**Adsorption of Copper (II), Cobalt (II) and Nickel (II) on Minim-Martap (Cameroon) bauxite: Kinetic and Equilibrium Studies.**

**ABSTRACT**

The influence of different parameters on the kinetics of Cu (II), Co (II) and Ni (II) ions adsorption on Cameroon bauxite was investigated. The bauxite was characterized using X-ray diffraction (XRD), Electric conductivity (EC), and Fourier transform infrared spectroscopy (FTIR) techniques. The influence of particles size, stirring speed, contact time, pH and temperature on the kinetics of the removal process was studied. The experiments results show that Cu (II), Co (II) and Ni (II) were significantly retained at a pH value of 5, 8 and 9 respectively, with corresponding removal efficiency of 97% for Cu (II), 99% for Co (II) and the 98% for Ni (II) 98%. Furthermore, the adsorption increases with decreasing particles size and increasing stiring speed. The Langmuir separation factor SL,shows a more favourable adsorption of the three heavy metals on bauxite The Temkin constant, *BT* , related to the heat of sorption for three metal ions were all less than 8 kJ/mol, indicating a physical removal mechanism. The adsorption of Cu (II) and Ni (II) on bauxite is endothermic while adsorption of Co (II) is exothermic. Cobalt removal was faster with pseudo-second order rate constant K2 (μmol.g1min-1) of0.861 compared to, 0.316 for both Cu (II) and Ni (II), and more favourable as given by the Langmuir equilibrium constant, KL(L/mmol) of 0.032 for cobalt, 0.007 for Nickel and 0.0011 for copper. Results of this study shows that different heavy metals simultaneously present in wastewater can effectively be removed with bauxite, particularly Cameroonian bauxite, a low cost material with over 95% efficiency for each metal.

**Key words:** Adsorption, bauxite, heavy metals, wastewater, Minim-Martap

1. **INTRODUCTION**

Among the pollutants largely research do to their certified toxicity, we can mention heavy metals or trace metallic element (TME) (Al, As, Cd, Cr, Co, Cu, Pb, Mn, Hg, Ni and Zn), the target organs are nervous system, marrow born, and other organs. The differents industrials wastes, the mining concentrator and sterile mining can be an important source of by heavy metals pollution do to the mining acid drainage (MAD). These mining pollutants naturally exist in the terrestrial crust, in more than their adjunction in different human activities as for example the combustion of coal and the petroleum, metallurgy, tannery, chemical fertilizers, insecticides, fungicides, etc.

 Environmental pollution can be natural, urban, agricultural or industrial origin. Previous work had showed that the mining exploitation waste are source of environmental pollution. In Cameroon among these waste, it has been notice that Cu (II), Co (II) and Ni (II) are toxics. Cu (II) is primarily used as a metal or alloy and is also present in fungicides and algaecides. It creates stress in the gastrointestinal and respiratory tracts. Excessive levels of Cu (II) may damage liver and kidney, and may be responsible for anaemia, immunotoxicity, and developmental toxicity. The co-carcinogenic character of Cu (II) is implicated in stomach and lung cancer (Moumin, 2022), Cu (II) can also cause a Wilson disease. An exposition to Co (II) can induce pulmonary affections, can caused nausea, vomiting and serious cardiac affections, Co (II) can be carcinogenic possible for it caused cancer when it’s introduce in one muscle under the skin (Krisna and Susmita, 2011). The World Health Organization has determined that drinking water should not contain more than 2 mg.L-1 of Cu (II), 1 mg.L-1 of Co (II) and 0,02 of Ni (II) (WHO,2017). It is then necessary to depollute effluents before throwing them out in the nature. In order to solve the problems of heavy metal pollution in the environmental, it is important to bring pragmatic solution to the issue.

 There are several methods for treatment of metals contaminated effluents such

as chemicals precipitation, filtration, reverse osmosis, ultrafiltration, electro-dialysis, coagulation flocculation and adsorption has been used to remove toxic metals in aquatic environment (Shahmohammadi and *al.*, 2011:Ghomri and *al.*, 2013; Tsamo and *al.*, 2018). However these methods are more appropriate in situation where heavy metals concentration are relatively high. They are sometimes high ineffective, or sometimes at high cost in situation where the heavy metal present in waste water are in low concentration (Khelifi, 2018).Adsorption with bauxite has been found to be effective for the elimination of Cu (II), Co (II) and Ni (II).

