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Biosorption of Lead (II) ions from aqueous solution using *Moringa oleifera* pods

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ABSTRACT

The adsorption of Pb^{2+} onto ground Moringa oleifera pods was studied under various conditions such as, pH, contact time, adsorbent dosage, and concentration of adsorbate. The adsorption process was checked for conformity with the Freundlich and Langmuir isotherms. From the adsorption experiments conducted, it was observed that the adsorption was pH, contact time, and adsorbate concentration dependent. The adsorption process was partly dependent on adsorbent dosage. It was also discovered that the adsorption did not conform to the Freundlich and Langmuir adsorption isotherms. Maximum percent adsorption obtained after contacting the Pb^{2+} aqueous solution with ground Moringa pods for 180mins was 48.4% at pH 7. This study revealed that Moringa pod is not a very good biosorbent for the removal of Pb^{2+} from wastewater at pH.

Keywords: Biosorption; Pb(II); *Moringa oleifera*; adsorption; Isotherms.

INTRODUCTION

Excessive release of heavy metals into the environment due to industrialization and urbanization poses great problem worldwide. Unlike organic pollutants, the majority of which are susceptible to biological degradation, heavy metal ions do not degrade into harmless end products [1].The increase in usage of heavy metals in industrial activities has occasioned their existence in wastewater. For example Lead and Cadmium is contained in the wastewater of industries such as electroplating, plastic and paint manufacturing, mining, metallurgical process, petrochemical process, batteries, and paper and pulp mills [2].

Despite the campaign against the use of lead in paints and as antiknock in petrol, appreciable quantities of lead from these products find their way into soils, rivers, aquatic life, and ultimately into humans causing damage to the central nervous system, kidneys, and reproductive system. In 2010, hundreds of deaths were recorded in Zamfara State, Nigeria due to lead poisoning. In view of the lethal effects associated with the ingestion (directly or indirectly) of lead and heavy metals generally, a lot of research is on going into fast, cost-effective, and neat ways to remove these toxic metals from our soils and water bodies.

Some methods employed in the removal of heavy metals from waste water include ion exchange, precipitation, ultra-filtration, reverse osmosis, phytoremediation etc. Of these methods, ion-exchange has proved to be the most effective, although it is expensive. Though it is very cheap to phytoremediate polluted soils and water bodies, yet the method is slow. A promising method for heavy metal removal from waste water is biosorption. Biosorption can be defined as the ability of biological materials to adsorb heavy metals from wastewater through metabolically mediated uptake and/or physicochemical uptake[3]. It is an effective and versatile method and can be easily adopted at low cost to remove heavy metals from large amount of industrial wastewaters. The basis for biosorption is the metal binding abilities of various biological materials. Recently, there is intensive study on the use of seeds, pods, and bark of plants (collectively called biomass) in removing heavy metals from waste water. Though many biomasses have proved efficient in adsorbing these metals, yet there is continuous research to discover more efficient ones. In addition, studies are been carried to ascertain the optimum conditions necessary for efficient removal of these metals from polluted sites.

Lead is a common contaminant in the natural environment that can enter the water column through geologic weathering and volcanic action, or by various anthropogenic practices including smelting, coal burning and use in gasoline, batteries and paint [4]. Though waterborne Lead concentrations do not normally exceed 0.6 μmol l^{-1}[5], levels as high as 4.3 μmol l^{-1} have previously been reported [6]. Contamination of water through anthropogenic practices is the primary cause of lead poisoning in fish [7].

In the discharge of metal ions in industrial effluent using bio-adsorption process has been an area of extensive research because of the presence and accumulation of toxic carcinogenic effect on living species. The most common and harmful heavy metals are Aluminum, Lead, Copper, Nickel, Chromium and Zinc. They are stable elements that cannot be metabolized by the body and get passed up in the food chain to human beings. When waste is disposed into the environment, a further long-term hazard is encountered. There are possibly more problems from these metals, which interfere with normal bodily function, than have been considered in most medical circles. Reviewing all of our vitamins and minerals has shown us that almost every substance that is useful can be a toxin or poison, as well. Metals are known primarily and almost exclusively for their potential toxicity in the body, though commercially they may have great advantages [8].

