Bentonite Clay as an Alternative Adsorbent for Removal of Heavy Metals in Wastewater

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ORIGINAL RESEARCH

Abstract- This study investigates the potential of bentonite clay as an alternative adsorbent for removing heavy metals from abattoir wastewater. Laboratory experiments were conducted to evaluate the effectiveness of bentonite clay in removing six heavy metals, including Lead, Chromium, Arsenic, Cadmium, Zinc and Iron. Results show that bentonite clay effectively removed all heavy metals, with removal efficiencies ranging from 75% to 95%. The study also found that the adsorption efficiency of bentonite clay increased with increasing initial metal concentration and decreasing pH of the solution. Freundlich and Langmuir models were used to predict the adsorption process, and the R^2 values for both models were similar. This suggests that both models were equally adequate or inadequate in describing the process. The study concludes that bentonite clay is a promising adsorbent for removing heavy metals from wastewater. It is recommended that the use of bentonite clay as an alternative adsorbent for heavy metal removal should be further explored and optimized, particularly in terms of operating conditions such as pH, contact time, and adsorbent dosage.

Keywords- Bentonite, Adsorption, isotherm, heavy metals

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1 INTRODUCTION

Regardless of large supplies of fresh water and the natural tendency of surface waters to cleanse themselves over time, the ever growing populations had resulted in outbreaks of life threatening diseases and this has been traced to pathogenic bacteria in the polluted water. Wastewater is simply used water discharged from homes, businesses, industries, commercial activities and institutions which is directed to treatment process. This wastewater is further characterized and defined according to its sources of origin (Rockson-itiveh and uyigue, 2021). Heavy metals are major pollutants in the wastewater of several industries such as agrochemical, petrochemical and fertilizers, manufacturing industries, distilleries, diaries. Heavy metals such as Chromium, Cadmium, Nickel and Lead are natural constituents of the Earth's crust with an adverse toxicity.

According to Abdie *et al.* (2016), the most common toxic ions in aqueous solutions responsible for particular problems were heavy metal ions, dyes, etc. Despite the fact that the human body needs small dose of heavy metals such as $Zn^{2+,}$ an excess of it may cause eminent health problem like depression, lethargy, neurological signs and increased thirst. Exposure to such toxic ions can cause health problems such as liver or kidney damage, Wilson disease, insomnia, cancer, diarrhea, nausea, vomiting, dermatitis, chronic asthma, coughing and headache (Alexander *et al.*, 2018). Removal of these toxic ions from wastewater is necessary for many health and environmental considerations.

Conventional methods such as reduction, precipitation, adsorption, oxidation and ion exchange, adsorption techniques are widely employed using the activated carbon as an adsorbent are effective but can be expensive (Daffi *et al.*, 2023), generate secondary waste, and may not be suitable for treating large volumes of wastewater (Suresh et al., 2015). Therefore, the search for alternative, cost-effective methods for heavy metal removal in wastewater is ongoing. One alternative approach is the use of natural adsorbents such as bentonite clay. Adsorption is a separation technique in which gas or liquid molecules are adsorbed on the surface of an adsorption solid. This separation process typically involves a metal (such as copper, lead, arsenic, chromium) of interest. The metal is dispersed in an aqueous phase that is being transported to the surface of the solid material (adsorbent) such as nanomaterials, biomaterials and activated carbon (Rockson-itiveh and Uyigue, 2021). The adsorbate interacts with the adsorbents either by physical or chemical forces.

In physical adsorption, the binding forces of interaction are the Van der Waals forces while in those of chemisorption involves chemical forces. (Kennedy *et a*l., 2018). Most commonly used adsorbent material is the activated carbon according to Suresh et al., 2015, but it proves to be expensive. Other adsorbent materials that have gained attention are volcanic ash, fly ash, bentonite clay. Bentonite clay has been found to be most economical adsorbent material because of its high efficiency in removing heavy metals, availability and it is environmentally friendly (Sheikh *et al* 2019). They of the montmorillonite group with a very high chemical and mechanical stability, varying surface and structural properties and contains smectite minerals (Tadesse, 2022). There exist various procedures for the removal of heavy metals from wastewater such as adsorption, membrane technologies etc, among which adsorption offers a better efficiency. The adsorption process is an efficient and effective method for the removal of a wide variety of toxic

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pollutants specifically heavy metals from wastewater and it regarded as the oldest most widely used procedure.