The principal adsorbants are: the active charcoal (Senthil and *al.*, 2009;Ouakou and Youssef, 2016), show high cost of production and regeneration, pure synthetics oxides such as the alumina and the silica gel (Minmane and *al.,* 2014) also show high cost of production, natural oxides such as clays, zeolites and bauxites (Marzouk, 2013;Tsamo and *al*, 2018; Moumin and *al,*2022). The clays and zeolites had made up of many studies, it exist a few works using bauxite as adsorbent for the elimination of heavy metals.

The adjustment of industrial process require to know kinetics and thermodynamics parameters and to predict if the reaction will be chemical or physical order. Some work on adsorption of only one cation by metallic oxides shows that kinetic is generally of the second order and adsorption is physical nature (Ghomri and *al.*, 2013; Senthil and *al.*,2009). The objectif of this study is the evaluation of kinetic and therdynamic adsorption of Cu (II), Co (II) and Ni (II) adsorption on Minim-Martap bauxite and their isotherms.

1. **MATERIAL AND METHODS**

**2.1 Sampling**

 Bauxite used in this work was collected at Tchabal Haleo (Minim-Martap) (Fig.1) with coordinates 06° 53' 14'' N and 12° 57'55'' E at 12m 74 altitude. The collection was done in boreholes dug during the bauxite exploration phase (Taylor and *al.*, 2018). Collected bauxite was crushed and grounded to fine powder particles. This is to increase the material’s surface area thereby, improving mineral extractability and increases Bayer process efficiency. The crushed bauxite was washed with distilled water to remove undesirable material such as residual clays, which have a deleterious effect on the efficiency of the Bayer process. The washed sample was then dried at 100 °C for 24 hours and used for characterization study and extraction of alumina. The bauxite was dried and sieve to obtain fraction of 50 μm, 100 μm and 500 μm.



**Fig. 1. Sampling area**

**2.2 Characterization of adsorbent**

The quantitative elemental composition (expressed as oxide) was determined by X-ray fluorescence (XRF). The FTIR spectroscopy using an Alpha-P IR spectrophotometer model of Bruker Company was used to identify surface functional groups. The resulting absorption bands were attributed respective functional groups by comparing them with those of bauxite samples and other functional groups reported in the literature. The point of zero charge PZC of bauxite particles was determined by acid-base titration (using 0,1 mol.L-1 of HCl and 0,1 mol.L-1 of NaOH)

* 1. **Adsorbents preparation**

─ The solution of cobalt of analytical type (CoSO4.7H2O) at 1 mmol/L has been prepare by dissolving 0.01405 g of hydrated cobalt with molar mass of 0. 281 g/mmol in 50 mL of distilled water at room temperature. The obtain solution was kept in a glass flask. This solution was used to prepare diluted solution of 0.2 mmol.L-1.

─ The solution of copper of analytical type (CuSO4.5H2O) at 1 mmol/L has been prepare by dissolving 0.0125 g of hydrated copper with molar mass of 0.250 g/mmol in 50 mL of distilled water at room temperature. The obtain solution was kept in a glass flask. This solution was used to prepare diluted solution of 0.2mmol.L-1.

─ The solution of nickel of analytical type (NiSO4.8H2O) 1 mmol/L has been prepare by dissolving 0.01404 g of hydrate nickel with molar mass of 0.299 g/mmol in

50 mL of distilled water at room temperature. The obtain solution was kept in a glass flask. This solution was used to prepare diluted solution of 0.2 mmolL-1.

* 1. **Batch Adsorption Studies**

 Adsorption experiments were allowed to take place in 250 mL stoppered Erlenmeyer flasks with 100 mL working solution. The contents of the flasks where uniformly mixed by a Thermostated bath shaker at 600 spm and at desired concentration pH and temperature. Effects of particles size, pH, temperature, agitation speed and initial concentration of adsorbate on the kinetics of adsorption were evaluated. pH adjustment was done using 0.1M HCl and 0.1M NaOH solution. Samples of the mixture were taken at predetermined intervals and then filtered through a Whatman N° 1 filter paper. The residual amount of Cu (II), Co (II) and Ni (II) in the filtrate was determined using a UV-Visible spectrophotometer (Spectroquant Pharo 100 M) at wave lengths of 699, 515 and 407 nm of Cu (II), Co (II) and Ni (II) respectively (color developed using their respective complexing agents). Analytical grade chemicals and reagents were used throughout the study.