Recent studies have shown that heavy metals can be removed using plant materials such as palm pressed fibers and coconut husk[9], water fern *Azolla filiculoidis*[10], peat moss[11], duck weed *Wolffia globosa*[12], lignocellulosic substrate extracted from wheat bran[13], *Rhizopus nigricans*[14], cork and yohimbe bark wastes [15] and leaves of indigenous biomaterials, *Tridax procumbens*[16]. Apart from the plant based material chemical modification of various adsorbents, phenol formaldehyde cationic matrices[17], polyethylonamide modified wood[18], sulphur containing modified silica gels [16] and commercial activated charcoals also employed[19].

The active agents in *Moringa oleifera* extracts responsible for coagulation were suggested as the cationic polypeptides [20][21]. Gassenschmidt *et al*.[22] reported the isolation from *M. oleifera* of a flocculating protein of 60 residues with molecular mass of about 6.5 kDa, isoelectronic point above pH 10, high levels of glutamine, arginine and proline with the amino terminus blocked by pyroglutamate, and flocculant capacity comparable to a synthetic polyacrylamide cationic polymer. However, a non-protein coagulant was also reported but not characterised [23].Earlier studies showed that *M. oleifera* seed powder is effective in Cadmium remediation of water [24][25] .Although the water clarifying properties of *M. stenopetala* have not been as extensively studied as those of *M. oleifera*, Jahn [20] reported that 100-150 mg/l of *M. stenopetala* was as effective in water clarification as 200 mg/l of *M. Oleifera*. Most recent studies have shown that *M. stenopetala* has the capacity to remove Lead from water [26].Furthermore, the studies showed that *M. stenopetala* is more effective in lead sorption from water than *M. oleifera*.

Hence, this study aim at investigating the potential of this low-cost biosorbent, M. oleifera seed for the removal of Lead from aqueous solution. Parameters such as pH, adsorbent dose, contact time and adsorbate concentration that might influence the adsorption efficiency were investigated.

MATERIALS AND METHODS

2.1 Materials

All reagents used were of analytical grade (BDH Laboratory supplies, Poole, England). The Moringa pods were obtained from Akure, Ondo State Nigeria. All pH measurements were done using a pocket pH tester (Surgifriend Medical, England). Agitation of the aqueous solution was done using a mechanical orbital shaker (Gallenkamp Registered Trademark, England). Whatman filter paper no.42 was used to separate the adsorbent from the aqueous solution after each experiment. The biosorbent was sieved using laboratory test sieve (Endecotts Limited London, England). During the treatment of the biosorbent, stirring was done using magnetic stirrer

(Surgifriend AM – 325DB). The Adsorption experiment was conducted at the Phytoremediation Research Laboratory of the Federal University of Technology, Akure, Ondo state, Nigeria.

2.2 Treatment of Biosorbent

After sourcing, the seeds were removed from the fruit (called drumsticks) then the seeds and pods were dried separately for about 2 weeks. When satisfactorily dried, the pods were grounded to powder using a mechanical grinder. The method described by Mubeena *et al*.[27] was modified and adopted in the treatment of the biosorbent. 80g of the biosorbent was treated with 1600ml, 0.1M HNO_3 with continuous stirring for 2 hours to remove metals from the biosorbent and increase its surface area. Then it was washed with 500ml distilled water, this was done in thrice then the sample was then sundried for about 6 hours. After the acid treatment, the adsorbent (about 50g) was extracted with 400ml methanol to remove inorganic and organic matter from the sorbent surface. This was carried out for 2 hours 30 minutes. The adsorbent pH was adjusted to 7 using 0.1M NaOH, washed with distilled water, oven – dried for about 1 hour, kept in an air – tight plastic container and put in a refrigerator at 4°C prior the analysis.

