Isotherm Modeling on the Equilibrium Sorption of Cadmium (II) from Solution by Agbani Clay

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***Abstract*– The main objective of this study was to remove Cadmium(II) ions from aqueous solution by adsorption unto Agbani clay as a low-cost adsorbent. The clay was used without chemical modification or treatment in order to maintain a low process cost. The effect of pH, initial Cadmium ion concentration and time were determined using batch adsorption technique. Maximum adsorption was recorded at a pH of 5.0 and equilibrium sorption was achieved within 50 minutes of the process. Equilibrium isotherm models applied showed the Freundlich isotherm model with the best regression coefficient R^2 of 0.9907, followed by the Temkin isotherm, (0.9220) and the least value was obtained with the Dubinin-Radushkevich, (0.8159) and Langmuir isotherm, (0.8158). The Langmuir isotherm constant (b) and the Freundlich constant (n) indicated a high affinity of Agbani clay for Cadmium(II) ions. A chemical adsorption process was indicated by the value of the apparent energy of adsorption (9.13KJ/mol) obtained from the Dubinin-Radushkevich isotherm. The experimental results indicated the potential of Agbani clay as a low-cost adsorbent for cadmium removal from industrial wastewaters.**

***Keywords* –** Agbani Clay, Cadmium, Equilibrium Modeling, Isotherm, Sorption and Temkin Model

I. INTRODUCTION

Metals and its associated compounds are useful in the industrial development of any Nation. Cadmium, just like other metals occur naturally in nature and is found in association with most zinc minerals. Cadmium is one of the most toxic metals because of the absence of a homeostatic control for this metal in the human body [1]. It has the potential to accumulate steadily in the human body when exposed through air, water or food sources. As a result of this accumulation in the body, it causes serious health problems to man, animals and aquatic life. Cadmium as a potent enzyme inhibitor causes kidney and liver damages. Crustaceans are sensitive to the toxic effects of cadmium and most animal species have shown this metal to be tetratogenic [2]. In recent years, one of the main objectives in the removal of cadmium and other heavy metals from wastewaters consist in the reduction of the concentration of these metals to very low levels. The techniques such as ion exchange, solvent extraction, membrane filtration, reverse osmosis, coagulation, precipitation and activated carbon adsorption are well known technologies for the treatment of waters rich in cadmium and other metallic species [3]. However, these techniques are expensive and sometimes ineffective especially when the concentrations of metals in solution are below 100mg/l. The problem of high cost involved in applying these techniques in the treatment of industrials wastewaters has limited their use in most development nations. As a result, Scientist over the world are engaged in the search for cheaper and more effective alternatives. Recently, many Science and engineering researchers and research groups have made use of low cost adsorbents for the removal of cadmium and other heavy metals from effluents. Adsorption unto these materials have been found to be effective, and include the use of clay [4]-[6], biomass materials [7]-[11], natural zeolite [12], Sepiolite [13], montmorillonite [14], [15], bentonite [16], [17] and Sawdust [18]. Emphasizing on the need for cheaper adsorbents, this work reports the use of Agbani clay for the removal of cadmium(II) ions from aqueous solution. This clay material is easily obtainable in Agbani, Nkanu west local government area of Enugu State, Nigeria. The influence of pH, Cadmium ion concentration and contact time were studied. Equilibrium isotherm models were applied to help the description of the adsorption process.

II. MATERIALS AND METHOD

A. Preparation of Adsorbent

The Adsorbent (Agbani clay) was collected from Agbani in Nkanu west local government area, Enugu, Nigeria. The clay was dispersed in excess amount of distilled water in a container, stirred vigorously to ensure proper dissolution and filtered to remove unwanted suspended particles. The filtrate was allowed to settle for 24hrs and excess water was decanted from the top. The clay obtained at the bottom of the container was sundried for several days to get rid of water molecules, then oven dried at a temperature of 105^0C for 2hrs in order to remove water molecules still present. The dried clay was grinded and passed subsequently through a 100µm mesh sieve. The sieved particles obtained were used for the adsorption process. The chemical composition of the clay was determined by classical method with the help of the Atomic Absorption Spectrophotometer (AAS) (Buck Scientific model 210VGP).

