Physico-Chemical Activation of South African Bentonite Clay and Impact on Metal Adsorption Capacity

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Abstract**—**The aim of the project is to investigate the influence of physico-chemical activation on the metal adsorption capacities of natural bentonite clay from the North West Province of South Africa. The clay has been characterized using XRF and XRD analysis, in order to determine the mineralogical and elemental composition of the clay. The following activation techniques have been investigated to determine the influence they have on the adsorption capacities of the clay: acid activation, heat treatment, time of treatment, type of acid and concentrations of the acids. The kinetic and isotherm models have been used to determine the adsorption behaviour of the activated and non-activated clays.

The clay adsorption capacity for the removal of Co(II) was improved after chemical treatment, but the adsorption capacity for the removal of Pb(II) was decreased after activation. The FTIR analysis has shown that the binding group mainly involved in the removal of metals is -CO.

This study informs on the suitable activation technique for the improvement of the adsorption capacity of the typical clay from the North West Province of South Africa.

Keywords**—**Bentonite clay, physico-chemical activation, metal adsorption, kinetic, isotherm

I. Introduction

HEAVY metals are commonly found in wastewater because of an increase in mining, metal finishing industry, textile manufacturing, electro painting, electroplating, coal combustion, refining of metals and the manufacturing of batteries. The wastewater that results from these industries usually contain Pb(II), Cu(II), Cd(II), Ni(II), Cr(VI) and Zn(II) [1]. The presence of these heavy metals in wastewater poses a growing risk to society, because some of the heavy metals are very toxic to the environment and have a high degree of toxicity for the living organisms [2]. The increased use of Co(II) in the nuclear power plants, mining, paint and electronic industries has led to an increase of Co(II) in water sources.

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Co(II) can cause paralysis, bone defects, low blood pressure and also diarrhoea [3]. Pb(II) exposure can cause serious health problems such as high blood pressure, kidney damage, learning deficiencies and also anaemia [4]. The removal of these metals from water is therefore extremely important, as the impact that they have on both the environment as well as living organisms can be significant. There are numerous processes available for the removal of metals from solutions, such as chemical precipitation, reverse osmosis, ion exchange, solvent extraction and adsorption. Adsorption however has become a preferred method for the metal removal, because it is a low cost and effective method [5]. Clays have a high cation exchange capacity, mechanical and chemical stability and low-cost, and are very accessible and abundant. Clays that are currently being used include bentonite, kaolinite, montmorillonite, smectite and beidellite [6]. The aim of this study is to determine the influence of acid activation on the metal adsorption capacities of bentonite clay focusing mainly on the influence of temperature, time and concentrations of acids.

II. Methodology

A. Materials

Bentonite clay

Natural bentonite clay was used during the course of the experiments. The bentonite clay used in this study has been collected from the Koppies District in the Freestate Province of South Africa. The clay was gently grinded to a powder form and then sieved to obtain a particle size <75 μm.

Reagents

The acids used to activate the clay were H_2SO_4 (98%, p.a., ACE) and HCl (36%, p.a., ACE). A stock solution of Pb(II) and Co(II) was prepared by dissolving the required amounts of $Pb(NO_3)_2$ (p.a., ACE) and $Co(NO_3)_2 \cdot 6H_2O$ (p.a., ACE) in distilled water.

B. Acid activation

The activation experiments were conducted in a batch system using flasks of 250 ml capacity. A clay/acid ratio of 0.02 was used. Thus, 2 g of clay was added to 100 mL of acid solution (H_2SO_4 or HCl) with concentrations of 0.5 M or 4 M. The solutions were heated (25°C or 80°C) while undergoing continues mechanical stirring for 1 h or 6 h at a speed of 200

rpm. After the stirring process the solutions were centrifuged for 10 minutes at 4000 rpm and washed with distilled water. The solutions were then oven dried at 80°C for 24 h until a constant weight was obtained.

C. Adsorption experiments

The adsorption experiments were conducted in a batch system using flasks of 250 ml capacity.