 The amount of Cu (II), Co (II) and Ni (II) adsorbed at time ‘’t’’and percentage removal of copper and cobalt were computed (Tsamo and *al*., 2018) according to the following equations:

***Q ad = (*** $\frac{C\_{0}-C\_{t}}{m}$***) x V*** (1)

 Where Q ad is the adsorption capacity at time ‘’t’’ mmol/g), C0 is the initial heavy metal concentration (mmol/L), Ct is the heavy metal concentration (mmol/L) at time t ‘’m’’ is the adsorbent weight (g) and V is the volume of the heavy metal solution (L). Percentage removal of heavy metal was calculated as:

***Q ad (%) = (*** $\frac{C\_{0}-C\_{e}}{C\_{0}}$***) x 100*** (2)

1. **RESULTS AND DISCUSSION**

**3.1 Physicochemical Characteristics**

The chemical composition of bauxite (Table 1) show that the bauxite is mainly constituted by aluminium oxides (48.87 %) showing the abundance of alumina Al2O3 follow by the iron oxide (16.77 %) which is responsible of the red colour of the samples,

**Table 1: Chemical composition of the bauxite sample**

|  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Minerals** | **Al2O3** | **Fe2O3** | **SiO2** | **CaO** | **K2O** | **Na2O** | **SO3** | **TiO2** | **Mn203** | **P2O5** | **PF** |
| **Composition** | 48.9 | 16.77 | 2.47 | 0.81 | 0.15 | 6.29 | 3.08 | 1.85 | 0.02 | 0,22 | 17.73 |

There is also oxides of Sodium (NaO2) 6.29 %, silicon SiO2 2.47 %, titanium 1.85 %.TiO2 and sulphur 3.08%, other oxides are consider as negligible with amount less than 1%.

The X-ray diffraction of the bauxite (Fig 2) is constituted principally of two types of kaolin Al2Si2O5(OH)4 (83.24%) and H4Al2Si2O9 (42.47%), mullite 67.32% and 83.92 % of gibbsite.

**Fig. 2. XRD patterns of Minim-Martap bauxite**

The FTIR spectra of bauxite is presented at Fig 3 and bands attributions in Table 2.



**Fig 3. IRTF spectra of bauxite**

**Table 2: Attribution of bands of vibration**

|  |  |  |  |
| --- | --- | --- | --- |
| **Type of Frequencies**   | **Observe values (cm-1)** | **Attributions**  | **References** |
| Stretching vibrations  | 3838.56 | Al–OH | [15] |
| 3735.5 |   |   |   |
| 3690.57 | Si–OH | [16] |
| 3648.79 |   |   |   |
| 3525.12 | O–H, H–O–H |  [5;16]  |
| 3447.29 |   |   |   |
| 3373.99 |   |   |   |
| Bending Vibration | 1010.48 | Si–O–Si | [5;16] |
| 965.75 |   |   |   |
| 913.01 |   |   |   |
| 792.12 | Si–O–Al | [16] |
| Stretching vibrations | 742.96 |   |   |   |
| 515.18 | Fe–O | [5] |
| 467.36 |   |   |   |
| 442.62 |   |   |   |
| 417.74 |   |   |   |

**3.2 Effects of particles size**

The effects of the particle on the kinetic adsorption of Cu (II), Co (II) and Ni (II) was

evaluated for the particles of size less than 50, 100 et 500 µm (Fig 4).

  

(b)

(a)



(c)

**Fig. 4. Effect of particles size on adsorption of Cu (II) (a), Co (II) (b)and (c) Ni (II). Conditions: C0 = 0.2 mmol/l, v = 600tr/min, T= 35°C, pH = 7.**

 the adsorption of particles of size <50 μm is about 92 % ,those size < 100 μm is about 70% and those of 500 μm about 60% for the three heavy metals. Particles size does not influence the equilibrium time, however the adsorbed quantity of Cu (II), Co (II) and Ni (II) decrease when the particles size increase. This is do to the fact that the specific surface of particles increase when their size decrease. Therefore for small particles the surface of contact between molecules is higher which induce one more high number of adsorption accessibles sites (Messouaf, 2017).

**3.3 Effect of pH**

 The pH of the solution is an important factor in the adsorption process

because its affect charge of the adsorbent surface and the degree of ionization and the specification of the adsorbate (Tsamo and *al*., 2018). The adsorption capacity of Cu (II), Co (II) and Ni (II) was evaluated for pH range from 5 to 8 (Fig 5)

 

(b)

(a)



(c)

**Fig. 5. Effect of pH on adsorption of Cu (II) (a), Co (II) (b) and Ni (II) (c)** **Conditions : C0 = 0.2 mmol/l, v = 600tr/min, T= 35°C, d < 50µm.**

The quantities of Cu (II) adsorbed decrease between pH = 5 and pH = 8, passing by 99% at pH = 5 to 95% at pH = 6 and reach 80% at pH =8, the maximum of adsorption of Cu (II) on bauxite appear at pH of 5 do to the speciation of metal. Similar observation has been reported by Krishna and *al.*, (2011) for the adsorption of Cu (II) on natural and activated clays. According to these authors, Cu (II) may be adsorbed as Cu2+, Cu(OH)+ and $Cu\_{2}(OH)\_{2}^{2+}$ at pH close to or < 5.1 Similar results were also reported by other authors (Arzu and Mehmet, 2006; Sana and *al.,* 2011).Eliot and Huang (Elimbi and *al.,* 2018) showed that the dominant species of copper at pH 3.0-5.0 were Cu2+ and Cu(OH)+, while at pH > 6.3 the species were insoluble Cu(OH)2.

