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Adsorptive Remediation of Heavy Metals from Industrial Wastewater using Modified Exhausted Neem Leaf

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The present work studied an efficient and cost-effective biosorbent prepared by chemical modification of exhausted Neem leaves. Amine functional groups were added to the surface of adsorbent using dimethylamine. The modified exhausted biowaste was used as adsorbent for sequestering heavy metal ions contained in industrial waste water as a function of varying pH values and contact time. Heavy metal concentration was determined before and after each contact time using atomic absorption spectrophotometer. The equilibrium adsorption results obtained obeyed the Langmuir isotherm and the kinetic data were found to best fit the pseudo-second order equation which indicates the biosorption mechanism. High adsorption rates were obtained at pH 5 with adsorption equilibrium that was gradually achieved in about 180 min. Studies found that the waste biomass with simple chemical treatment had a high efficiency for the removal of heavy metals contained in industrial wastewater and could be a promising green adsorbent.

Key words: Adsorption kinetics, Industrial wastewater, Modified exhausted biowaste, Biosorbent, Sorption capacity

INTRODUCTION

Enhanced economic activities in industries around the globe have also contributed negatively to the environment with resultant deterioration of the ecosystem due to pollutions (Jonathan *et al.*, 2009). The past decades have seen revolutions in industrial technology which have engaged the versatile use of heavy metal owing to its significance in processes. Heavy metal ions are highly mobile in solution hence, insufficient treatment of effluents from industries transfers the heavy metals into the ecosystems; whose accumulation possess a threat to the environment and human health (Dursun, 2006; Mohammadreza and Abdolmajid, 2015). Paramount among the effects of the accumulation of heavy metals within the ecosystems is the rapid depletion of immunological defenses as its concentration exceeds a certain quotient in humans. This depletion is responsible for numerous diseases that plague the humans like the Wilson's disease, anemia, encephalopathy, hepatitis, liver damage, dermatitis or chronic asthma and cancer caused by ingestion of heavy metals like cadmium, chromium, lead, copper and mercury among others (Jonathan *et al.*, 2009; Dursun, 2006; Mohammadreza and Abdolmajid, 2015; Sajjad *et al*., 2009;David and Minati, 2018). Water pollution as a result of heavy metal contamination from uncontrolled industrial wastewater is still a serious environmental concern owing to its toxicity, minimal biodegradability, and access into the food chain (Afroze and Sen, 2018). Remediation of heavy metal ions from industrial wastewater have engaged techniques such as ion flotation and exchange, precipitation, membrane-related process, electrochemical technique and biosorption process (Dursun, 2006; Mohammadreza and Abdolmajid, 2015; Sajjad *et al*., 2009;David and Minati, 2018; Afroze and Sen, 2018; Deng*et al.*, 2007; Jarup, 2003; Preetha and Viruthagiri, 2007). However, the challenge of most conventional methods includes low remediation efficiency in the presence of minute heavy metal concentration, cost effectiveness, use of toxic chemicals in some methods among others(Deng, *et al.*, 2007; Jarup, 2003).The adsorption process is considered a reliable remediation technology for wastewater contaminated with heavy metals as regards its high efficiency towards very small concentrations, cost effectiveness and operational simplicity (Park *et al.*, 2006). This makes the biosorption process a future technique considering several factors discussed later in this work. In another adsorption case, adsorbents with great porosity such as activated carbon, ion exchange resins and chelating ion exchange resins suffer micro-pore blockage from very fine solid particles contained in the effluents thereby, decreasing the effectiveness of the adsorbent aside its negative cost effectiveness (Jarup, 2003).