Adsorption with activated clays

The adsorptive solutions were prepared by dissolving Pb $(NO_3)_2$ and $CoCl_2 \cdot 6H_2O$ in distilled water. The working solutions contained 50 ppm of Pb(II) or 50 ppm of Co(II). An amount of 0.2 g of the activated adsorbent was added to 50 mL of the adsorptive solution and continuously stirred for 2 h at a speed of 200 rpm. The mixture was then centrifuged for 10 minutes at 4000 rpm and Pb(II) or Co(II) ions remaining in the supernatant were determined by ICP analysis. The same experimental procedure was followed using the non-activated clay. The adsorption capacity at equilibrium was calculated using the equation below:

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

Where: q_e is the amount of Pb(II) or Co(II) adsorbed per unit mass of the adsorbent (mg/g); C_o is the initial Pb(II) or Co(II) concentration in the solution (mg/L); C_e is the Pb(II) or Co(II) concentration at equilibrium (mg/L); m is the amount of bentonite (g); V is the solution volume (L).

The Pb(II) or Co(II) ions adsorbed at a particular time interval was calculated using the following equation:

$$q_t = \frac{(C_o - C_t)V}{m}$$

Where: q_t is the amount of Pb(II) or Co(II) adsorbed at a certain time (mg/g); C_t is the Pb(II) or Co(II) concentration at a particular time (mg/L).

Adsorption with different initial metal concentrations

The activated clays (using HCl or H_2SO_4) with better adsorption of Pb(II) and Co(II) ions were further used to adsorb Pb(II) and Co(II) ions from solutions containing 30, 50, 70 and 100 ppm of Pb(II) or Co(II) ions. A fixed amount of 0.2 g of clay was added to 50 ml of the adsorptive solutions. The adsorption process was carried out for 2 h while undergoing continues mechanical stirring. The mixture was then centrifuged and the residual metal concentration in the supernatant was determined by ICP analysis.

Adsorption of metals at various contact times

The activated clays (using HCl or H_2SO_4) with better adsorption capacity were used in this set of experiment using solutions containing 50 ppm of metal. A fixed amount of 0.2 g of clay was added to 50 ml of the adsorptive solution. The adsorption process was carried out for 15, 30, 60, 90 and 120 minutes while undergoing continues mechanical stirring. The mixtures were then centrifuged and the residual metal concentration in the supernatant was determined by ICP analysis.

D. Characterization

The bentonite clay was grinded to a powder form and sieved to obtain a particle size <75µm. The mineralogical composition of the clay was determined by X-ray diffraction analysis (XRD); The diffractometer used was a Philips model X'Pert pro MPD, at a power of 1.6 kW used at 40 kV, programmable divergence and anti-scatter slits; primary Soller slits: 0.04 Rad; 2θ range: 4-79.98; step size: 0.017°. The chemical composition of the clay was determined through X-ray fluorescence analysis (XRF); The XRF was used to identify the elements in the clay; it was performed on the MagiX PRO & SuperQ Version 4 (Panalytical, Netherland) with a rhodium (Rh) anode used in the X-ray tube and operated at 50 kV and current 125 mA; at power level of 4 kW. The Fourier Transform Infrared Spectroscopy (FTIR) was used to investigate the structural changes of the clay that has undergone acid activation. The ATR_FTIR (Perkin-Elmer Spectrum 100 spectrometer) was used at a spectral range of 4000-500 cm^{-1} with a resolution of 4 cm^{-1}.

E. Isotherm and kinetic models

Freundlich and Langmuir isotherms were used to determine the adsorption affinity of the bentonite clay for cobalt and lead. The linear expression of the Freundlich model is as follow:

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

Where: q_e is the concentration of metal at equilibrium in solid form (mg/g); C_e is the concentration of metal at equilibrium in the solution (mg/L); k_f is the adsorption capacity measured (mg/g); *n* is the intensity of adsorption.

The linear expression of the Langmuir model is as follow:

$$\frac{C_e}{q_e} = \frac{1}{b q_m} + \frac{C_e}{q_m}$$

Where: C_e is the metal equilibrium constant (mg/L); q_e is the adsorbed metal at equilibrium in (mg/g); q_m is the Langmuir constant associated with adsorption capacity (mg/g); *b* is the Langmuir constant associated with the energy during adsorption (L/mg).

Two adsorption kinetics were used namely pseudo-first and -second order kinetics. The pseudo-first order is expressed by the following equation:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303}$$

Where: q_e is the adsorbed metal at equilibrium (mg/g); q_t is the adsorbed metal at equilibrium at time t (mg/g); k_1 is the rate constant for the first order adsorption (min^{-1}).