However, due to the high cost of commercial activated carbon, research has been conducted on the use of more cost-effective adsorbents such as bentonite clay. Bentonite is a naturally occurring clay mineral that has a high surface area and can adsorb a variety of heavy metals from aqueous solutions. Its low cost, abundance, and high efficiency make it a promising candidate for the treatment of heavy metal-contaminated wastewater. Bentonite clays is an attractive adsorbent as it is relatively cheap and also abundant in the earth, with very high internal surface area and high porosities. The structure of the clay is composed of numerous tetrahedral and octahedral layers of Si, Al, Mg and layers of oxygen, hydroxyl groups, respectively (Kennedy et.al., 2018). These layers are separated by pockets of interlayer space with either positively charged or negatively charged dangling surface groups. This configuration allows for adsorption of unwanted cations, anions or other molecules from contaminated water (Kennedy *et al*., 2018).

Several studies have investigated the use of bentonite clay in removing heavy metals from wastewater with little or minimal efficiency. For example, Abdi et al., (2016) studied the adsorption of lead (Pb), cadmium (Cd), and nickel (Ni) by bentonite clay in batch experiments. They found that the removal efficiency increased with increasing initial metal concentration and decreasing pH. They also found that the Langmuir model provided the best fit to their experimental data, indicating that adsorption occurred through monolayer coverage. Liu and Zhang (2019) conducted a comprehensive review on the use of bentonite-based materials for heavy metal removal from wastewater. They reported that bentonite-based materials have been used to remove a wide range of heavy metals, including lead, cadmium, copper, zinc, and chromium.

Ramesh and Gandhimathi (2016) did a work on the use of modified bentonite clay for Chromium (Cr) removal from industrial wastewater. They out that the adsorption capacity of bentonite clay in removing Cr was enhanced as the clay is being modified with sodium dodecyl sulfate (SDS). As literature has shown that the efficiency of bentonite clay for the removal of heavy metals from wastewater can be enhanced with the appropriate additives, this research utilizes sulphuric acid to modify the bentonite clay as a means of enhancing the efficiency and effectiveness of the adsorption capacity of the clay. Overall, the research presented in this paper contributes to the ongoing efforts to develop sustainable, cost-effective methods for heavy metal removal in wastewater treatment. However, further research is needed to optimize the use of bentonite clay for heavy metal removal in different types of waste water and to evaluate its potential for large-scale applications.

2 MATERIALS AND METHODS

2.1 ADSORPTION USING BENTONITE CLAY

The University of Portharcourt Laboratory provided all the reagents for this experiment, which were all of analytical grade. As the adsorbent for adsorption, exceptionally pure bentonite powder (Aluminium silicate hydrate) was purchased. Using the atomic absorption technique type AA-6800, the amounts of the heavy metals under investigation were determined. Concentrated nitric acid (63%) was of high quality and was acquired from the laboratory as buffer solutions of pH 4, 7, and 9 for the calibration of pH-meters.

2.2 ACTIVATION OF BENTONITE CLAY

Bentonite powder was dissolved in 60% H_2SO_4 for the purpose of activation. The temperature and contact time were also taken into consideration throughout the activation procedure in accordance with Emam (2013). At temperatures of approximately 75°C, 85°C, and 100°C for 12 hours, the activation process was carried out using a mechanical stirrer spinning at 200 rpm. After washing the mixture with distilled water to remove excess unreacted acid and bring it to neutrality, it was dried. The dried bentonite was crushed into small particles and prepared for usage after drying to a temperature of about 80^oC (Tadesse, 2022).

2.3 BATCH ADSORPTION TEST ON BENTONITE CLAY

Batch experiments were used to study the heavy metal adsorption by the adsorbents. It was decided to set up an adsorption column, which consisted of a 500 ml separating funnel clamped by a retort stand over a 500 ml graduated measuring cylinder with an open end and a perforated beaker on top for equitable distribution of the effluent as shown in Figure 1.0 below. To keep the bentonite contained, the base of the cylinder is clipped with filter paper measuring 1.8 mm. The 250ml beaker that served as the setup's collector was then put underneath it. Weighting 19.6g of bentonite into the adsorption column resulted in a packed height of 1.3 cm. The contact time was then recorded after 150 ml of wastewater had been added to the column via the separating funnel and controlled with the help of the tap. The surfactant from the adsorption column was then filtered using a 90mm filter paper to remove any bentonite particle that must have escaped into the surfactant. The residual heavy metals were determined by atomic absorption spectrophotometer (AAS) analysis.