B. Specific Surface Area Determination

The specific surface area of Agbani clay was determined using the methylene blue absorption test method [19]. 2g of Agbani clay was dissolved in 200ml of deionized water, 10 ppm of methylene blue solution was added to the solution and agitated in a shaker for 2hrs. It was then kept for 24hrs for equilibrium to be attained, after which 10ml aliquot was taken and centrifuged. The amount of methylene blue adsorbed was then determined by the use of the UV/visible spectrophotometer (Spectrumlab 752s). Also, 20, 30, 40, 50, 60 and 70 ppm solutions of methylene blue were added sequentially and the previous steps repeated. A graph of concentration of methylene blue added versus the amount of methylene blue adsorbed was used to identify the point of complete cation replacement. The specific surface area (SSA) was calculated from the amount of methylene blue absorbed at the optimum point of cation replacement using (1).

$$SSA = \frac{[{}_{M}M_{B}].[A_{V}].[AMB]}{319.98} \times \frac{1}{Ms} \qquad (1)$$

Where ${}_{M}M_{B}$ is the amount of methylene blue absorbed at the point of complete cation replacement, A_V is the Avogadro's number (6.02×10^{23}), *Ms* is the mass of adsorbent (clay) and *AMB* is the area covered by one methylene molecule (assumed to be 130Å^2).

C. Batch Sorption Experiment

The reagents used in this study were of analytical grade. De-ionized water was used for preparing and dilution of all solutions. A stock solution of Cadmium(II) of concentration 500mg/l was prepared by dissolving appropriate amount of $Cd(NO_3)_2$ in de-ionized water. From the stock solution, lower concentrations of 20, 40, 60, 80 and 100mg/l were prepared by accurate dilutions. The pH of each solution was adjusted to the required experimental value by the use of the pH meter to determine the pH and the drop wise addition of 0.1M NaOH or 0.1M HNO_3 until the desired value was obtained. The sorption experiment was conducted using the batch method to determine the effect of pH, initial Cadmium ion concentration and adsorption time. The influence of pH was performed in the range 1 to 8, initial Cadmium ion concentration in the range 20-100mg/l and a time interval of 10 to 120 minutes was used to determine the equilibrium time. In each case the parameter to be studied was varied while other parameters were kept constant. The study was carried out by adding 2g of the clay to 20m/l of a given solution of metal ion at room temperature of 27^0C. At the end of the contact time required, the solution was filtered and the filtrate analyzed for residual cadmium(II) ion concentration using the AAS. This was done for each experiment in a particular study, the experiment was repeated in each case and the mean value was calculated to minimize errors. The adsorption uptake capacity of the clay for cadmium(II) ions was calculated using (2).

$$qe = v[Co\text{-}Ce]/m \qquad (2)$$

Where *qe* (mg/g) is the equilibrium adsorption capacity of the clay for cadmium ions, *Co* (mg/l) is the initial cadmium ion concentration in solution, *Ce* (mg/l) is the concentration of cadmium ions remaining in solution at equilibrium, *v* (liters) is the volume of solution used and *m* (g) is the mass of clay used.

III. RESULTS AND DISCUSSION

A. Clay Characterization

The result for the chemical characterization of Agbani clay is shown in Table 1. The analysis was carried out by the classical method and the use of the Atomic Absorption Spectrophotometer (AAS). The main constituents of the clay are SiO_2 and Al_2O_3 , while other elements are present in little amounts.

Table I: Chemical Characterization of Agbani Clay

Composition	% by weight
SiO_2	50.3
Al_2O_3	26.09
CaO	1.93
MgO	1.77
Na_2O	1.35
Fe_2O_3	2.31
K_2O	1.01
TiO_2	0.56
MnO	0.81
Loss on Ignition	13.87
Surface Area (m^2/g) 18.32	

B. Influence of pH

The characterization of the effect of initial pH of solution on adsorption is necessary for an accurate evaluation of equilibrium parameters; this has been reported to be one of the most important parameters in the sorption of metal ions [20]. The net charge on the adsorbent is determined by the pH which in turn determines whether the metal ions can bind to the surface or not. Adsorption process is reversible in the presence of mineral acid, due to its ability to regulate the net charge on the adsorbent. The result for the effect of pH on adsorption of Cadmium(II) by Agbani clay is shown in fig.1. Maximum adsorption was obtained at pH 5.0, at pH values greater than 7.0 metals can be precipitated due to the formation of several hydroxyl low soluble species such as $Cd(OH)_2$ and $Cd(OH)_3^-$. pH 5.0 was used as the optimum pH for subsequent studies, since at this pH, maximum uptake capacity was achieved and metal precipitation avoided.