The pseudo-second order can be described by the following equation:

$$\frac{t}{q_t} = \frac{1}{k_2 {q_e}^2} + \frac{t}{q_e}$$

Where: q_e is the adsorbed metal at equilibrium (mg/g); q_t is the adsorbed metal at equilibrium at time t (mg/g); k_2 is the rate constant for the second order adsorption ($g/mg.min^{-1}$).

adsorption of Pb(II) by clay. The results obtained are given in Figure 1 (a, b, c, d). The activation conditions in these figures affect differently the adsorption capacity of the clay, however the higher adsorption capacity (q_e = 11.32 mg/g) as exhibited in Figure 1 (a) is obtained following pretreatment of clay with H_2SO_4, while treatment with HCl resulted in better adsorption capacities for most of the activation conditions. Figure 1 (b) shows the influence of the activation time on the capacity of clay to adsorb Pb(II). The shorter activation time of 1 h showed better results than the 6 h activation of the clay. The influence of heat treatment can be observed in Figure 1 (c), the activation at lower temperature of 25°C resulted in much higher adsorption capacities than the activation at 80°C. Figure 1(d) shows the influence of the acid

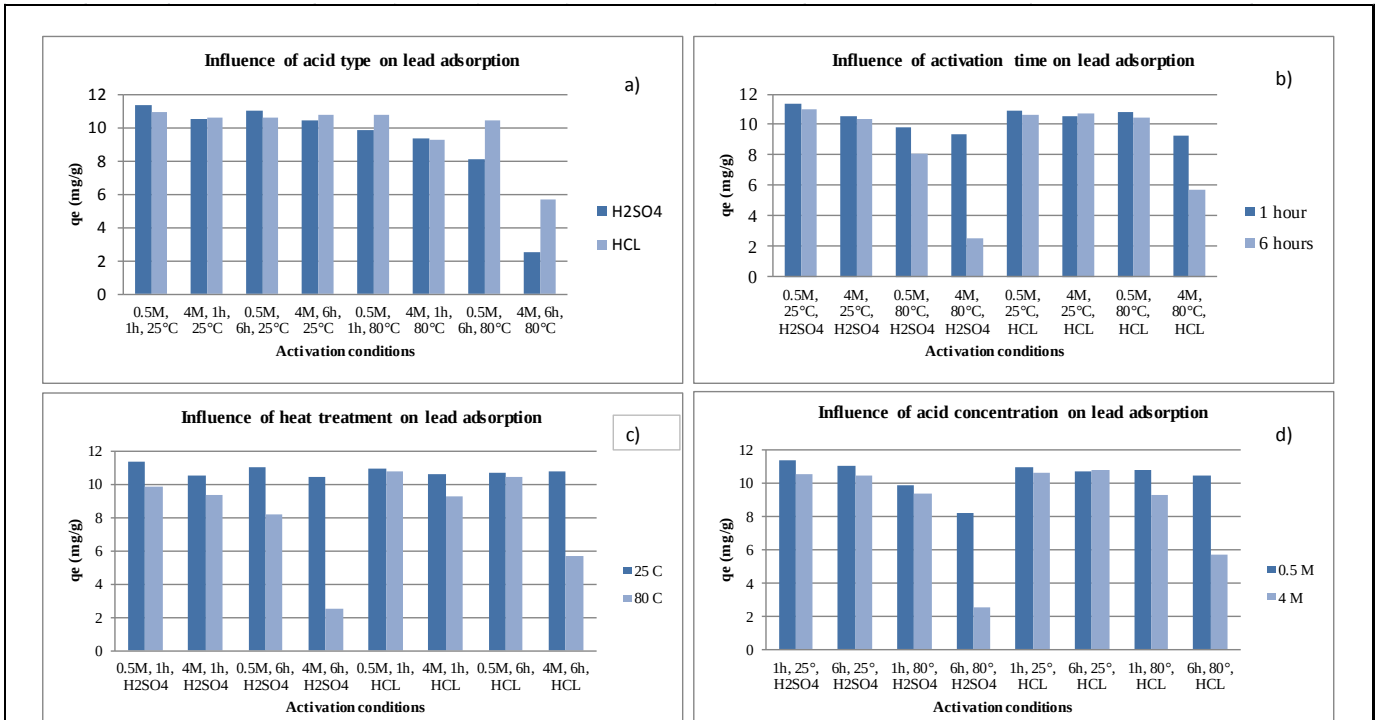

Fig. 1 Clay adsorption capacity under various activation conditions: a) Influence of acid type on Pb(II) adsorption; b) Influence of activation time on Pb(II) adsorption; c) Influence of heat treatment on Pb(II) adsorption; d) Influence of acid concentration on Pb(II) adsorption.