2.3 Biosorption Experiments: pH studies, contact time, adsorbent dosage and concentration of Pb^{2+}

The influence of pH on Pb^{2+} ion biosorption was studied by introducing 0.5g of adsorbent into 250ml conical flasks containing 50ml of 50ppm lead solution. 0.1M NaOH and 0.1M HCl were used to adjust the pH during the study. The pH range of interest was 4 – 9 and three hours was the duration of the agitation at 200rpm. After agitation, the solution was filtered using Whatman filter paper no. 42. Then they were refrigerated until the metal analysis was done. For contact time study, 0.5g of adsorbent was introduced into 250ml conical flasks containing 50ml, lead solution with initial concentration of 50ppm at pH 7. The contact time ranged from 30mins – 180mins.The study on adsorbent dosage was conducted by varying the quantity of the adsorbent from 0.3g – 0.8g. Time for agitation was 3 hours while aqueous solution was maintained at pH 7. Concentrations ranging from 20ppm – 70ppm were used for the pH study. Time for agitation was 3 hours while aqueous solution was maintained at pH 7. The percentage adsorption was determined using the equation below:

$$\frac{Co - Ca}{Co} X\, 100$$

Where C_o= is the initial concentration of solution, C_a = concentration of solution after adsorption.

The residual Pb^{2+} ion concentrations resulting from these experiments were determined by using Perkin Elmer model 3110 Atomic Absorption Spectrometer.

2.4 Statistical analysis

Each experiment was conducted in triplicate to ensure the reproducibility of results. All data represent the mean of three independent experiments. Statistical analyses were performed using the statistical functions of Microsoft Excel version Office XP (Microsoft Corporation, USA).

RESULTS AND DISCUSSION

3.1 Effect of pH

The effect of pH on adsorption of Pb^{2+} by Moringa pods as presented by Fig.1 is divided into three phases. First, there is a sharp decrease in percent adsorption from 47.53% to 46.92% between pH 4 and 5. Second, a sharp increase in percent adsorption from pH 5 – 7 is observed, with maximum adsorption (48.4%) experienced at pH 7. Finally, the amount adsorption decreases sharply from 7 – 8, then slowly between 8 and 9. pH is an important parameter for adsorption of metal ions from aqueous solution because it affects the solubility of the metal ions, concentration of the counter ions on the functional groups of the adsorbent and the degree of ionization of the adsorbate during reaction[28].

The reduced adsorption efficiency of Lead ion removal with a decrease in pH could be attributed to the presence of H^+ ions in the mixture, which compete with Lead (II) ions for the binding sites. This finding agrees with that reported by Oboh and Aluyor [8] where sour sop seeds were used as the biosorbent. Similar observation have also been reported by some researchers [29,30,31].The second phase of the adsorption results agree with work done by Oboh and Aluyor [8] where sour sop seeds were used as the biosorbent. They observed that the adsorption of Pb^{2+} by sour sop seeds were highest at pH 7. Kanaan and Veemaraj [31] also carried out similar studies using bamboo dust and commercial activated carbon (CAC) as adsorbents, observed that Pb^{2+} experience maximum adsorption at pH 7.2.