Fig.1: Batch Adsorption Column set-up for the experiment

The removal efficiency of the adsorbed heavy metal concentration was estimated by taking percentage of the difference between the initial and final concentrations

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with respect to the initial concentration as show in equation 1.0.

Removal Efficiency= $(C1 - C2)/C1 \times 100$………… (1)

Where C_1 and C_2 is the initial and final concentrations in mg/l of the heavy metals.

2.4 ADSORPTION MODELS

The Langmuir and Freundlich isotherm models were used to fit the experimental data in this investigation.

2.4.1 Langmuir Isotherm Model

$$C\_e/q\_e = C\_e/q\_m + \frac{1}{k_L q_m} \qquad (2)$$

Where Ce is the equilibrium concentration of heavy metal, qe is the amount of the heavy metals adsorbed (mg/g), q_m is the maximum coverage capacity (mg/g) and K_L is the lamgmuir constant for adsorption (L/mg), V is the volume of the adsorbate (mL), m is the mass of the adsorbent. 1/ $q_m$and 1/ K_Lq_m are the slope and intercept respectively from the plot of Ce/qe versus Ce.

2.4.2 Freundlich Isotherm Model

$$q_e = K_F {C_e}^{1/n} \qquad (3)$$

where qe is the amount of metal ion adsorbed per actual amount of adsorbent (mg/g), Ce is equilibrium concentration (mg/l), K_F and n are Freundlich equilibrium constants which are obtained from linear plot of lnqe versus lnCe. where 1/n is a heterogeneity parameter, the smaller 1/n, the greater the expected heterogeneity.

3 RESULTS AND DISCUSSIONS

3.1 PHYSICOCHEMICAL CHARACTERISTICS OF THE ADSORBENT

The physiochemical characteristics of the adsorbent were assessed using the methods and procedures mentioned in the methodology. The exchangeable cation and excess hydroxyl groups in the montmorillonite structure influenced the pH of natural calcium bentonite to be alkaline in nature. As more OH were lost as a result of the thermal processing during calcination, the pH decreased as well as the point of zero charge. Because raw bentonite has more hydroxyl groups than calcined bentonite, its point of zero charge is larger. Buffer solutions of pH 4, 7 and 9 was used for the calibration of pH-meters alongside a stirring speed of 200rpm. The specific gravity of pure montmorillonite mineral has been discovered from literature to vary between 2 and 2.7 and it decreases as water content increases. It is observed that the specific surface area greatly increased as heat is being applied during treatment to remove impurities of carbonates, water organic compounds and hydroxyl groups. Table 1 shows a summary of the physicochemical properties of the bentonite clay.

Table 1. Physicochemical properties of bentonite clay

Property	Mean Value
Specific Gravity	2.50
Moisture Content	9.86
Ph	8.4
Activation Temperature	**Specific Surface Area M²/G**
75	84
85	162
100	204

3.2 BENTONITE CLAY IMPACT

Table 2.0 shows the heavy metal content of analysed wastewater collected from the slaughter house before and after adsorption treatment. The results showed that the heavy metal content of the wastewater with respect to Chromium Cr is maximum in sample 2 (33.48) while Cd is minimum in sample 1 at (1.58). The overall heavy metal levels are of the following order: Zn>Cr>Fe>Pb>As>Cd. These values are far above the WHO discharge standard for wastewater effluent discharge. The results obtained after treatment showed that the treatment process performance was maximum as majority of the parameters has > 90% performance. This implies that bentonite clay is highly efficient as an adsorbent for wastewater treatment involving Cadmium, Chromium, Arsenic and Lead. The removal percentage followed the order: Cd>As>Cr>Pb> Zn>Fe. These results performed better than those of Mona Karnib et al 2014 while using activated carbon as an adsorbent.

In their experiment, a maximum removal percentage of 86 % was attained for Cadmium and 24% for Chromium. The effectiveness of bentonite clay is traceable to the its internal and external surface areas for cation exchange, high cation exchange capacity, large specific surface area, and the presence of exchangeable cations. These properties make it a promising candidate for wastewater treatment containing heavy metals. It has been reported that the expanding layer of aluminosilicate with different surface exchangeable cations such as Calcium, Sodium, Magnesium, and Potassium provides the affinity and capacity for bentonite adsorption (Alexander et.al 2018). Rezapour et.al 2014 studied the application of raw HCl^- and $H_2SO_4^-$ activated bentonite as adsorbents for the removal of Zn^{2+} and Pb^{2+} from aqueous solution, it was shown that activated bentonite with sulfuric and hydrochloric acids provided maximum adsorption of Pb and Zn ions with efficiencies of about 98% and 55% respectively which is in line with the current studies.