III. Results And Discussion

A. Characterization of the adsorbents

The XRD analysis revealed the mineralogical composition of the bentonite clay, containing mainly quartz, montmorillonite, bentonite and kaolinite. The chemical elements identified by XRF analysis included SiO_2 (62.89%), Al_2O_3 (18.68%) and Fe_2O_3 (10.86%).

B. Effect of activation on the adsorption capacity of clay

Adsorption of lead by activated clay

The bentonite clay was activated under different activation conditions to investigate the influence of the type of acid, acid concentration, activation time and heat treatment on the

The activation did not improve the adsorption capacity of bentonite clay for the removal of Pb(II). The adsorption capacity (q_e) of the non-activated bentonite clay was 11.6 mg/g which is slightly higher than the highest adsorption capacity (q_e = 11.32 mg/g) of the activated clay (0.5 M of H_2SO_4, 25°C, 1 h).

Activated clays cobalt adsorption

Figures 2 (a, b, c, d) exhibit the adsorption of cobalt by the activated clay. From Figure 2 (a), it can be observed that the highest adsorption capacity (6.22 mg/g) was achieved following pretreatment with HCl.

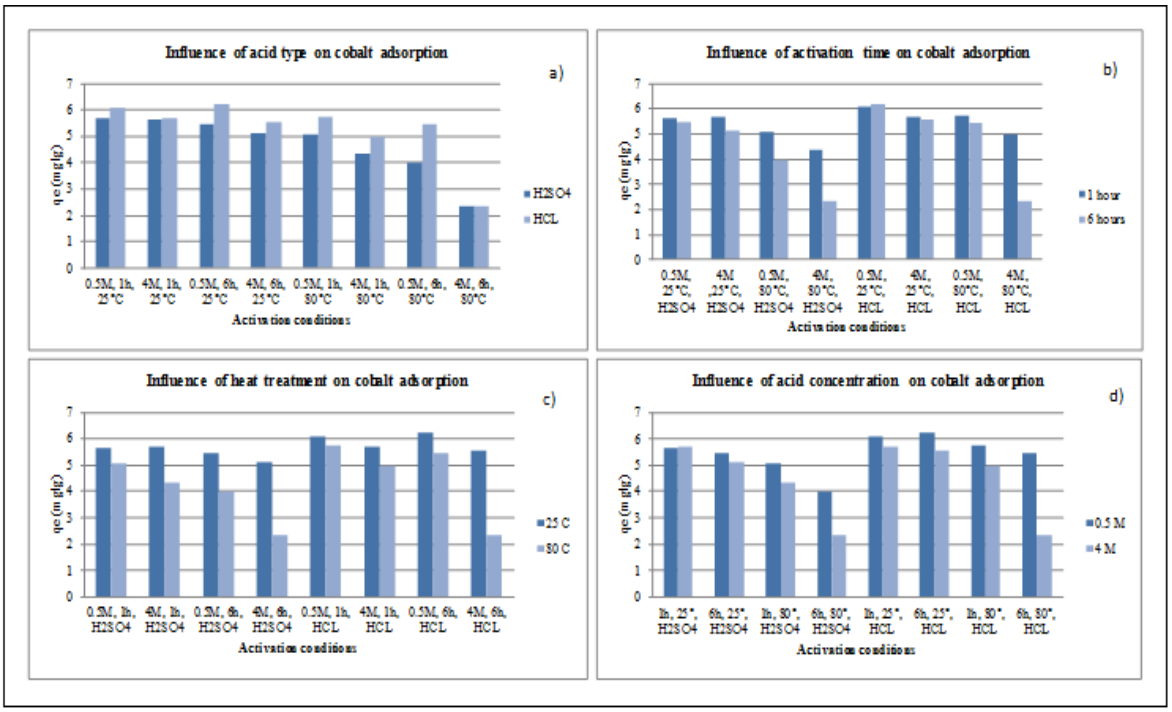

Fig. 2 Activated clays: a) Influence of acid type on Co(II) adsorption; b) Influence of activation time on Co(II) adsorption; c) Influence of heat treatment on Co(II) adsorption; d) Influence of acid concentration on Co(II) adsorption

