Pb(II) from aqueous solution. Acid-activation led to an increase in the adsorption capacity brought about by increasing the surface area. Several factors are affecting the adsorption of metal ions onto adsorbents, however, the pH solution is a significant impact on the adsorption of metals ions. Thus the experimental data were better fitted with Langmuir linear model compared to Freundlich linear model. This indicated that while the interactions were predominantly chemical, the adsorption sites were non-uniform and nonspecific. Such a study could also help to establish the adsorptive capacity of these adsorbents for actual industrial effluents contaminated with different heavy metal ions.

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REFERENCES

1. D. H. Kumar, K. Sessaiah, A. V. R. Reddy, M. M. Rao and M. C. Wang, *Journal of Hazardous Materials*, **174**, 831(2010), DOI:10.1016/j.jhazmat.2009.09.128
2. A. Allwar, *Rasayan Journal of Chemistry*, **12(2)**, 598(2019), DOI:10.31788/RJC.2019.1225090
3. V. Obuseng, F. Nareetsile and H. M. Kwaambwa, *Analytica Chimica Acta*, **730**, 87(2012), DOI: 10.1016/j.aca.2012.01.054
4. S. Tunali, S. Arslan, T. Alp, D. Arslan and T. Akar, *Chemical Engineering Journal*, **185-186**, 82(2012), DOI:10.1016/j.cej.2012.01.032
5. M. Riaz, R. Nadeem, M. Asif, T. Mehmood and K. Rehman, *Journal of Hazardous Materials*, **161(3)**, 88(2009), DOI:10.1016/j.jhazmat.2008.03.096
6. H. S. Ibrahim, N. S. Ammar, M. Soylak and M. Ibrahim, *Spectrochimica Acta. Partie A*, **96**, 413(2012), DOI:10.1016/j.saa.2012.05.039
7. K. Mohanty, D. Das and M. N. Biswas, *Adsorption*, **12(2)**, 119(2006), DOI:10.1007/s10450-006-0374-2
8. K. G. Bhattacharyya and S. S. Gupta, *Advances in Colloid and Interface Science*, **140**, 114(2008), DOI:10.1016/j.cis.2007.12.008
9. D. M. Manohar, B. F. Noeline and T. S. Anirudhan, *Applied Clay Science*, **31**, 194(2006), DOI: 10.1016/j.clay.2005.08.008
10. D. L. Guerra, R. Viana and C. Airoidi, *Inorganic Chemistry Communications*, **11**, 20(2008), DOI: 10.1016/j.inoche.2007.09.029
11. S. Sen gupta and K. G. Bhattacharyya, *Indian Journal of Chemical Technology*, **16(6)**, 457(2009)
12. K. G. Bhattacharyya and S. Sen, *Separation and Purification Technology*, **15 July**, 388(2006), DOI: 10.1016/j.seppur.2005.12.014
13. K. G. Bhattacharyya and S. Sen, *Applied Clay Science*, **41**, 1(2008), DOI: 10.1016/j.clay.2007.09.005
14. S. Sen and K. G. Bhattacharyya, *Applied Clay Science*, **30**, 199(2005), DOI: 10.1016/j.clay.2005.03.008
15. G. Suraj, C. S. P. Iyer and M. Lalithambika, *Applied Clay Science*, **13(4)**, 293(1998), DOI: 10.1016/s0169-1317(98)00043-x
16. C. R. Theocharis, K. J. S. Jacob and A. C. Gray, *Journal of the Chemical Society, Faraday Transactions 1: Physical Chemistry in Condensed Phases*, **84(5)**, 1509(1988), DOI: 10.1039/f19888401509
17. O. Allahdin, M. Wartel, G. Tricot, B. Revel and A. Boughriet, *Microporous and Mesoporous Materials*, **226**, 360(2016), DOI:10.1016/j.micromeso.2016.02.028
18. A. S. R. P. A. Cristina Volzone, G. John, Thompson, A. Melnitchenko and J. Ortiga, *Clays and Clay Minerals*, **47(5)**, 647(1999), DOI:10.1346/ccmn.1999.0470511
19. D. De Engenharia, E. Polit cnica, U. D. S. Paulo and S. P. Sp, *Quimica Nova*, **24(3)**, 345(2001)
20. S. Letaief and C. Detellier, *Canadian Journal of Chemistry*, **6**, 1(2008), DOI:10.1139/v07-130