At lower pH values, the solution is highly acidic which results in a net positive charge on the active sites of the clay. The metal ions thus compete with protons on the active sites leading to a reduction in the uptake of cadmium ions by the clay. Also, the protonation of the active sites on the clay reduces the number of negatively charged sites available for cadmium ons to bind; hence a decrease in adsorption. As the pH of the solution increased, the active sites becomes de-protonated and free for cadmium ions to bind, this reduces the competition between metal ions and protons leading to an increase in adsorption with increase in pH, similar result has been reported [20].

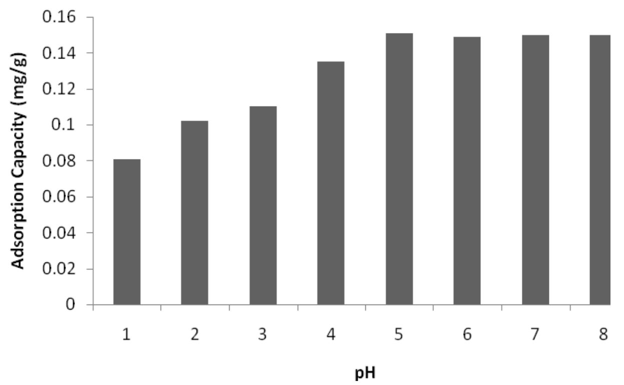

Fig. 1: Effect of pH on the sorption of cadmium(II) by Agbani clay (conc, 20mg/l, time, 2hrs, temp, 300K)

C. *Influence of Initial Cadmium Ion Concentration*

The effect of initial Cadmium ion concentration was performed at initial concentration of 20-100mg/l, since most techniques of heavy metal removal are usually ineffective at these concentrations. As shown in fig. 2, the amount of cadmium adsorbed increased with increase in initial cadmium concentration. This is expected because at higher initial concentration more efficient utilization of active sites is envisaged due to a greater driving force by a higher concentration gradient. The increase in concentration leads to increase in collision between the cadmium ions and the active sites, which is a major factor in kinetics for increase in the rate of chemical reactions. Also this increase is due to higher availability of cadmium ions for sorption. These sorption characteristics indicate that surface saturation is dependent on the initial metal ion concentration, as this determines the amount of metal ions adsorbed by the clay in the presence of available active sites. Other researchers obtained similar results [21], [22].

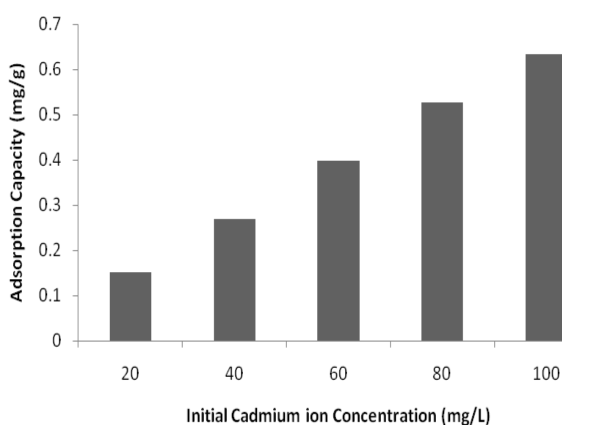

Fig. 2: Effect of cadmium ion concentration on its adsorption by Agbani clay (pH, 5.0, time, 2hrs, temp, 300K)

D. *Effect of Adsorption Time*

The effect of time on the sorption process was investigated to determine the rate at which sorption takes place and the equilibrium time. The kinetics of metal sorption governs the rate, which determines the residence time, and it is one of the important characteristics defining the efficiency of an adsorbent [23]. The result on the effect of time on the removal of cadmium(II) ions by Agbani clay is presented in fig.3. As observed a rapid increase in adsorption with increase in time was obtained within the first thirty minutes after which the rate of adsorption became slower up to 50minutes. After 50minutes, there was no significant change in the rate of adsorption up to 120minutes which showed that equilibrium was attained. Sorption experiments were conducted at a contact time of 2hrs to ensure equilibrium attainment. The fast uptake capacity obtained at the initial stage may be explained by an increased availability in the number of active binding sites on the adsorbent surface. The slow and insignificant adsorption observed as time progresses is due to the fact that every adsorbent has a limited number of active sites which becomes occupied with time [24].