Figure 2 (b) shows the influence of the activation time on the capacity of clay to adsorpb Co(II). The shorter activation time of 1 h showed better results than the 6 h activation of the clay. The influence of heat treatment can be observed in Figure 2 (c), the lower temperature of 25°C showed much higher adsorption capacities than the activation at 80°C. Figure 2(d) shows the influence of the acid concentration on the adsorption capacities of the clays. The treatment with lower concentration (0.5 M) of acid resulted in much higher adsorption capacities than the activation with the higher acid concentration of 4 M.

The activation of clay in this case improves its adsorption capacity. The non-activated clay showed an adsorption capacity of 4.04 mg/L while the highest adsorption capacity achieved by the activated clay (0.5 M of HCl, 25°C, 1 h) was equal to 6.22 mg/g.

C. Adsorption isotherms models

To study the isotherm models, the adsorption process was carried out at 25°C for 2 h by varying the initial concentrations of Pb(II) and Co(II) in the ranges previously defined.

The adsorption data were fitted on the linearly Langmuir equation. The values of q_m and b were determined from the intercept and the slope of the line obtained by plotting C_e/q_e versus C_e.

The Langmuir plots for the adsorption of Co(II) and Pb(II) are given in Figures 3 (a, b). The calculated values for the adsorption by non-activated and activated clays are given in Table 1. The Figures of the different clays showed similar patterns for both Pb(II) and Co(II). In the case of lead adsorption, the clay activated with HCl showed the best fit as confirmed by the value of the coefficient of determination (R^2) equal to 0.99. For the Co(II) adsorption, the clay activated with H_2SO_4 had the best fit with R^2 equal to 0.944. The plots of the adsorption of Pb(II) and Co(II) on non-activated clay gave relatively low R^2 values equal to 0.916 and 0.741, respectively, indicating that there was no perfect fit with the Langmuir model.

TABLE 1
ISOTHERM PARAMETERS FOR THE ADSORPTION OF PB(II) AND CO(II) ONTO THE CLAYS

Isotherm	Adsorbent	Isotherm constants	Pb(II)	Co(II)
Langmuir	non activated clay	q_m (mg/g)	24.938	NA
		b	0.372	NA
		R^2	0.916	0.741
	HCL best activated	q_m (mg/g)	18.587	11.933
		b	0.161	0.031
		R^2	0.990	0.918
	H_2SO_4 best activated	q_m (mg/g)	19.960	10.672
		b	0.195	0.033
		R^2	0.989	0.944

Freundlich model

The adsorption of Pb(II) by non-activated clay fitted (R^2 equal to 0.944) the Freundlich model; while there was no fit using the clay activated with HCl and H_2SO_4 with the R^2 values equal to 0.86 and 0.87 respectively. The Co(II) adsorption did not fit the Freundlich model when using the non-activated clay, the clay activated with HCl or H_2SO_4, the R^2 values equal to 0.508, 0.881 and 0.895 respectively.