Biosorption is one of the emerging green technologies which utilizes naturally occurring waste materials as heavy metals sequestering agents from aqueous solutions. Biosorbents, especially biomass waste is presently a promising future environmental remediation method for recovering and removing metals from aqueous solutions bearing its attendant numerous advantages (Katsutoshi *et al.,* 2017). Some of the advantages of the biosorption method of remedying heavy metals from the environment include cost effectiveness, high efficiency and minimal sludge production, regeneration of biosorbent and possible recovery of the metal ions (Mohammadreza and Abdolmajid, 2015). These natural sorbents function through the molecular structures with different functional groups located at the waste biomass surface such as carboxylates, hydroxyls, nitro- derivatives, phosphate among others which are considered the active regions responsible for metal sorption. Although the sorption capacities of waste biomass biosorbent have been reported to be unsatisfactory regarding sorption capacities which can be successfully enhanced efficiently by chemical modification of the biosorbent surface (Bindra *et al.*, 2016). Available literature has shown that biomass waste as well as microorganisms can function as biosorbent for heavy metals in several environments at various pH values, some researchers have used waste agricultural biomass to remedy heavy metals from industrial wastewaters, especially those of cellulosic materials which did show good biosorption capacities (Hayder *et al.*, 2020). Several agricultural products are known to contain within their molecular structures active sites that include hemicellulose, lignin, lipids, proteins and hydrocarbons among others which are active sites for interaction for metal ions. The good adsorption efficiency of agricultural waste biomass according to Renu *et al* (Renu *et al.,* 2017) could be attributed to the presence of acetamido, alcoholic, carbonyl, phenolic, amido, amino, and sulfhydryl functional groups. Biosorption might be considered to be a fast chemical process which might involve passive ad non-metabolic pathway of binding between the biosorbent and the heavy metal in coordinate complex chelates (Jonathan *et al.*, 2009). The chelating ligand process might follow a single or combination of these routes; electrostatic interaction, ion exchange and complexation , micro-precipitation, coordinate chelationand/oradsorption, (Hannatu *et al*., 2020)

Similarly, Katsutoshi Inoue *et al*(Katsutoshi *et al.*, 2017) stated that biomass with an insignificant adsorption behavior can be activated into a highly efficient adsorbent by subjecting them to chemical treatments as in the case of changing chitin to chitosan via simple hydration using concentrated sodium hydroxide solution which in turn improves its sorption capacity remarkably. Moreover, wastes of several biomass have an affinity that target particular metal ions at particular environmental conditions thus, modifying the biomass waste chemically with relative active species becomes pertinent. Chemically modified biomass have been studied in respect of the search for efficient biosorbent and reports show that the introduction of more N-functional groups on the surface of biosorbent favors effective chelation mechanism of heavy metals from aqueous solutions (Bindra *et al.*, 2016). In this study, Modified exhausted biowaste (MEB) was investigated as a biosorbent for the treatment of heavy metals contaminated in industrial wastewater. The exhausted biomass chemical pre-treatment method was engaged to enhance its surface adsorptive capacity without limiting the cost effectiveness or eco-friendly advantages of the biosorbent. The modified biosorbent was tested for sorption capacity under the adsorption behavior of effect of solution pH value, sorption isotherm and kinetics of adsorption were investigated and discussed to clarify the optimum operating conditions.

2. MATERIALS AND METHODS

2.1. Wastewater Analysis and Biosorbent Preparation

The industrial wastewater was obtained from a cosmetics industry, Medicus Ind. Ltd. Kano state, Nigeria. The industrial wastewater which was used as the working solution was analyzed for the presence of Pb^{2+} and Zn^{2+} ions. In all experimental works, the pH of the solutions was maintained by using 0.1 M HNO_3 and 0.1 M NaOH solution while Hanna Instrument (±0.5) was used for pH measurements. 0.1 M solution of 2-[4-(2-hydroxymethyl)-1-piperazinyl] ethane sulphonic acid [HEPES] was used as the reaction buffer (Bindra *et al.*, 2016). Neem leaf was obtained from its natural habitat in Yelwa, Bauchi State, dried in the open air and grounded. About 250 g of the grounded leaf was put into teabags and immersed in hot distilled water to exhaust (until a clear filtrate is obtained) and then, dried and sieved with a 212 μm sieve. The residue (biowaste) was treated with acid to remove adhered soluble substances and further enhance its surface biopolymeric properties (David and Minati, 2018). The acid-treated biowaste was neutralized by thoroughly washing with distilled. The resulting charred biowaste was mixed with thionyl chloride at ambient temperature for 4 hrs, filtered and washed sufficiently with cold water (8 ^{0}C) to terminate further reaction. Absolute ethanol was used to rewash the residue to ensure removal of unreacted substance and dried in an oven at 40 ^{0}C before reacted with dimethylamine in presence of sodium carbonate at 80 ^{0}C for 5 hrs. After cooling, the mixture was filtered and washed with 0.1 M HCl followed by distilled water and ethanol. The MEB which was sourced from Neem leaf was left to dried and stored prior to usage. All the chemicals used were of analytical grade (AR) and double distilled water was used wherever necessary for the experimental works. The heavy metal ions concentration before and after the adsorption process was determined by atomic absorption spectrophotometer (AAS)AA320N shanghais general analytical instruments.