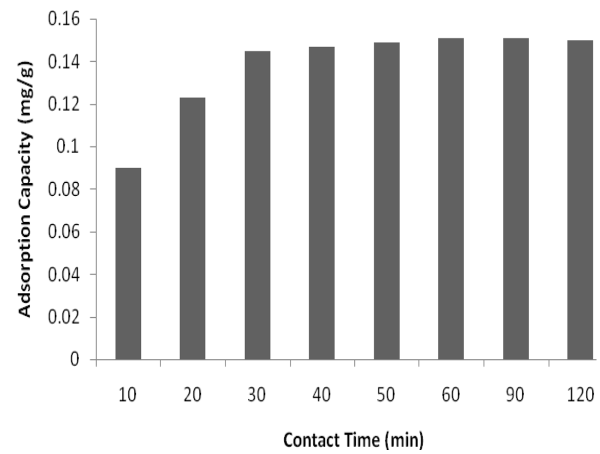

Fig. 3: Effect of contact time on the adsorption of cadmium(II) by Agbani clay (pH, 5.0, conc, 20mg/l, temp, 300K)

E. *Equilibrium Isotherm Modeling*

The adsorption isotherm was obtained from the data deduced from effect of initial Cadmium ion concentration. These isotherms are generally used to establish the relationship between the amount of metal ion adsorbed and its equilibrium concentration in solution. The degree of the adsorbent (Agbani clay) affinity for the adsorbate (cadmium ions) determines its distribution between the solid and liquid phases. These adsorption isotherms are used as functional expressions capable of simulating favorable adsorption uptake capacity as long as environmental parameters such as pH, initial metal ion concentration and contact time are carefully controlled during experiments. The Langmuir, Freundlich, Dubinin-Radushkevich and Temkins isotherm were applied in this study. Although these isotherms shed no light on the mechanism of adsorption, they are useful for comparing results from different sources on a quantitative basis, providing information on the adsorption potential of a material with easily interpretable constants.

Table 2: Equilibrium Isotherm Parameters

Langmuir Isotherm Model					
qm	**b**	**R^2**			
1.427	0.02	0.8158			
Langmuir R_L values					
R_L	0.71	0.56	0.45	0.38	0.33
Co	**20**	**40**	**60**	**80**	**100**
Freundlich Isotherm Model					
1/n	**n**	**Kf**	**R^2**		
0.725	1.38	0.05	0.9907		
Dubinin-Radushkevich Model					
q_D	**B_D(mol^2/kJ)**	**E**	**R^2**		
0.48	0.006	9.13	0.8159		
Temkin Isotherm Model					
B	**A**	**R^2**			
0.239	0.318	0.922			

F. *Langmuir Isotherm*

The Langmuir isotherm is used for monolayer adsorption onto a surface containing a finite number of identical binding sites [25]. The linearized form of the Langmuir equation is given in (3).

$$Ce/qe=Ce/qm+1/qmb \qquad (3)$$

Where *qm* is the maximum adsorption capacity for a monolayer coverage, *b* is a coefficient related to the affinity between the sorbent and the sorbate. The constants *qm* and *b* were obtained from the slope and intercept of the plot of Ce/qe against Ce shown in Fig. 4 and the Langmuir isotherm parameters are given in Table 2. The constants *b* expresses the affinity between the adsorbent and adsorbate [26]. The low value of *b* obtained indicated that Agbani clay has a high affinity for cadmium ion. An important characteristic of the Langmuir isotherm is expressed in a dimensionless constant equilibrium parameter R_L. The R_L value indicates the shape of the isotherm and is given in (4).

$$R_L = 1/[1+bCo] \qquad (4)$$

According to Mckay et al [27], R_L values between 0 and1 indicates a favorable adsorption process, 1 indicates a linear adsorption, 0 indicates irreversible adsorption, while an R_L value greater than 1 signifies an unfavorable adsorption process. This implies that the adsorption of Cd(II) on Agbani clay is a favorable adsorption as the R_L values obtained at all initial concentrations lie between 0 and 1. This suggest the applicability of this clay material for Cadmium(II) removal.