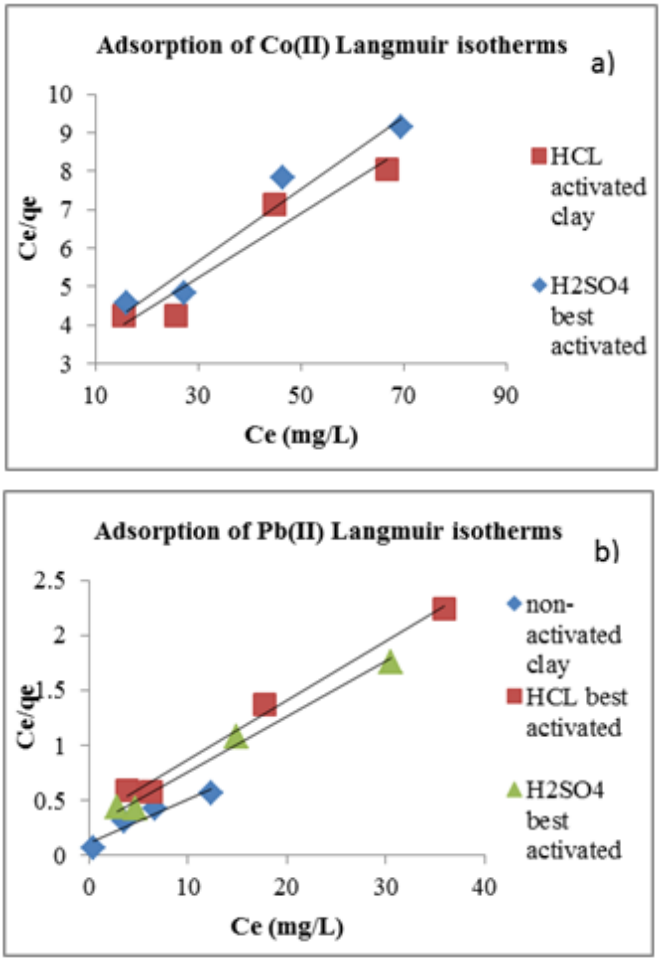

Fig. 3 Langmuir isotherm; a) Adsorption of Co(II); b) Adsorption of Pb(II).

Adsorption affinity

The b value determined from the Langmuir model has been reported to positively correlate to the strength of the binding sites [7]. The b values obtained for the adsorption of Pb(II) was higher than for the adsorption of Co(II) both for clay activated with HCl (Pb(II), 0.161; Co(II), 0.031) and the clay activated with H_2SO_4 (Pb(II), 0.195; Co(II), 0.033); implying that the activated clays had higher affinity for Pb(II) than Co(II). The FTIR analysis was then used to determine the binding groups involved in the adsorption of the two metals; Figure 5 below shows the wavelength shift that may have resulted from the binding of the metal on the clay.

A shift of band can be observed in the zone 1000-1300 as Pb(II) or Co(II) bind to the activated clay; it is therefore likely that the –Co is involved in the binding of both metals. The affinity of the clay for Pb(II) in this case is likely to be dependent on the chemical property of the metal. According to Sag et al. [8], metal ions with higher atomic weight can generate higher momentum energy, which may promote the adsorption of the metal ion by increasing the probability of effective cohesion between the metal ion and the sorbent surface; it therefore ensues that a higher atomic weight leads to higher adsorption preference by the sorbent.

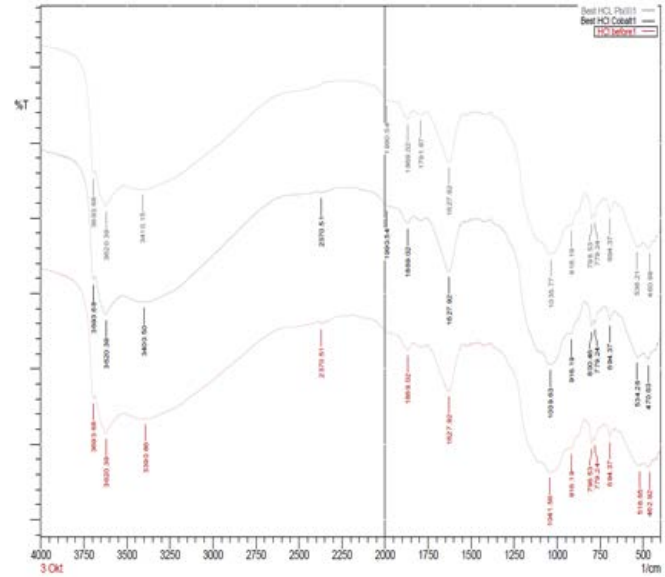

Fig. 4 FTIR analysis of the binding of Pb(II) and Co(II) on non-activated and activated clays

D. Adsorption kinetics model

Pseudo-second order

The pseudo-second order model was applied for the kinetic study of the adsorption of Pb(II) and Co(II) onto the clays. The plot of t/q_t vs t which can be seen in Figures 5 (a, b) showed a good fit for the adsorption of Pb(II) and Co(II) onto the clays as indicated by the R^2 values. The kinetic parameters for the adsorption of Pb(II) and Co(II) onto the three adsorbents are given in Table 2. The R^2 values that were obtained for the Pb(II) adsorption are 0.999 for the non-activated clay as well as for the clay activated with HCl and 0.998 for the clay activated with H_2SO_4. The adsorption capacity of the clay was higher for the removal of Pb(II) than for the removal of Co(II).