2.2. Adsorption Consideration

Adsorption processes often contain the simultaneous existence of both physical and chemical adsorption processes occurring side by side. The adsorption experiments were studied by using batch sorption experiments (Katsutoshi *et al.,* 2017). All the experiments were performed at room temperature and 120 rpm on a mechanical shaker with 25 mg of MEB in 250 ml reaction beakers containing 20 ml of industrial wastewater at varying pH and 0.1 M HEPES buffer. The effect of solution pH value and contact time was studied. The adsorption efficiency A% of MEB was calculated by using equation 1 , (Hannatu *et al*., 2020)

$$A\% = \frac{C_i - C_e}{C_i} \times 100 \qquad 1$$

where C_i and C_e are the concentration of metal ions (mg/L) before and after adsorption experiments respectively.The amount of metal adsorbed as sorption capacity q_e (mg/g) wascomputed by using equation 2 (Katsutoshi *et al.,* 2017)

$$q_e = \frac{C_i - C_e}{W} \times \mathrm{V} \qquad 2$$

where V is volume of metal solution (L) and W is weight of adsorbent (g).

3. RESULTS AND DISCUSSIONS

3.1 Adsorption Considerations

Figure 1 and 2 shows the adsorbance efficiency of MEB for Pb and Fe ions contained in industrial wastewater respectively. Increased consciousness for safeguarding the aqueous environment has increased the search alternative technology for remedying industrial wastewater. The use of bio-adsorbent as an alternative method for remedying contaminated industrial wastewater has advantages of simple application process, easy operation, wide applicability, renewable source as well as possible heavy metal recovery which make the whole process extremely convenient for large-scale use (Jiefu, 2018).The initial adsorption rate was gradual for all studied pH values but mostly leveled off at about 180 min of contact time which could be the probable effect of modifying MEB surface. This observation however, had an exception at pH 5 which tends to increase with increase in contact time till about 225 min for both Pb and Fe ions sorption. . This might be due to the availability of higher number of active adsorption sites on the surface of adsorbent at pH 5 which was seen as the optimum operating pH for the sorption of these heavy metals. Adsorption for pH 3 and 11 however, became slower with an increase in contact time of the experiment as a result of the mobility of ions and/or contention for the adsorbent active sites with other ions in solution. Biosorption is rate-dependent process considered to be a fast physical and chemical processes occurring simultaneously. The sorption capacity for the experimental work is presented in Figure 3 and 4 which reveals that adsorption increased with time till a limiting equilibrium state was obtained around 135 min of reaction time. This suggests that the adsorption rate was a fast process and spontaneous however, adsorption was seen to increase with increase in pH up to pH 9 as seen in Figure 4 for Fe ion sorption. This effect was seen to agree with the idea that the hydrogen ions in the solution compete with the adsorbate at low pH (Katsutoshi *et al.,* 2017).. pH of a solution regulates the speciation of metal ions as well as dissociative action of functional groups on the adsorbent surface with regards to metal sorption onto adsorbent surface(Davoud *et al.*, 2020).Solution pH is a basic factor in the aqueous behavior since it affects the surface functional group of the adsorbent and the solubility of ions in aqueous solutions. As observed from Figure 3 sorption capacity was reached around 90 min of reaction while desorption set in at higher contact time for Pb ions. A reversed path was observed for the sorption of Fe ions in Figure 4 where increased contact time increased sorption capacity at pH 9.