For a fixed amount of bauxite, adsorption is not only dependent on initial Co (II) and Ni (II) concentration, but is also influenced by pH of the aqueous solution range of 1.0 to 8.0 (Krisna and *al.*, 2011). However, the experiments could not be carried out beyond pH 8.0 as the solubility of Co (II) rapidly decreases resulting in separation by precipitation. So between pH = 5 to pH = 8 we note that the quantity of Co (II) and Ni (II) adsorbed increase passing to 60 % at pH 5 to 80 % at pH 8.

**3.3 Effect of the temperature**

 The study of the influence of the temperature on the kinetic of adsorption of Cu (II), Co (II) and Ni (II) on the bauxite was investigated for the temperatures of 25 °C, 35 °C and 45 °C respectively and under the optimized conditions for each metals and adsorbent (Fig. 6).

 

(b)

(a)



(c)

**Fig. 6: Effect of the temperature on adsorption of Cu (II) (a), Co (II) (b)****and Ni (II) (c), Conditions: C0 = 0.2 mmol/L, v = 600tr/min, pH = 7, d< 50 μm.**

The adsorption data at different temperatures indicated that there are significant changes in the metal adsorption. When the temperature of the solution raised from 25 °C to 45 °C, the Cu2+, Co2+ and Ni2+ adsorption yield onto bauxite increase from 70 %, 65 % and 72 %, to 99 %, 95 % and 99.7% at the end of contact period of 60 min, respectively for the three heavy metals. Each raise of 10 °C in the temperature shortens the equilibrium time required about 40 min. Similar results were found by Arzu and Mehmet (2006) who have investigated copper, cadmium and lead adsorption onto pyrite and sulphide. In addition Sana and *al*. (2011) had reported that adsorption of Cu (II), Cd (II) and Pb (II) onto Triticum aestivum increases with the increasing temperature. Consequently, it can be concluded that the adsorption of Cu2+, Co2+ and Ni2+ ions onto bauxite is endothermic. In addition, the increases in metal adsorption by the increasing temperature suggest that the mechanism governing the adsorption process may be chemical origin.

**3.4 Effect of stirring rate**

 The influence of stirring rate is used as important factor in this process. In fact, it contribute to the distribution to the adsorbate in adsorbent and the determination of the maximal adsorbed quantity (Chouchane and *al.*, 2016). The stirring rate on adsorption of Cu (II), Co (II) and Ni (II) was evaluated for the stirring rate of 300 spm, 600 spm and 1000 spm (Fig 7).

 

(a)

(b)



(c)

**Fig. 7. Effect of the agitation on adsorption of Cu (II) (a), Co (II) (b) and Ni (II) (c).** **Conditions: C0 = 0.2 mmol/L, pH = 7, T=35°C, d< 50µm.**

Optimum of stirring for Cu (II), Co (II) and Ni (II) was found to be at 600 spm with the percentage of 70% for Cu (II), 85% for Co (II) and 56 % for Ni (II) , while this value fall to 45%, 60% and 37% for Cu (II), Co (II) and Ni (II) respectively at 1000 rpm. It is because at very slow stirring rate the adsorbent accumulates at the bottom reducing the contact surface area of the adsorbent with the adsorbate. Also at very high speed, centrifugal forces operate resulting in desorption of the adsorbate (Sana and *al.*, 2011). This observation suggest that the interaction between bauxite and metal molecules is insufficient at lower stirring rate constraining the solid-liquid mass transfer of Cu (II), Co (II) and Ni (II) on the bauxite. Stirring rate surpassing 600 rpm yielded marginal increments in Cu (II), Co (II) and Ni (II) removal efficiency, indicating of the reaction gradually approach the equilibrium.

Similar results was also reported by Xuying and *al.*, (2024) on the adsorption of Zn (II) and Cu (II) in acid mine drainage by fly ash loaded nano-FeS. Consequently, considerating all factors, a stirring rate of 600 rpm was chosen for subsequent experiments.