TABLE II
KINETIC PARAMETERS FOR THE ADSORPTION OF P(II) AND CO(II) ONTO THE ADSORBENTS

Kinetic model	Adsorbent	Kinetic parameters	Pb(II)	Co(II)
Pseudo second order	non activated clay	k_2	-0.048	-0.032
		q_e (calc)	12.253	5.473
		q_e (exp)	11.587	3.982
		R^2	0.999	0.987
	HCL best activated	k_2	0.030	0.018
		q_e (calc)	11.050	6.075
		q_e (exp)	10.938	6.345
		R^2	0.999	0.992
	H_2SO_4 best activated	k_2	0.023	0.012
		q_e (calc)	11.320	5.675
		q_e (exp)	11.521	6.211
		R^2	0.998	0.995

Irrespective of the type of bentonite clay used, it was also observed that the adsorption capacity calculated from the pseudo-second order kinetic plot was closer to the experimental values and always higher for the adsorption of Pb(II), this confirms the affinity determined using the Langmuir model.

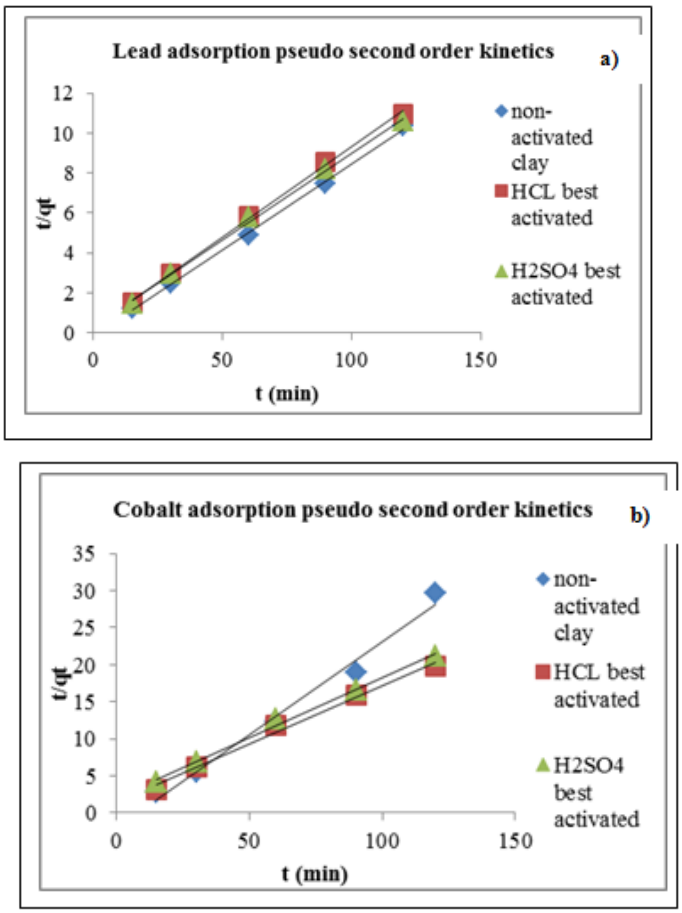

Fig. 5 Pseudo second order kinetics; a) Pb(II) adsorption; b) Co(II) adsorption

IV. Conclusion

The activation of the clay decreased the adsorption capacity of the clay for the removal of Pb(II), but increased the capacity for the adsorption of Co(II). The clay activated with HCl showed the highest adsorption capacity for the removal of Co(II) while the clay activated with H_2SO_4 was better for the removal of Pb(II). The optimum adsorption conditions (0.5 M, 1 h and 25°C) are suitable for cost effective pretreatment of clay and therefore attractive. The adsorption behaviour of the activated clays could be predicted using the Langmuir model while the Freundlich model was suitable for the non-activated clay, implying an homogenous binding on the activated clay and an heterogeneous binding on the non-activated clay; a faster adsorption on the former is therefore expected..

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Dr Elvis Fosso-Kankeu has been the recipient of several merit awards.