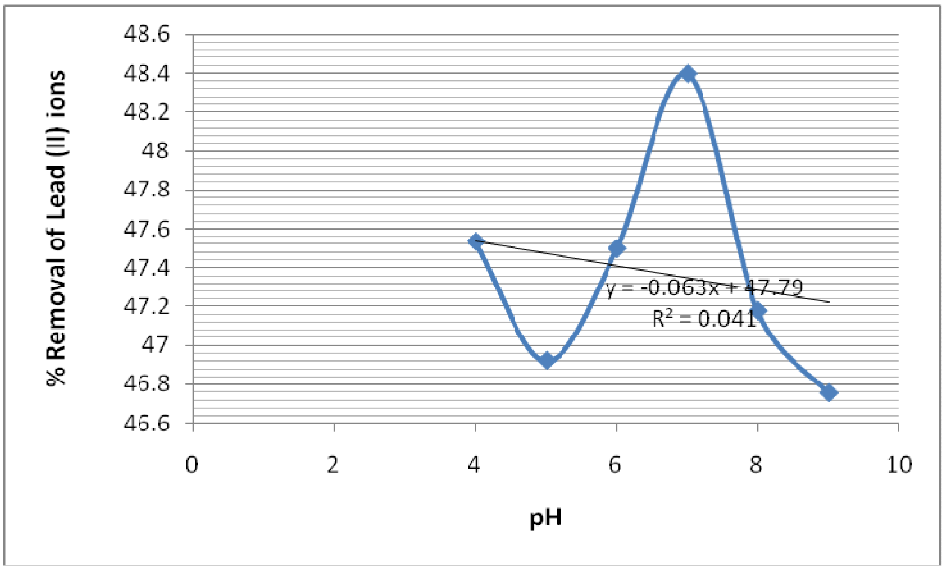

Fig. 1 Removal of lead (II) ions from aqueous solutions (50 ml) at different pH using Moringa pods as biosorbent for 3 hours.

3.2 Effect of Contact Time

The percentage removal of Pb^{2+} by the Moringa pod adsorbent with time is shown in Fig 2. From the result of the adsorption experiment the highest adsorption of Pb^{2+} of 47.22% was achieved at the end of 180 minutes. For Moringa pods, there was a progression in the rate of adsorption but it was not linear at any time. Also, from Fig. 2, it was observed that the rate of adsorption increased significantly for Pb^{2+} between 40 – 60 min of contact time. This result is important, as equilibrium time is one of the important parameters for an economical wastewater treatment system.

Oboh and Aluyor [8] in their work on biosorption of Lead using sour sop seeds, Kannan and Veemaraj [31] using bamboo dust and commercial activated carbon as adsorbent[29], all reported that the contact time was directly proportional to amount of Lead ions adsorbed from aqueous solution.

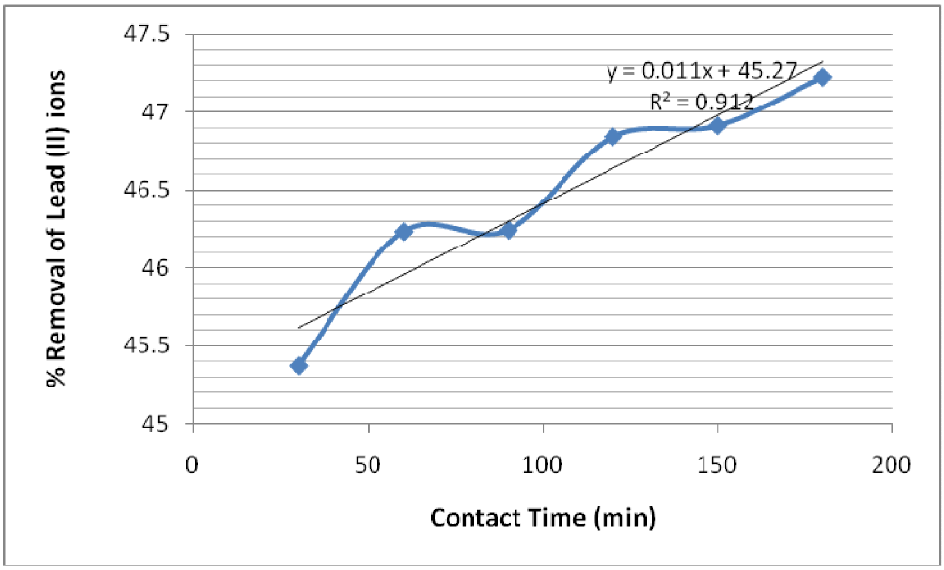

Fig. 2 Removal of Lead (II) ions from aqueous solutions (50 ml, pH 7) with time using Moringa pods (0.5 g) as biosorbent

3.3 Effect of Adsorbent Dosage

The effect of the adsorbent dosage on the removal of Pb^{2+} from aqueous solution was investigated by varying the dosage of the adsorbent from 0.3 – 0.8g. It is expected that an increase in the dosage of adsorbent should yield a corresponding increase in the amount of metal ion adsorbed onto the surface of the adsorbent since there will be more sites for the adsorbate to be adsorbed. Therefore competition for bonding sites between molecules of the adsorbate should decrease with increase in dosage of the adsorbent.