**3.5 Effect of the initial concentration**

 The initial concentration of the pollutant can have an important influence on the capacity of retention of solid support. In the aim of study the fact of initial concentration following values 0.2, 0.8 and 1.6 mmol/L has been considered. The results are presented on the Fig 8. The results show that the increasing of the Cu (II), Co (II) and Ni (II) concentration tend to increase the capacity of adsorption of heavy metals. In the beginning of the experiment, Cu (II), Co (II) and Ni (II) fixed in the actif sites of the bauxite till the complete saturation (stage of saturation). The high concentration of Cu (II) permit to increase the transfer of the mass of the metal toward the actives sites of adsorbent which increase by follow the motive force of gradient of concentration. This phenomenon influence the capacity of the adsorption.

It has been noted that the presence of the actifs groups as OH and AlO‒ onthe bauxite sites. These groups attack directly the positive charges of the metals which have as consequence the formation of the complex (Tamari, 2021).

 

(b)

(a)



(c)

**Fig. 8. Effect of initial concentration on adsorption of Cu (II) (a), Co (II) (b) and Ni (II) (c) on bauxite****. Conditions : T = 35 °C, Va = 600 spm, pH = 7, d< 50µm.**

**3.5 Adsorption Kinetics**

Adsorption kinetics studies to determine the efficiency of adsorption. Pseudo-first-order, pseudo-second-order and intraparticle diffusion models have been

Widely used to study the rate-limiting step of the adsorption process. The Pseudo-first-order kinetic model in its linearized form is given by the Largergren equation as

**Ln (*qe ‒ qt*) = ln*qe* ‒*k1t*** (3)

Where *qt* is adsorption capacity *(mmol.g-1)* at time *t (min), qe* is the equilibriumadsorption capacity *(mmol.g-1)* and *k1* is the pseudo-first-order equilibrium rateconstant *(min-1).*

The linear regression of Ln (*qe ‒ qt*) in function of t give R2 of 0.76 and 0.49 respectively for the adsorption kinetics of Cu (II), Co (II) and Ni (II). Consequently, calculated qe values did not match with the experimental values thus, indicating unsuitabililty of this model compared to other models. Similar finding concerning psedo-first-order modelling of adsorption on bauxite were reported by Arsu and Mehmet, (2006).

 

(b)

(a)

**Fig. 9. Second order (a) and intraparticle models (b)**

The pseudo-second-order kinetic model expression is as follows:

$\frac{t}{qt}=\frac{1}{k\_{2}q\_{e}^{2}}+\frac{t}{q\_{e}}$(4)

Where *K2*(g.*mmol-1.min-1)* is the pseudo-second-order constant. The second-order rate constant, computed and experimental *qe* and correlated coefficient values from second order plots of different parameters for kinetics of adsorption of Cu (II), Co (II) and Ni (II) on bauxite given in Table 3 (Fig 9). The experimental and calculated values were well correlated and R2 values were above 98% for the three heavy metals. The reaction speed out in two stapes the first one is the diffusion of the particles to surface and the second the surface reaction.

**Table 3. Parameters of pseudo second order model and intraparticle diffusion**

|  |  |  |
| --- | --- | --- |
|  | **2ème ordre** | **Diffusion intraparticulaire** |
| **R2** | **K2** | **R2** | **kint**  | **C** | **D** |
| **(mmol.g1min-1)** | **(mmol.g-1min-0.5)** | **(mmol.g-1)** | **(cm2/s)** |
| **Cu**(II) | 0.989 | 0.316 | 0.98 | 0.096 | 1.12 | 1.87.10-8 |
| **Co**(II) | 0.998 | 0.861 |  0.93 | 0.001 | 0.035 | 1.87.10-8 |
| **Ni**(II) | 0.999 | 0.316 | 0.92 | 0.026 | 0.91 | 1.08.10-9 |

The transfer of solute is generally characterised either by step external mass transfer or intraparticle diffusion or the two them. To study the existence of the intraparticle diffusion during the adsorption, the most equation used is the given by Weber and Moris (1963)

***qt = kd.t0.5 + C***(5)

where *kd* (*mmol/g min1/2*) is the diffusion rate constant and *C* (*mmol/g*) represents the thickness of the boundary layer. Fig 9 show the linear form of the second order and the intraparticle models (Table 1).

When the intraparticle diffusion is the only step of limitation of the speed in the entire adsorption process, then the curve qt in function of t1/2 pass through the origin (Deng and Shin, 2015). In our case the lines coming from the function Q ad = f (t1/2) on the Fig 7 does not pass through the origin, which show that the diffusion of Cu (II), Co (II) and Ni (II) in the pores is not the only mechanism that limitate the kinetic of the sorption, hence this model does not describe the adsorption of these metals on bauxite sample used.