G. *Freundlich Isotherm*

The Freundlich isotherm model assumes that the removal of metal ions occurs on a heterogeneous adsorbent surface and can be applied to multilayer adsorption [28]. This isotherm was applied in order to determine the adsorption intensity of the adsorbent for the adsorbate. The linear form of the Freundlich isotherm equation is expressed in (5).

$$lnqe = [1/n]lnCe + lnKf \qquad (5)$$

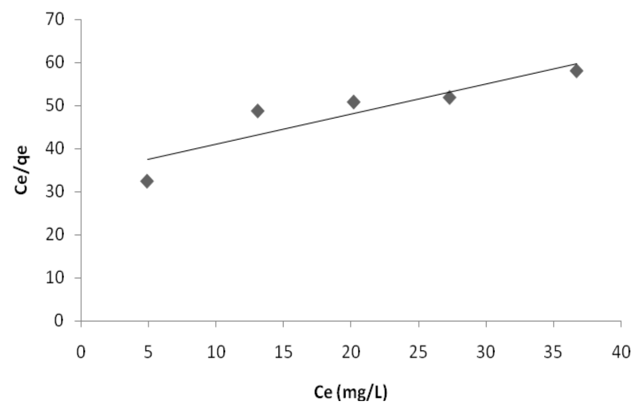

Fig. 4: Langmuir isotherm model on the adsorption of cadmium (II) by Agbani clay (pH, 5.0, time, 2hrs, temp, 300K)

Kf is a constant describing the adsorption capacity (L/g) and *n* is an empirical parameter related to the adsorption intensity, the plot of lnqe against lnCe is shown in fig.5 and the Freundlich isotherm parameters obtained are given in Table 2. The constants *n* and *Kf* were obtained from the slope and intercept respectively. The value of the regression coefficient (R^2) obtained, 0.9907 showed that this isotherm gave a good and better fit to the experimental data than the Langmuir isotherm. One important characteristic of the Freundlich isotherm is its ability to give an appropriate description of equilibrium data over a restricted range of concentration. According to Kadirvelu and Namasivayam, [29], the value of *n* between 1 and 10 represents a beneficial adsorption process, The value of *n* obtained (1.38) lies within this range which implies that Agbani clay has a high affinity for cadmium(II) ions in solution.

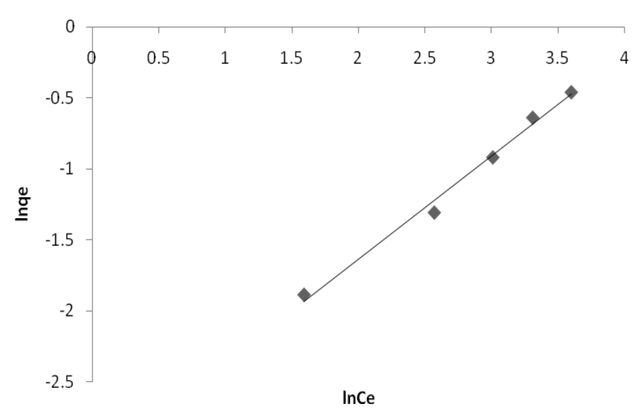

Fig. 5: Freundlich isotherm model on the adsorption of cadmium(II) by Agbani clay (pH, 5.0, time, 2hrs, temp, 300K)

H. Dubinin-Radushkevich Isotherm

The Dubinin-Radushkevich (D-R) isotherm model was applied to the data in order to deduce the heterogeneity of the surface energies of adsorption and the characteristic porosity of the adsorbent [30]. The linear form of the D-R isotherm is given in (6).

$$lnqe = lnq_D - B_D[RTln(1+1/Ce)]^2 \qquad (6)$$

The apparent energy of adsorption, *E* was calculated using (7).

$$E=1/(2B_D)^{1/2} \qquad (7)$$

The constants q_D(mol/g) is the D-R constant representing the theoretical saturation capacity and B_D(mol^2/J^2) is a constant related to the mean free energy of adsorption per mol of the adsorbate, *R* is the ideal gas constant, (8.314J/molK) , *T*(K) is the temperature of adsorption and *E*(kJ/mol) is the mean free energy of adsorption per molecule of the adsorbate when transferred to the surface of the solid from infinity in solution [31]. The plot of lnqe against $[RTln(1+1/Ce)]^2$ is shown in Fig. 6 and the constants q_D and B_D were calculated from the intercept and slope respectively. The D-R isotherm parameters are given in Table 2. This plot as indicated from the regression parameter R^2 (0.8159) showed that this isotherm did not provided a very good fit to the experimental data. If the value of *E* lies between 8 and 16kJ/mol the sorption process is a chemisorptions one, while values of below 8kJ/mol indicates a physical adsorption process [32]. The value of the apparent energy of adsorption (9.13kJ/mol) obtained indicated chemisorptions between Agbani clay and cadmium ions.