From Fig. 3 this trend was inconsistent and therefore suggests that the use of Moringa pod as adsorbent partly depend on its dosage in aqueous solution. This assertion is supported by Elaigwu *et al* [30]. Whereas other works done by Oboh and Aluyor [8] using sour sop seeds, Reddy *et al*[29] using Moringa bark and varying adsorbent dosage from 0.1 – 1g, Tangjuank *et al*[32] using activated carbon prepared from cashew nut shells, and others reveal a direct proportional relationship between the adsorbent dosage and percent adsorption.

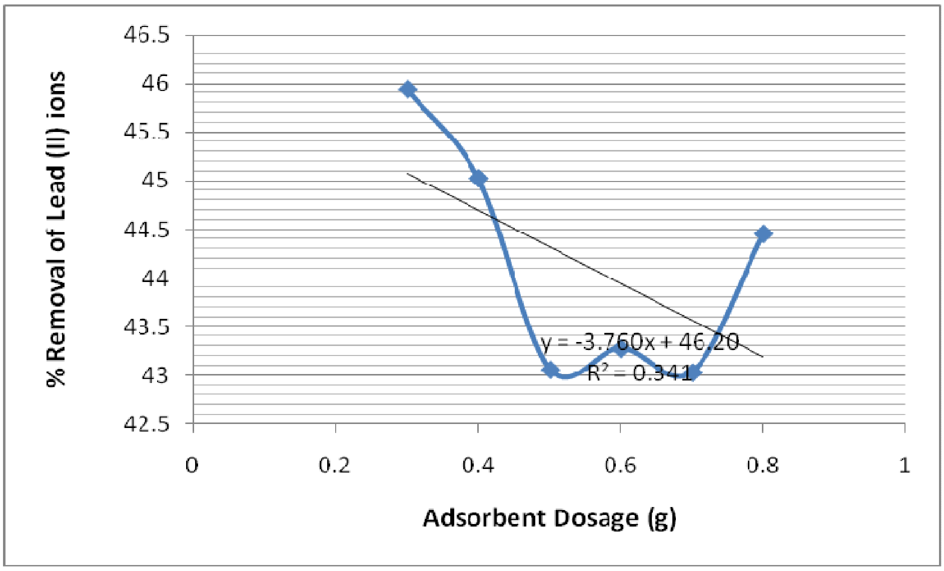

Fig. 3 Removal of Lead (II) ions from aqueous solutions (50 ml, pH 7).

3.4 Effect of Initial Concentration of Pb^{2+} Aqueous Solution

From Fig 4, increase in adsorbate concentration resulted in corresponding increase in percent adsorption. It was observed that this trend could also suggest that increase in adsorbate concentration results in increase in number of available molecules per binding site of the adsorbent thus bringing about a higher probability of binding of molecules to the adsorbent (i.e. the probability of chemical interaction between the adsorbent and the adsorbate is enhanced by reason of the high availability of molecules of adsorbate in solution). The overall trend is consistent with the observed phenomenon. Similar works by Elaigwu *et al*[30], Hashem[33] and Karaca *et al*[34] supported this assertion.

3.5 Adsorption Isotherms

It is expected that the adsorption of Pb^{2+} on Moringa pods should correlate with Freundlich and Langmuir isotherms since it is possible for more than one layer of the metals ions to accumulate on the adsorbent's surface. From the findings this assertion is not supported. Elaigwu *et al* [30] reported that the adsorption of Pb^{2+} onto activated carbon prepared from cow dung was not really dependent on adsorbent dosage lending credence to this observation.