**3.6 Adsorption Isotherms**

 The study of the equilibrium adsorption isotherms (Fig 10) is fundamental in

the determination of adsorption capacity and the nature of adsorbate‒adsorbent interactions (Saravanan and Suda, 2014).



**Fig. 10. Adsorption Isotherms of Cu (II), Co (II) and Ni (II) on bauxite**

Adsorption isotherms are mathematical model that describe the distribution of the adsorbate specie among liquid and solid phases, based on a set of assumptions that are related to the heterogeneity/homogeneity of the solid surface, the type of coverage, and the possibility of interaction between the adsorbate specie (Shahmohammadi and *al*., 2011). In this study, equilibrium data were analyzed using the Freundlich, Langmuir and Temkin isotherms expression Table 2..

**3.6.1 Freundlich model**

 The Freundlich (1906) equation is an empirical equation based on adsorption on a heterogeneous surface. The equation is commonly represented as:

$Lnq\_{e}=LnK\_{F}+\frac{1}{n}LnC\_{e}$(6)

Where *Ce* (*mmol/L*) is the equilibrium concentration and qe (mmol/g) is the amount adsorbed metal ion per unit mass of the adsorbent. The constant n is the Freundlich equation exponent that represents the parameter characterizing quasi-Gaussian energetic heterogeneity of adsorption surface (Basal and Goyal, 2005). KF (L/mmol) is the Freundlich constant indicative of the relative adsorption capacity of the adsorbent. The Freundlich exponent, n, should have values lying in the range of 1 to 10 for classification as favorable adsorption (Chantawong and *al.*, 2003). The Freundlich model was chosen to estimate the adsorption intensity of the sorbate on the sorbent surface. The experimental data from the from the batch sorption study of the metal ions on bauxite were plotted logarithmically (Fig. 11) using the linear Freundlich isotherm equation.

 The linear Freundlich isotherm constants for Cu (II), Co (II) and Ni (II) on bauxite are presented in table II. The Freundlich isotherm parameter 1/n measures the adsorption intensity of metal ions on the bauxite. The high 1/n value of Cu (II) (0.92) Co (1.06) and NI (II) (1.78), indicating the preferential sorption of Co (II) than Cu (II) and Ni (II) than Co (II) probably due to smaller ionic radius and secondly shows the ability of the bauxite to remove the three metal ions from solution even at high concentrations. The ultimate adsorption capacity *KF*, of the adsorbent was calculated from the isothermal linear regression equation. The *KF* value of NI (II) (0.8) is grater than that of Cu (II) (0,58 L/g) and Co (II) (0,41 L/g) suggesting and confirming that NI (II) has greater adsorption tendency towards the bauxite than the Cu (II) and Co (II). **3.6.2 .Langmuir model**

The Langmuir (Langmuir 1918) model assumes that uptake of metal ions occurs

on a homogenous surface by monolayer adsorption without any interaction between adsorbed ions. The Langmuir equation may be written as:

$q\_{e}=\frac{q\_{m}K\_{L}C\_{e}}{1+K\_{L}C\_{e}}$(7)

Eq (8) can be expressed in its linear form as:

$\frac{C\_{e}}{q\_{e}}=\frac{C\_{e}}{q\_{m}}+\frac{1}{K\_{L}q\_{m}}$(8)

Where *qe* is the amount of heavy metal adsorbed (*mmol/*g), *Ce* is the equilibrium concentration of the metal ion (*mmol/L*), *qm* represent the maximum amount of adsorbed metal ion per unit per unit mass of sorbent corresponding to complete coverage of the adsorptive sites (*mmol/g*), *KL* is the Langmuir constant related to energy of adsorption (*L/mmol*).

 The Langmuir isotherm model was chosen for the estimation of maximum adsorption capacity corresponding to complete monolayer coverage on the bauxite surface. The plot of specific sorption (*Ce/qe*) against the equilibrium concentration (*Ce*) for Cu (II), Co (II) and Ni (II) are shown Fig. 9 and the linear isotherm parameter, *qm*, *KL*, and the coefficient of determination are presented in table II. The sorption capacity, qm, which is a measure of the maximum of sorption capacity corresponding to complete monolayer coverage showed that the bauxite had the mass capacity for Cu (II) (0.25 mmol/g) more than Co (II) (0.04 mmol/g) and Ni (II) (0.03). The adsorption coefficient, *KL* that is related to the apparent energy of sorption for Ni (II) (0.070 L/mmol) than Cu (II) (1.1.10-3 L/mmol) and Co (II) (-3.2.10-3 L/mmol) The data in table 4 (Fig 11) further indicated that, the effectiveness of bauxite in sorption of the three heavy metals from an aqueous system was Cu (II) > Co (II) > Ni (II). This preferential sorption behaviour could be explained in terms of ionic radii of metal ions (Cu (II) = 74.5 pm, Co (II) = 73 pm and Ni (II) = 69 pm). The element with larger ionic radius will compete faster for exchange sites than those of smaller ionic radius.