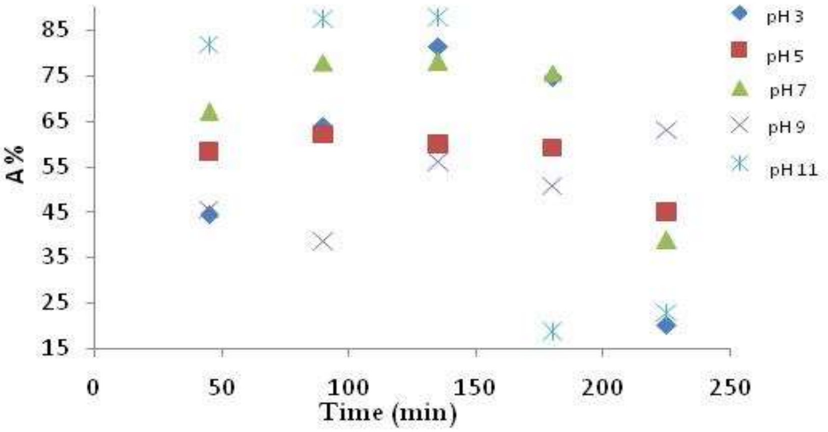

Figure 1: Effect of pH on adsorbance for Pb ions removal from wastewater as a function of contact time

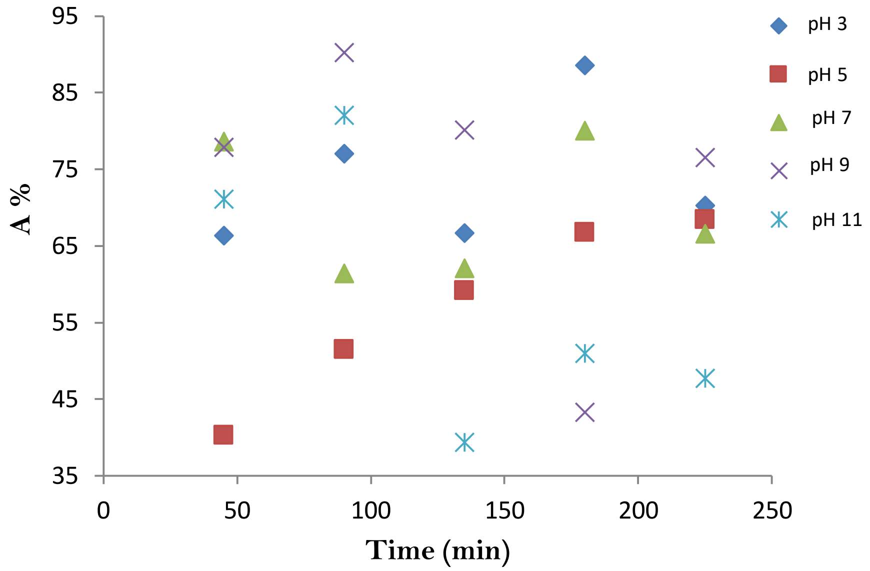

Figure 2: Effect of pH on adsorbance for Fe ions removal from wastewater as a function of contact time

The increase of sorption capacity with increase of solution pH is suspected to be the effect of any surface charges on the adsorbent and the degree of ionization of the solution (Prasad and Freitas, 2000). At low pH, it is known that H^+ ions which are highly mobile would compete with the metal ions in solution for active binding sites while at high pH all the binding sites may be protonated or precipitates as metal hydroxides. This causes a decrease in the sorption of heavy metal ions at the adsorbent surface. Moreover, high pH values lows the concentration of H^+ions and also decreases solubility of metals ions which enhances metal ion sorption on the surface of the adsorbent. As observed from Figure 3, it is suspected that further increase in pH caused precipitation of the heavy metals as their hydroxide causing a decrease in the sorption action of the adsorbent.