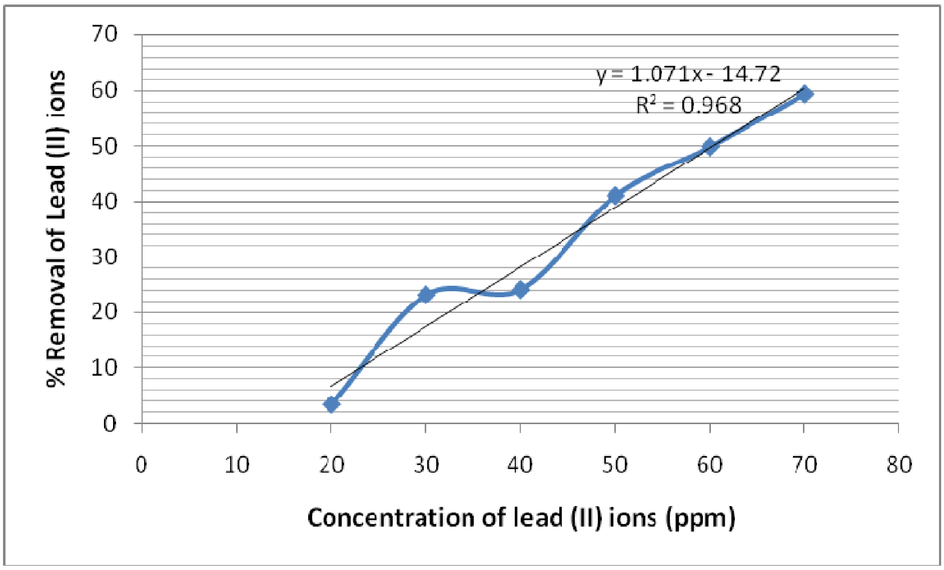

Fig. 4 Removal of Lead (II) ions from aqueous solutions (50 ml, pH 7) with time using Moringa pods (0.5 g) as biosorbent. Agitation time was 3 hours.

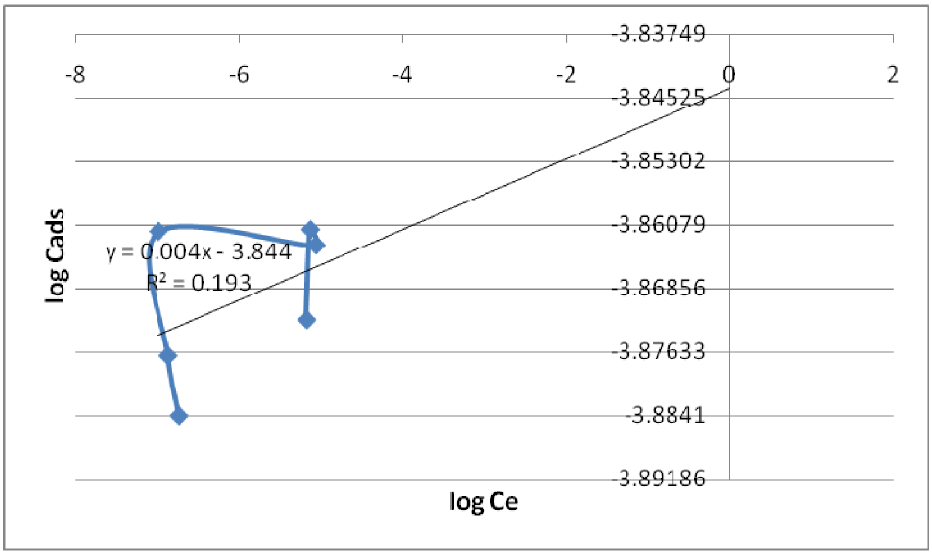

Fig. 5 Freundlich sorption isotherms of Pb^{2+} onto 0.5 g Moringa pods/50 cm^3 of sorbate, 180 min agitation time at pH 7 and room temperature.