 



**Fig. 11. Lineary forms of isotherms of Langmuir (a), Freundlich (b) et Temkin (c)**

Furthemore favorability of adsorption of the three metal ions on the bauxite was tested using the essential features of the Langmuir isotherm model, expressed in terms of a dimensionless constant called separation factor *SF*, which is defined by the following relationship:

***SF = 1/(1 + KLC0)*** (9)

Where *KL* (L/mmol) is Langmuir isotherm constant and *C0* is initial metal ion concentration. The *SF* value for the adsorption of Cu (II), Co (II) and Ni (II) on bauxite at initial concentration of 20 mmol/L (lowest concentration studied) and 600 mmol/L (highest concentration studied) are listed in Table 4. The separation parameter for the three metals are near to the unity which indicates the favorable adsorption of heavy metals for bauxite. However, *SF* value of Cu (II) > Co (II) = Ni (II) indicates that in a mixed metal ion system, Cu (II) will compete for binding sites faster than Co (II) and Ni (II).

**3.6.3 Temkin model**

The Temkin isotherm equation assumes that the heat of adsorption of all the molecules in layer decreases linearly with coverage due to adsorbent-adsorbate interactions, and that the adsorption is characterized by a uniform distribution of the bonding energy (Temkin, 1940). The Temkin isotherm is represented by the following equation:

$q\_{e}=\frac{RT}{b}Ln (K\_{T}C\_{e})$(10)

Equation (10) can be expressed in ist linear form as:

$q\_{e}=B\_{T}LnK\_{T}+B\_{T}LnC\_{e}$(11)

Where, T is the absolute temperature (K), R is the universal gas constant (8.314 J/mol.K), *KT* is the equilibrium binding constant (L/mmol), *bT* is the variation of adsorption energy (kJ/mol). *BT* is Temkin constant related to the heat of adsorption (kJ/mol).

 The Temkin adsorption isotherm model was chosen to evaluate the adsorption potentials of the adsorbent for adsorbates.

The Temkin isotherm plot for the three metal ions are presented in Fig. 11 and the isotherm parameters is given in Table 4.

The Temkin adsorption potential, *KT*, of bauxite for Cu (II), Co (II) and Ni (II) are 0.037, 0.035 and 0.090 L/mmol respectively indicating bauxite-metal ion indicating that the equilibrium of adsorption of Ni (II) is better than that of Cu (II) and Co (II). The Temkin *BT,* related to the heat of sorption for the three metal ions were 0.042, 0.038 and 0.005 kJ/mol. It has been reported by Ho and *al*. (1996), that the typical range of bonding energy for ion-exchange

mechanism is 8-16 kJ/mol. The low values in this study indicates a weak interaction between adsorbent and adsorbate, supporting that it is not ions exchange mechanism in the present study. There is different sites but distributed in the homogenous manner in the surface of adsorbent.

**Table 4 : isotherm parameters of Langmuir, Freundlich et Temkin**

|  |  |  |  |
| --- | --- | --- | --- |
|  | **Langmuir** | **Freundlich** | **Temkin** |
| **Cations** | **R2** | **KL****(L/mmol)** | **qm****(mmol/g)** | **SL** | **R2** | **n (g/L)** | **Kf** | **R2** | **KT****(L/mmol)** | **B****(kJ/mol)** |
| Cu (II) | 0.97 | 0.0011 | 0.25 | 0,99 | 0.96 | 1.09 | 0.58 | 0.90 | 0.037 | 0.042 |
| Co (II) | 0.94 | -0.032 | 0.04 | 1,01 | 0.91 | 0.94 | 0.41 | 0.90 | 0.035 | 0.038 |
| Ni (II) | 0.94 | 0.007 | 0.03 | 0.99 | 0.96 | 1.78 | 0.79 | 0.98 | 0.09 | 0.005 |

**3.7 Adsorption thermodynamics parameters**

 Thermodynamic parameters like change in free energy (∆G°), enthalpy (∆H°) andentropy (∆S°) were studied to investigate the nature of the process and the parameters were evaluated using the equations:

**∆G° = ‒ RT lnKD**(12)

**Ln KD = ∆S°/R ‒ ∆H°/RT** (13)

Where *R* is the universal gaz constant (8.314 J. mol-1 K-1), *T* is the temperature of the medium (K), and *KD* is the distribution coefficient, obtained from equation:

***KD = qe/Ce***(14)



**Fig. 12. The Van’t Hoff plot of 1/T Vs lnKc**

The table 5 presents the thermodynamic parameters related to Fig12.