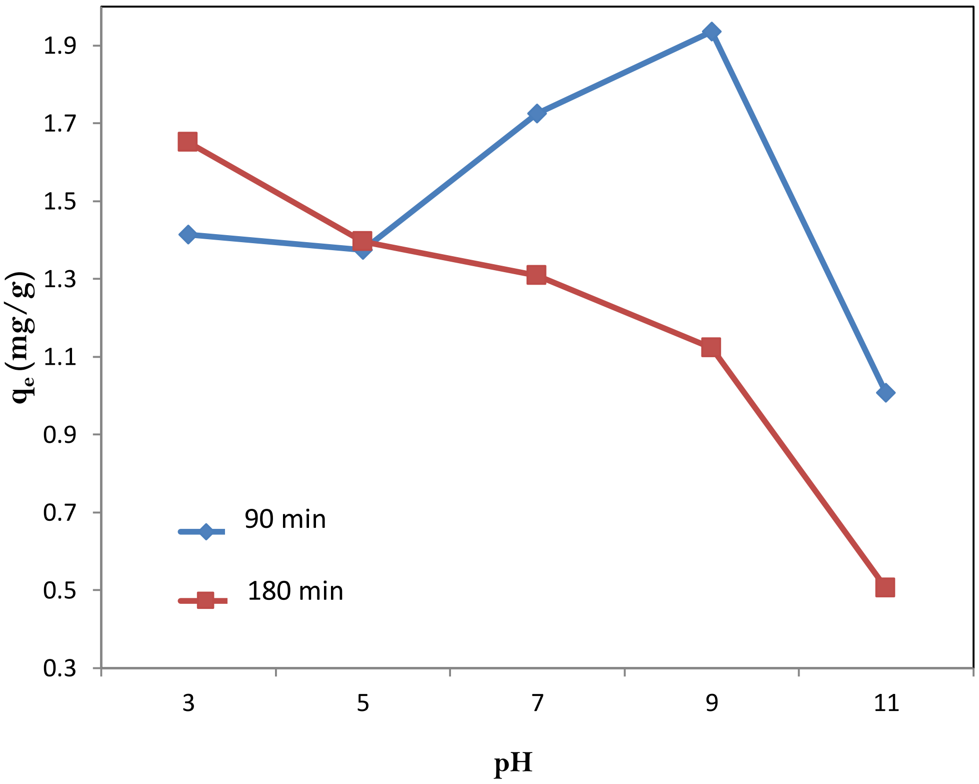

Figure 3: Sorption capacity for Pb ions removal from wastewater as a function of pH at different contact time

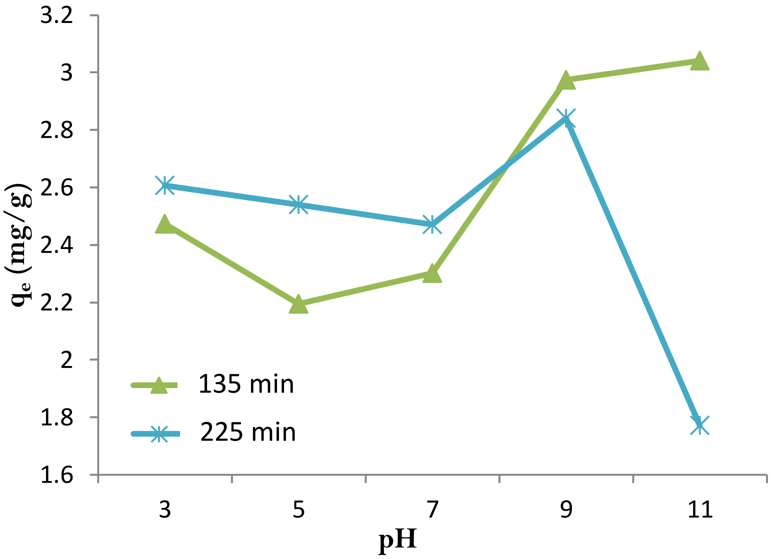

Figure 4: Sorption capacity for Fe ions removal from wastewater as a function of pH at different contact time

Itcan be seen from the obtained results that MEB can be an effective adsorbent for dissolved metal ions out of industrial wastewater solutions with quick and high efficiency, hencecan be ideal for the treatment of high volume and low concentration complex wastewaters (Jianlong and Can, 2009).

3.2 Adsorption kinetics and isotherm

Adsorption kinetics concerns the rate of solute removal at the solid–solution interface which over sees the residence time of the adsorbent in the solution. In the present study, kinetic studies were carried out in batch reactions using various pH values and contact time to ascertain the order of reaction and rate-limiting step. Although several adsorption kinetic models exist, the present study employed the best fit which was found to be the pseudo-second order rate model. According to Balarak *et al*(Davoud, *et al*., 2020) pseudo-second-order kinetic model most suites the study of biosorption kinetics of heavy metals and quantification of the rate limiting step kinetics.

