Langmuir and Freundlich Isotherm Models of Defatted Neem Seed Cake on Lead (ll) Nitrate in an Aqueous Medium

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Abstract: - **Defatted neem seed cake was adopted as a material for eliminating lead from the aqueous medium without any modification. Two isotherm adsorption models (Langmuir and Freundlich) were applied to evaluate the models of defatted neem cake adsorption processes.**

Freundlich models strongly supported the adsorption interaction between the adsorbate (lead) and the sorbent (neem seed cake) with a regression correlation of 0.9051 and Langmuir with 0.2472.

Defatted neem seed cake is a promising, cheap and eco-friendly agro material that can effectively be used to remove lead heavy metal from aqueous medium.

Keywords: **Defatted neem cake, Lead, Langmuir, Freundlich, The aqueous medium**

I. INTRODUCTION

Lead is commonly found in tap water significantly from natural sources with domestic plumbing system connections contain lead. Leaching from Polyvinyl chloride (PVC) pipes also contains result in high lead concentrations in drinking water.

The quantity of lead released depends on some factors, such as the presence of pH, dissolved oxygen, Chloride, temperature, water softness and standing time of the water [1,2]

Although lead can be leached from lead piping indefinitely, it appears that the leaching of lead from soldered joints and brass taps decreases with time [3]

Environmental Protection Agency, 1989. Soldered connections in recently built homes fitted with copper piping can release enough lead (210–390 μg/l) to cause intoxication in children [4]

The level of lead in drinking-water may be reduced by corrosion control measures such as the addition of lime and the adjustment of the pH in the distribution system from <7 to 8–9 [5,6].

Lead can also be released from flaking lead carbonate deposits on the lead pipe and from iron sediment from old galvanized plumbing that has accumulated lead from lead sources.

Lead is a cumulative general poison, with infants, children up to 6 years of age, the fetus and pregnant women being the most susceptible to adverse health effects. Its impacts on the central nervous system can be very devastating.

Overt signs of acute intoxication, including dullness, restlessness, irritability, poor attention span, headaches, muscle tremor, abdominal cramps, kidney damage, hallucinations, loss of memory and encephalopathy, occur at blood lead levels of 100–120 μg/dl in adults and 80–100 μg/dl in children. Signs of chronic lead toxicity, including tiredness, sleeplessness, irritability, headaches, joint pain, and gastrointestinal symptoms, may appear in adults at blood lead levels of 50–80 μg/dl. After 1–2 years of exposure, muscle weakness, gastrointestinal symptoms, lower. scores on psychometric tests, disturbances in mood and symptoms of peripheral neuropathy were observed in occupationally exposed populations at blood lead levels of 40–60 μg/dl [7]

Renal disease has long been associated with lead poisoning; however, chronic nephropathy in adults and children has not been detected below blood lead levels of 40 μg/dl [8,9]

Damage to the kidneys includes acute proximal tubular dysfunction and is characterized by the appearance of prominent inclusion bodies of a lead–protein complex in the proximal tubular epithelial cells at blood lead concentrations of 40–80 μg/dl [10].

The carcinogenicity of lead in humans has been examined in several epidemiological studies, which either have been negative or have shown only very small excess mortalities from cancers. In most of these studies, there were either concurrent exposures to other carcinogenic agents or other confounding factors such as smoking that were not considered [11,12]. A study on 700 smelter workers (mean blood level 79.7 μg/l) and battery factory workers (mean blood level 62.7 μg/l) indicated an excess of deaths from cancer of the digestive and respiratory systems [13], the significance of which has been debated [14]. There was also a non-significant increase in urinary tract tumors in production workers. In a study on lead smelter workers in Australia, no significant increase in cancers was seen, but there was a substantial excess of deaths from chronic renal disease [15]. The International Agency for Research on Cancer (IARC) considers that the overall evidence for carcinogenicity in humans is inadequate for lead [16], but that inorganic lead compounds are probably carcinogenic to humans [17].