21. C. A. Ríos, C. D. Williams and M. A. Fullen, *Applied Clay Science*, **43(2)**, 228(2009), DOI: [10.1016/j.clay.2008.09.014](https://doi.org/10.1016/j.clay.2008.09.014)
22. J. Thompson, *Clays and Clay Minerals*, **32**, 233(1984)
23. J. G. Thompson and P. F. Barron, *Clays and Clay Minerals*, **35(1)**, 38(1987), DOI: [10.1346/ccmn.1987.0350105](https://doi.org/10.1346/ccmn.1987.0350105)
24. K. O. Adebowale, I. E. Unuabonah and B. I. Olu-Owolabi, *Journal of Hazardous Materials*, **b134**, 130(2006), DOI: [10.1016/j.jhazmat.2005.10.056](https://doi.org/10.1016/j.jhazmat.2005.10.056)
25. A. Basker, P.S. Syed Shabudeen, S. Daniel and P.V. Kumar, *Rasayan Journal of Chemistry*, **7(1)**, 1(2014)
26. D. W. Astuti, N. H. Aprilita and M. Mudasir, *Rasayan Journal of Chemistry*, **13(2)**, 845(2020)
27. H. Ucun, Y. K. Bayhan, Y. Kayab, A. Cakici and F. Algurb, *Desalination*, **154**, 233(2003), DOI: [10.1016/s0011-9164\(03\)80038-3](https://doi.org/10.1016/s0011-9164(03)80038-3)
28. C. Kadirvelu and K. Namasivayam, *Advances in Environmental Research*, **7**, 471(2003)
29. B. Yu, Y. Zhang, A. Shukla, S. S. Shukla and K. L. Dorris, *Journal of Hazardous Materials*, **80(1-3)**, 33(2000), DOI: [10.1016/s0304-3894\(00\)00278-8](https://doi.org/10.1016/s0304-3894(00)00278-8)
30. V. K. Gupta, C. K. Jain, I. Ali, M. Sharma and V. K. Saini, *Water Research*, **37**, 4038(2003), DOI: [10.1016/s0043-1354\(03\)00292-6](https://doi.org/10.1016/s0043-1354(03)00292-6)
31. H. Revathi, A. Xavier, M.D. Kumar, T. Saranya, A. Kaviyarasu and T. Murugan, *Rasayan Journal of Chemistry*, **12(2)**, 719(2019), DOI: [10.31788/RJC.2019.1225094](https://doi.org/10.31788/RJC.2019.1225094)
32. T.W. Seow and C.K. Lim, *International Journal of Applied Engineering Research*, **11(4)**, 2675(2016), DOI: [10.1007/s11356-015-5880-x](https://doi.org/10.1007/s11356-015-5880-x)
33. E. I. Unuabonah, K. O. Adebowale, B. I. Olu-owolabi, L. Z. Yang and L. X. Kong, *Hydrometallurgy*, **93**, 1(2008), DOI: [10.1016/j.hydromet.2008.02.009](https://doi.org/10.1016/j.hydromet.2008.02.009)
34. S. Rengaraj, K. Yeon, S. Kang, J. Lee, K. Kim and S. Moon, *Journal of Hazardous Materials*, **92**, 185(2002), DOI: [10.1016/s0304-3894\(02\)00018-3](https://doi.org/10.1016/s0304-3894(02)00018-3)
35. S. Lin, Z. Song, G. Che, A. Ren, P. Li, C. Liu and J. Zhang, *Microporous and Mesoporous Materials*, **193**, 27(2014), DOI: [10.1016/j.micromeso.2014.03.004](https://doi.org/10.1016/j.micromeso.2014.03.004)

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