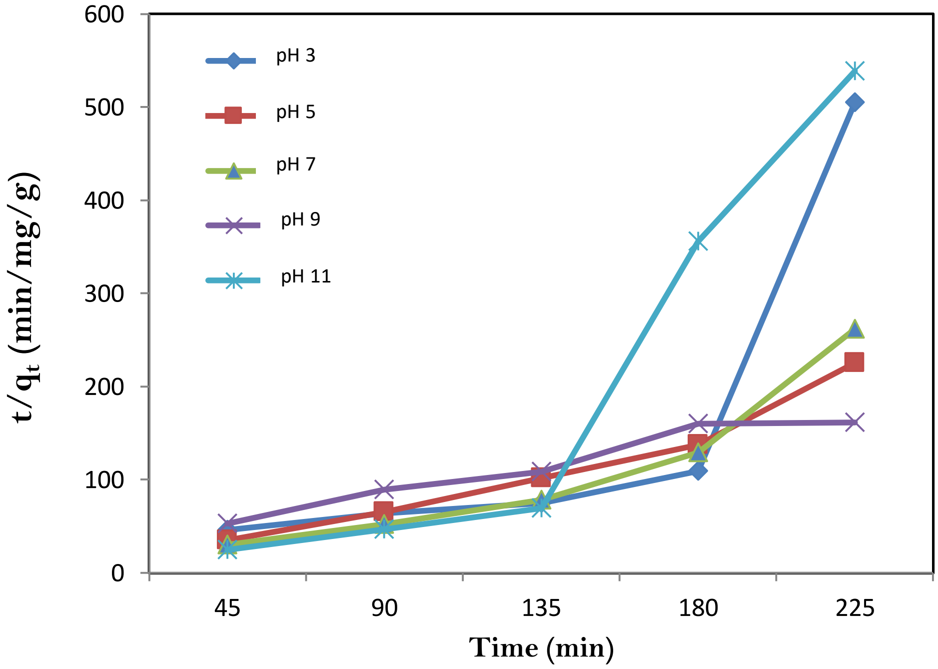

Figure 5: Pseudo-second order kinetics plots for Pb ions adsorption at different pH as a function of contact time.

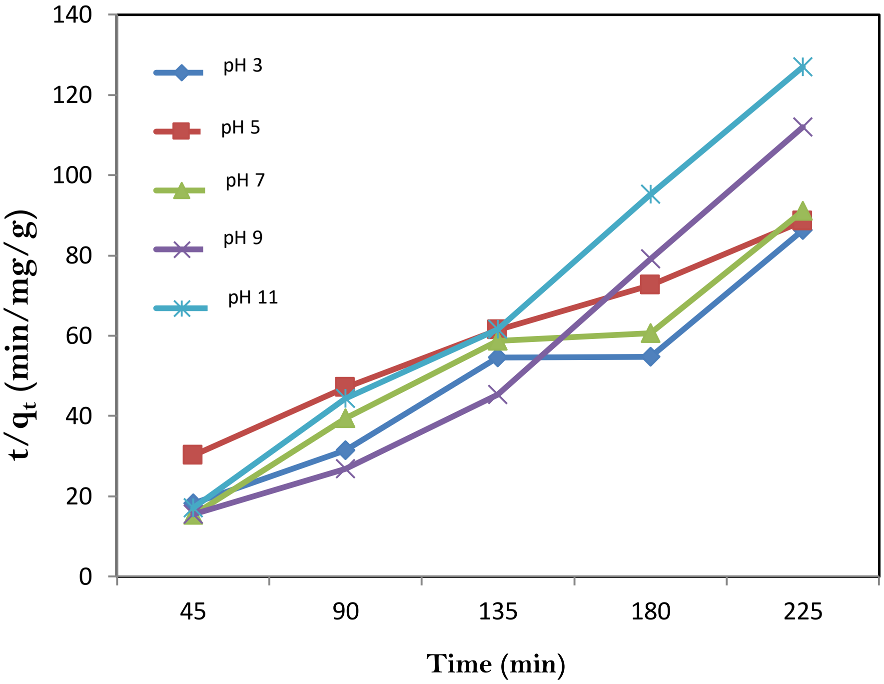

Figure 6: Pseudo-second order kinetics plots for Fe ions adsorption at different pH as a function of contact time.