Some of the most effective methods to remove lead from contaminated water are precipitation stabilization, ion exchange, and adsorption [18]. Most of these methods have drawbacks, such as high capital and operating costs or disposal of metal waste, and are not appropriate for small industries. For these low concentrations of metal ions in wastewater, the adsorption process is recommended for their removal [19]. Activated carbon is one of the most commonly used adsorbents. It is composed of carbonaceous material having a developed porosity, inner surface and a relatively high mechanical strength, which makes it suitable for the removal of heavy metals from wastewater [20].

With respect to these facts, the demands and requests for activated carbon are increasing. Currently, cheap agricultural wastes without or with few modifications and processing are considered promising adsorbents for heavy metals due to their high surface areas, and chemical natures microporous surface character [19]. Moreover, they are cheaper and easily available materials.

Neem defatted cake is the solid residue obtained by pressing the neem seed and fertilizer currently used as natural or processed into a more stable biomaterial [21]

In recent times, these neem seed cakes, both natural and modified, have been tested as biological absorbers for heavy metals [22]. The transformation of this waste into a useful absorbent helps not only the removal of heavy metals from the environment but also to prevent solid waste. Neem defatted seed cake; a biomaterial residue produced by neem oil extraction was adopted as sorbents for lead in an aqueous medium.

II. EXPERIMENTAL

2.1 Neem Sorbents Preparation and Characterizations

The neem seed cake used for this experiment was obtained from Neem laboratory, National Research for Chemical Technology Zaria Kaduna State, Nigeria. It was dried at ambient temperature and grounded with a porcelain mortar and pestle. It was then soaked in n-hexane for an hour to ensure complete oil extraction. It was dried in a vacuum oven at 60ºC for 8h after which a good dryness was achieved.

It was finally washed thoroughly with distilled water, dried at 105ºC for 8h and sieved to obtain the desired particle size (200um) [28]. Ash content, elemental analysis, pH and iodine number, and AAS were determined

2.2 Preparation of pbNo3 solution

10g lead nitrate in a 500ml beaker with 1L of distilled water.

2.3 pH

The pH measurements were made using a HI 9813-5 pH meter with 1g of the sorbent material in 25ml of distilled water.

2.4 Ash content

The ash content of all samples was obtained after burning a given amount of material in the presence of air at 550 ± 25ºC for 3 h and was calculated on a dry basis [23].

2.5 Elemental Analysis

Determination of Nitrogen and carbon contents of the sorbent material using ASTM D5373-93 methods [57]

2.6 AAS

The digested solution was measured by Atomic Absorption Spectrophotometry (Unicam Solaar 939).

2.7 Iodine number

The iodine number is defined in terms of the milligrams of iodine adsorbed by 1 g of material when the iodine equilibrium concentration is 0.01 M [24].

A standard iodine solution (0.05M) is treated with three different weights of material under specified conditions. The amount of iodine adsorbed (in milligrams) per gram of carbon at a residual iodine concentration of 0.01M is reported as the iodine number. [29]

2.8 Sorption isotherms

2.8.1 Langmuir isotherm

The Langmuir adsorption isotherm predicts that adsorption takes place at specific homogeneous sites within the adsorbent, and it has been used successfully for many adsorption processes of monolayer adsorption. The linearized Langmuir equation

is: $1/q_e = 1/q_m + 1/q_m.KL$

Where Ce is the equilibrium concentration of the adsorbate (mg/L), qc is the amount of adsorbate adsorbed per unit mass of adsorbate (mg/L) and q0 and b are Langmuir constants related to adsorption capacity and rate of adsorption, respectively.

2.8.2 Freundlich model

The Freundlich isotherm which is an empirical equation used to describe heterogeneous systems can be expressed in its logarithmic form as:

loge(qc) = logeCe + logekf

Where Kf and 1/n are Freundlich constants related to adsorption capacity and adsorption intensity of the biosorbent respectively. qc is the quantity adsorbed at equilibrium (mg/g), Ce is the equilibrium concentration of the adsorbate (defatted neem seed cake).