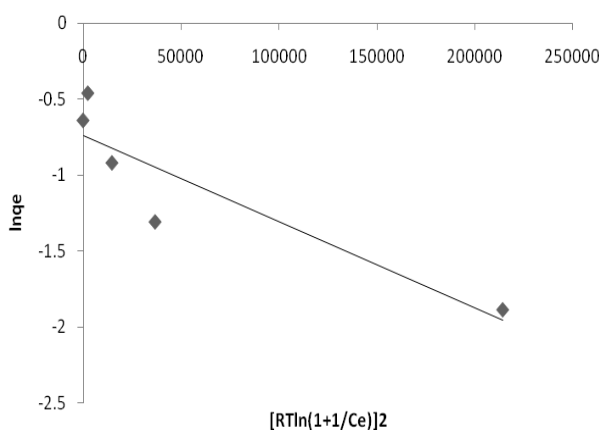

Fig. 6: Dubinin-Radushkevich isotherm model on the adsorption of cadmium(II) by Agbani clay (pH, 5.0, time, 2hrs, temp, 300K)

I. Temkins Isotherm Model

The Temkins isotherm model was also applied to the experimental data, unlike the Langmuir and Freundlich isotherm models, this isotherm takes into account the interactions between adsorbents and metal ions to be adsorbed and is based on the adsorption that the free energy of adsorption is simply a function of surface coverage [33]. The linear form of the Temkins isotherm model equation is given in (8).

$$qe = BlnA + BlnCe \qquad (8)$$

Where *B*= [RT/b_T] in (J/mol) corresponding to the heat of adsorption, *R* is the ideal gas constant, *T*(K) is the absolute temperature, b_T is the Temkins isotherm constant and *A* (L/g) is the equilibrium binding constant corresponding to the maximum binding energy. This isotherm was applied by a linear plot of qe against lnCe shown in fig.7 and the constants *B* and *A* were calculated from the slope and intercept respectively. The Temkins isotherm parameters *A*, *B* and R^2 are presented in Table 2. Again, looking at the regression R^2 obtained (0.922), it is seen that this isotherm is applicable to the description of equilibrium data. However, comparing the isotherms applied, the Freundlich gave the best fit, followed by the Temkin isotherm and then the least fit was obtain with the Dubinin-Radushkevich and Langmuir isotherms.

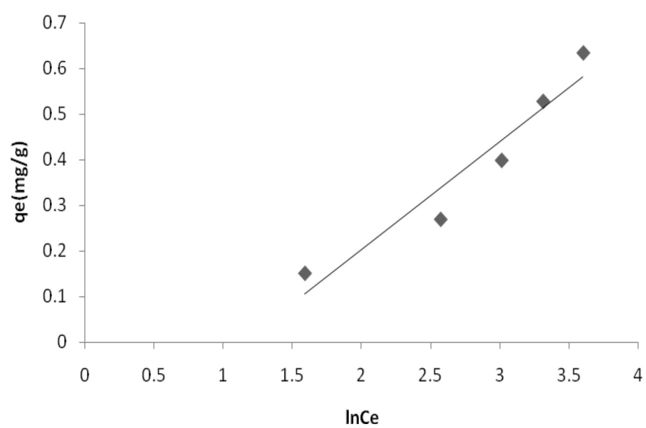

Fig. 7: Temkin isotherm model on the adsorption of cadmium(II) by Agbani clay (pH, 5.0, time, 2hrs, temp, 300K)

IV. CONCLUSION

The experimental result obtained showed the applicability of Agbani clay as a low cost adsorbent for treating industrial wastewaters contaminated with Cadmuim ions, this clay material can be used in Nigeria and other nations for Cadmuim removal from effluents without chemical modification, as chemical modifications or other forms of treatment may increase the cost of application.

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