The pseudo-second order kinetic model was used to describe the probable mechanism of MEB biosorption of Pb and Fe ion from wastewater. As shown in Figure 5 and 6, the plot of estimated t/q_t(min/mg/g) and associated contact time (min) at varying pH values at room temperature for MEB sorption action and it is obvious that the kinetic models well described the sorption of Pb and Fe ions. The coefficients of correlation (R^2) of pseudo-second-order kinetic model in Figure 5 was found to high at pH 5 for Pb (R^2 = 0.995768)while that of Figure 6 was found to be high at pH 9 for Fe (R^2 = 0.94661) sorption. The plots having high R^2 value indicate the applicability of pseudo-second order model as the mechanism of adsorption which is largely physisorption and probable there were occurrences of chemisorptions during the sorption action of MEB for Pb and Fe ions.The sorption mechanism of biomass can consist of several steps which include chemisorption, complexation, adsorption on surface, diffusion through pores and ion exchange (Hannatu *et al.*, 2020). Ding *et al* (Ding*et al.*, 2012)in their studies believed that ion exchange mechanism was the main heavy metal biosorption process rather than complexation with functional groups on the biosorbent surface however, as observed from Figure 5 and 6, the modification of the biomass revealed that metal ion sorption engaged enhanced ion exchange mechanism with induced functional groups which are suspected to engage complexation. The main assumption of pseudo-second order kinetic model is that the rate limiting steps may be a chemical sorption involving forces through exchange or sharing of electrons between the metal ions and the biomass (Prasad.and Freitas, 2000). The obtained result shown in Figure 5 and 6 revealed that MEB exhibited good number of electrostatic interaction and sharing of electrons between the metal ions and the biomass.The sorption capacity was seen to increase with increase in contact time with an optimum observed for pH 9 for Pb ion sorption while pH 5 solution was optimum for Fe ion sorption. The difference in optimum pH values for the heavy metal ions is ascribed to the mobility of Pb and Fe ionsin solution while the difference in sorption capacity for the studied metal ions is based on their mobility in solution which is affected by solution pH 5.