 **Table 5: Thermodynamic parameters of adsorption of heavy metals**

|  |  |  |  |
| --- | --- | --- | --- |
|  | **∆G° (kJ/mol)** | **∆H° (kJ/mol)** | **∆S° (kJ/mol)** |
| **Metals** | **298 K** | **308 K** | **318 K** |
| Cu (II) | 6,16 | 6,58 | 6,85 | 4,15 | 0,08 |
| Co (II) | 5,93 | 4,00 | 6,54 | -3,12 | 0,03 |
| Ni (II) | 6,75 | 8,23 | 9,17 | 31,05 | 0,07 |

The interaction of adsorbent with adsorbate can be grouped into two using the magnitude of enthalpy: chemical adsorption and physical adsorption. The enthalpy value of physical adsorption is < 40 kJ.mol-1 (Sun and Wang, 2010). The enthalpy values of adsorption of Cu (II), Co (II) and Ni (II) on bauxite match the physical adsorption. (∆H°) has positive value for the adsorption of Cu (II) and Ni (II) onto the bauxite which signified that the adsorption of Cu (II) and Ni (II) is endothermic while its value is negative for adsorption of Co (II) which shows that the adsorption of Co (II) onto bauxite is exothermic. Increased randomness at the solid-solution interface during the adsorption of metal ions was shown by the positive values of ∆S° which reflected the affinity bauxite for Cu (II), Co (II) and Ni (II) ions.

1. **CONCLUSION**

The characterization of the BMM by XRF showed the presence of alumina (Al2O3) 48.87 %, the oxides of iron (Fe2O3) 16.77 %, Sodium (NaO2) 6.29 % silicon SiO2 2.47 % and titanium 1.85 %.The kinetic study shows that particles with size less than 50µm, had the best adsorption results for the three heavy metals than those with size of 100µm and 500 µm. The quantity of the metal adsorbed by bauxite increased with agitation speed till 600 tr/min, and decrease on higher speed (1000tr/min). The adsorption of Cu (II) onto bauxite increased between pH 3 and pH 5 then decreased at pH, while adsorption of Ni (II) and Co (II) increase between pH 3 and pH 8. When the temperature of the solution is raised from 25 °C to 45 °C, the Cu2+, Co2+ and Ni2+ adsorption yield onto bauxite increase from 70 %, 65 % and 72 %, to 99 %, 95 % and 99.7% at the end of contact period of 60 min, respectively for the three heavy metals. The results show that the increasing of the Cu (II), Co (II) and Ni (II) concentration tend to increase the capacity of adsorption of heavy metals which pass from 0.9 to 17.3; 1.9 to 19.3 and 0.6 to 10.1 for Cu (II), Co (II) and Ni (II) respectively. The isotherms obtained for the three heavy metals followed the Langmuir, Freundlich and Temkin models. The separation parameter *SF* value of Co (II) (1.00) > Cu (II) (0.99) and Ni (II) (0.99) indicates that in a mixed metal ion system, Cu (II) and Ni (II) will compete for binding sites faster than Co (II).The results obtained through application of the first, second order and intraparticle models for the adsorption of Cu (II), Co II) and Ni (II)on bauxite follow the linear variation given by the pseudo-second order and intraparticle kinetics equation. The study on the behaviour of the three heavy metals in solution revealed that, Cu (II) ions are more adsorbed than Co (II) and Ni (II) with 0.25; 0.04 and 0.03 mmol/g respectively for the three heavymetals the sepation factor *SL*show the favorable adsorption of the three heavy metals on bauxite The Temkin constant, *BT* , related to the heat of sorption for three metal ions were 0.042; 0.038 and 0.004 kJ/mol for Cu (II), Co (II) and Ni (II) respectively, this values was less than 8 kJ/mol which shows the non-ion-exchange mechanism, the graph of isotherms of the three heavy metals was also found to be the C-form. The enthalpy values of adsorption of Cu (II), Co (II) and Ni (II) on bauxite match the physical adsorption. (∆H°) has positive value for the adsorption of Cu (II) and Ni (II) onto the bauxite which signified that the adsorption of Cu (II) is endothermic while its value is negative for adsorption of Co (II) which shows that the adsorption of Co (II) onto bauxite is exothermic. Increased randomness at the solid-solution interface during the adsorption of metal ions was shown by the positive values of ∆S° which reflected the good affinity of bauxite for Cu (II), Co (II) Ni (II) ions.

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