Freundlich sorption isotherm is the most commonly used empirical expression describing the sorption from solutions and deals with surface heterogeneity, exponential distribution of active sites of sorbent and their energies towards sorbate [35] and is given in the form of linearized equation below:

$$\log Cads = \log Cm + \frac{1}{n}\log Ce \qquad 4.1$$

where $\frac{1}{n}$ is a characteristic constant related to sorption intensity; C_{ads}, C_e and C_m represent adsorbed amount (mol g^{-1}), residual concentration of sorbate in solution at equilibrium (mol dm^{-3}) and sorption capacity of sorbent (mmol g^{-1}), respectively. It was observed that the adsorption of Pb^{2+} on Moringa pods does not conform to Freundlich isotherm. Fig. 5 presents the observation when the adsorption of Pb^{2+} was checked for conformity with Freundlich isotherm.

The Langmuir model represents monolayer sorption on a set of distinct localized sorption sites having the same sorption energies independent of surface coverage with no interaction and no steric hindrance between sorbed molecules and incoming molecules. The sorption data are also subjected to the following linearized form of Langmuir equation:

$$\frac{Ce}{Cads} = \frac{1}{Qb} + \frac{Ce}{Q} \qquad 4.2$$

Where Q represent sorption saturation capacity (mmol g^{-1}), indicating a monolayer coverage of sorbent with the sorbate, b elucidate the enthalpy of the sorption (dm^3 mol^{-1}), independent of temperature and C_{ads} and C_e are as defined earlier. Result revealed that the adsorption of Pb^{2+} onto Moringa pods does not conform to Langmuir isotherm (Fig. 6).

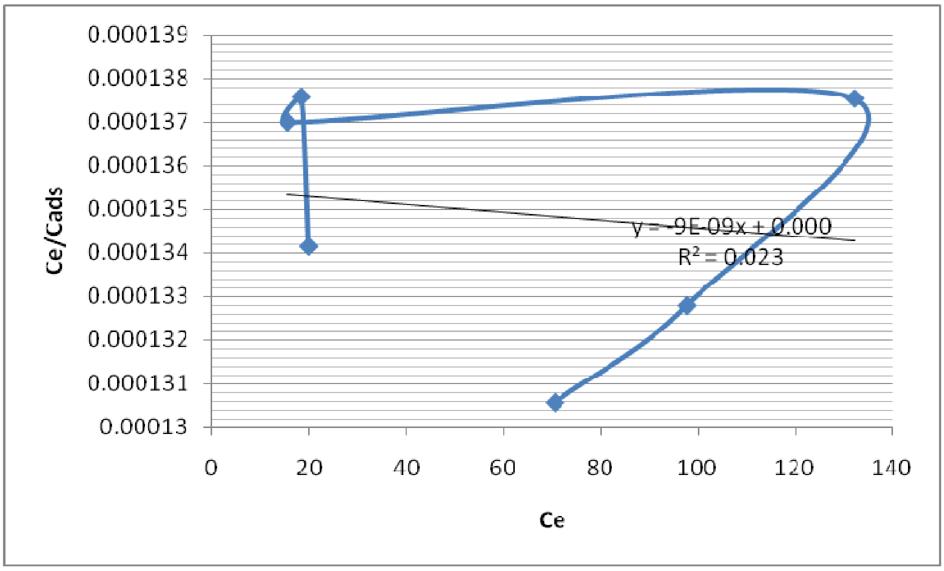

Fig. 6 Langmuir sorption isotherm of Pb^{2+} onto 0.5g Moringa pods/50 cm^3 of sorbate, 180 min agitation time at pH 7 and room temperature

CONCLUSION

The fine Moringa pods were ineffective in removal of Pb^{2+} ions from its aqueous solution. Maximum percent adsorption of Pb^{2+} ions was 48.4%, which is low when compared with adsorption efficiency of other biosorbents, for example, the adsorption efficiency of Moringa bark for Ni (II) is about 98% [29]. The obtained results showed that the biosorption of Lead ions was dependent on experimental parameters, such as contact time, initial concentration, and pH of Pb^{2+} solution. Percent removal of Pb^{2+} was independent of adsorbent dosage used. The adsorption of Pb^{2+} on Moringa pods do not correlate with the known adsorption isotherms.

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