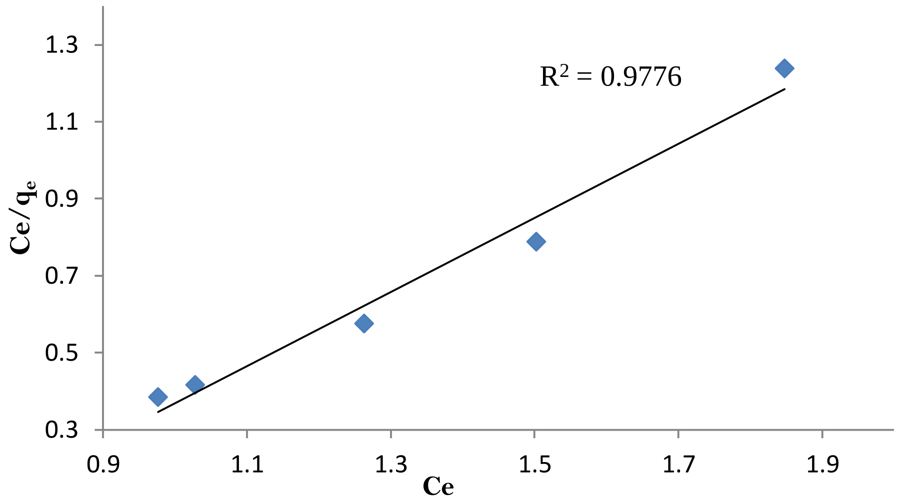

Figure 7: Plot of Langmuir Isotherm for the adsorption of Fe ions at pH 5

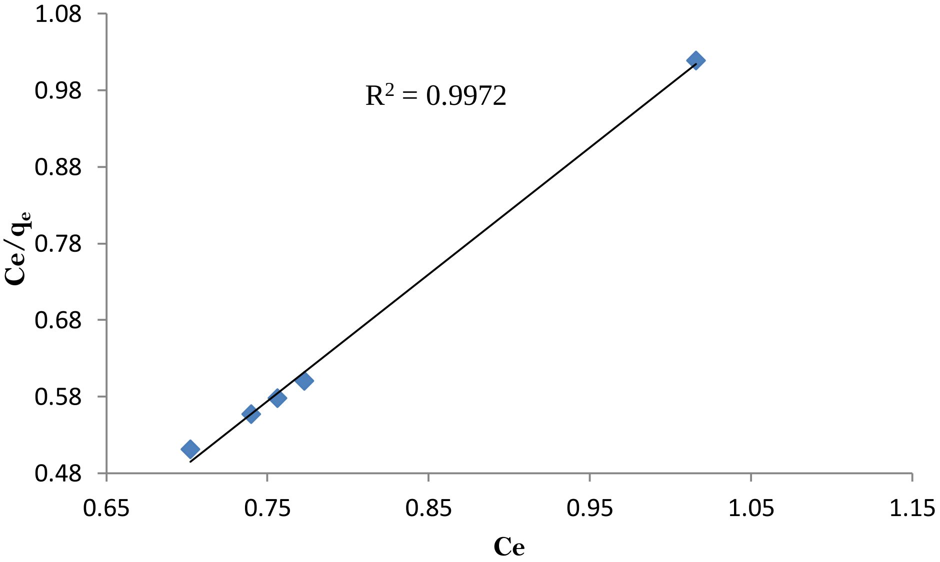

Figure 8: Plot of Langmuir Isotherm for the adsorption of Fe ions at pH 5

The Langmuir Isotherm is presented in Figure 7 and 8 for Pb and Fe ion sorption at pH 5. The linearity of the plot with high R^2 reveals that Pb and Fe ion sorption by MEB obeys Langmuir Isotherm which suggests ion exchange mechanism along a homogenous MEB surface. Langmuir Isotherm points to a dominant ion exchange mechanism based on a homogenous surface. It is assumed that the surface of the sorbent forms a monomolecular sorption layer with active sites energetically equal. The Isotherm could be defined using equation 3 (Jonathan *et al.*, 2009)

$$q = \frac{q_{max} b C_{eq}}{1 + bC_{eq}} \qquad 3$$

and the linear form of Langmuir formula is defined using equation 4 (Jonathan *et al.*, 2009)

$$\frac{C_{eq}}{q} = \frac{1}{q_{max} b} + \frac{1}{q_{max}} C_{eq} \qquad 4$$

where C_{eq} is the ion concentration in solution at equilibrium (mg/L); q is the amount of accumulated metal (mg/g); q_{max} is the maximum metal sorption (mg/g) and b is the ratio of adsorption and desorption rates (mL/mg)

The plot of C_{eq}/q versus C_e gives linear graph with q_{max} and b obtained from the slope and intercept. The sorption capability of MEB was enhanced via chemical modification to favor factors such as chemical state of active sites, the binding energy and number of available sites among others. According to Langmuir, saturation capacity (q_{max}) of the sorbent is assumed to conform to the total number of fixed identical active sites and however,this should be independent of the surrounding temperature. MEB heavy metal sorption activity engaged ionic exchange with electrostatic interaction mechanism which involved its charged groups with the metallic cations. The sorption mechanism is assumed to takes place within two successive period: a passive and quick uptake of heavy metal ions which is followed closely by an active and very slow uptake period (Jonathan *et al*.,2009; Prasad and Freitas, 2000). The initial process is expected to be physical adsorption or ion exchange mechanism with latter involves a chemisorption . The data from the Langmuir plot supports the findings that MEB could be used effectively as a suitable alternative for removal and possible recovery of heavy metals ions from industrial wastewater.

CONCLUSION

Increasing emphasis on the use of materials owing to their cost efficiency, regeneration ability, high adsorption efficiency, and minimal chemical sludge makes it future green adsorbents. The study investigated the use of exhausted waste leaf which was chemically modified to sequester heavy metal ions from industrial wastewater. The obtained data revealed that MEB sufficiently sequestered heavy metal ions through ion exchange mechanism which was dependent on the pH of the solution. The sorption was found to establish equilibrium after 135 minutes of contact time among various pH values indicating that MEB followed rapid attainment of phase equilibrium along with high sorption capacity values. Adsorption kinetics followed a pseudo-second-order kinetic model and the equilibrium adsorption results obeyed Langmuir Isotherm. The mechanism of sorption of Pb and Fe ions by MEB was largely by ion exchange with minimal chemisorption at the biosorbent solution interface which occurred at constant temperature and equilibrium solute concentration of the wastewater.

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DISCLOSURE STATEMENT

Conflict of interests: The authors declare that they have no conflict of interest.
Author contributions: All authors contributed equally to this work.
Ethical approval: All ethical guidelines have been adhered.
Sample availability: Samples of the compounds are available from the author.

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