The adsorption efficiency of bentonite clay was seen to increase with an increasing initial metal concentration, which can be ascribed to the increased availability of metal ions for adsorption. However, at high initial metal concentrations, the adsorption efficiency of bentonite clay decreased, which can be attributed to the saturation of adsorption sites on the surface of the clay. The usage of bentonite clay as an adsorbent for removal of heavy metal from wastewater has several advantages over other conventional adsorbents, such as low cost, abundant availability, and environmental friendliness. However, further studies are needed to optimize the operating

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conditions and to assess the feasibility of using bentonite clay at a larger scale. Additionally, the potential risks related with the disposal of spent bentonite clay should be evaluated to ensure that the use of bentonite clay does not cause any environmental harm. Table 2 below shows the removal percentages and heavy metal concentrations before and after treatment with bentonite powder.

Table 2. Percentage Removal and heavy metal compositions before and after treatment with bentonite sample

Heavy metal	Formula	Initial Composition (Mg/l)	Final Composition (Mg/l)	Percentage Removal	WHO Standard
Lead	Pb	13.20	0.48	96.4	0.2
Cadmium	Cd	1.58	0.002	99.9	0.01
Chromium	Cr	25.03	0.81	96.8	0.02
Arsenic	As	3.74	0.04	98.9	0.05
Zinc	Zn	19.14	2.02	89.4	5.0
Iron	Fe	5.02	1.14	77.3	5.0

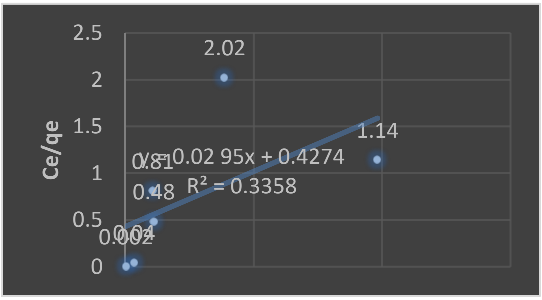

Fig. 1: Graph of Langmuir isotherm for the adsorption process

Table 3. Summary of isotherm model

Isotherm	Parameter
Langmuir	
Q_{max} mg/g	33.89
K_L L/mg	0.069
R^2	0.3356
Freundlich	
KF	61.26
N	1.464
R^2	0.3317

Adsorption isotherm usually is to fit the equilibrium data for the experiment and this serves as a medium of comparing the adsorption efficiencies at different operating conditions. Table 3 shows the summary of adsorption isotherm model. During this study, the Freundlich and Langmuir models were used to predict the adsorption model. An R^2 value of 0.3317 for the Freundlich isotherms indicates that the model explains 33.17% of the variation in the experimental data. This value is very similar to the R^2 value of 0.3356 for the Langmuir isotherm suggesting that both models may be similarly adequate or inadequate in describing the adsorption process. It is important to note that R^2 alone is not sufficient for evaluating the goodness of fit of a model to experimental data and other metrics and statistical test is recommended to fully access the fitness of this model.

4 CONCLUSION

Based on the obtained results from the experiment of batch adsorption, it can be established that bentonite clay is a promising adsorbent for the removal of heavy metals from wastewater. The adsorption efficiency of bentonite clay was seen to increase as the initial metal concentration increases. The Langmuir and Freundlich isotherm provided a good fit to the data of the experiment, which reveals that the adsorption of heavy metals onto bentonite clay follows a monolayer adsorption and a chemisorption process, respectively.

5. RECOMMENDATION

Based on the findings of this study, several recommendations can be made:

1. The use of bentonite clay as an alternative adsorbent for heavy metal removal should be further explored and optimized, especially with respect to operating conditions such as pH, contact time, and adsorbent dosage.
2. Future studies should be focused on the feasibility of using bentonite clay on a larger scale, such as in pilot-scale experiments and field applications.
3. The performance of bentonite clay should be compared with other conventional adsorbents to evaluate its effectiveness and cost-effectiveness.
4. The risks associated with disposing spent bentonite clay should be evaluated to ensure that the use of bentonite clay for heavy metal removal does not cause any environmental harm.
5. Finally, techniques should be initiated for the regeneration and reusability of spent bentonite clay should be investigated to reduce the cost and environmental impact of the adsorption procedure.

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