III. RESULTS AND DISCUSSION

3.1 Table 1. Physico chemical and elemental compositions of defatted neem seed cake.

Parameter	Neem Cake
pH	6.4
Ash content (%)	14
C (%)	41
N (%)	4.5
Iodine Number (mg/l)	140
Ca (%)	2.4
Mg (%)	0.7
K (%)	1.5
Fe (ppm)	875
Mn (ppm)	40
Zn (ppm)	55
Cu (ppm)	15.7
P (%)	0.6
S (%)	0.8

Results above present the defatted neem cake to be acidic in pH which is a justification for chains of organic acids embedded in this biomaterial. The ash content is indicative of its richness in plant nutrient. Iodine number has a significant amount of value which means the level of c-c unsaturation of this material. This is a good advantage as a biosorbent material as it is a relative indicator of porosity in a carbonaceous material [25].

It varies with changes in carbon raw material, processing conditions, and pore volume distribution [25]. As iodine number gives an indication on micro porosity (pores less than 1 nm in diameter), higher iodine numbers reflect better development of the micro porous structure and higher adsorption abilities for low-molar-mass solutes [26, 27]

3.2 Sorption isotherms

3.2.1 Langmuir isotherm

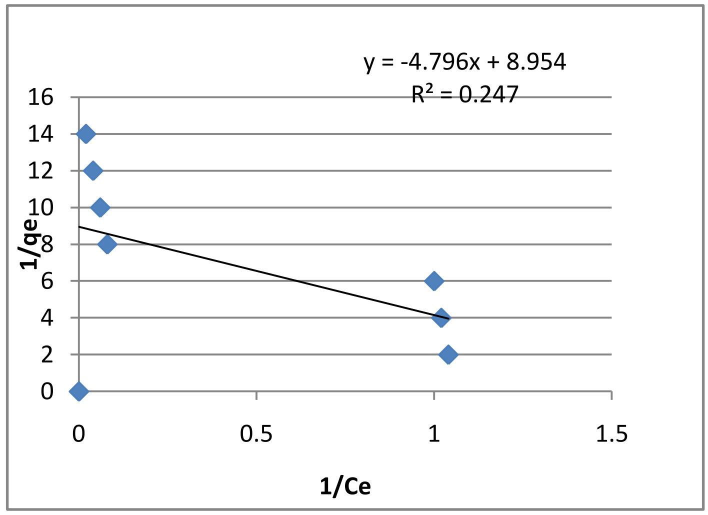

Figure l. Langmuir isotherm of defatted neem seed cake against lead (Pb) in an aqueous medium

The plotting does not give straight line meaning that, the adsorption of lead with defated neem seed cake does not comply with the Langmuir model of adsorption. In other words, this might imply that the sorption mechanism is not a homogenous distribution of the adsorbate on the surface of the neem cake. The correlation value of R2 (0.2472) indicated the type of isotherm to be unfavorable (RL>1).

3.2.2 Freundlich model

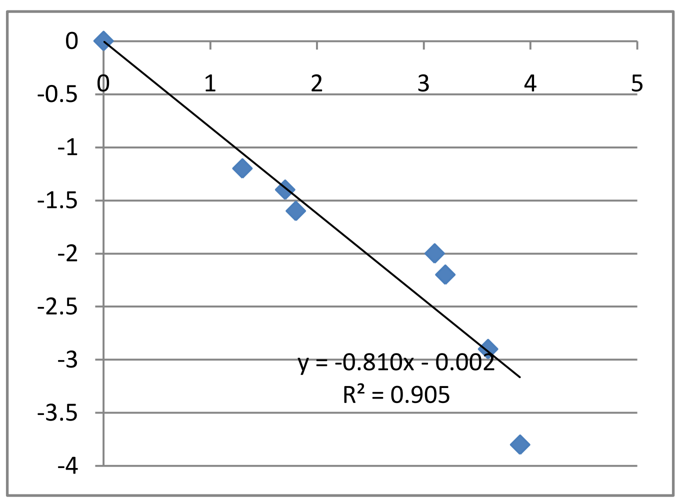

Figure ll. Freundlich adsorption isotherm of defatted neem seed cake against lead (Pb) in an aqueous medium

The plot of log qc against logCe provides a straight line with correlation coefficients of 0.9051 showing that the sorption of lead strongly obeys the Freundlich isotherm more than that of the Langmuir isotherm.

3.2.3 Estimated isotherm constants

Model	Slope	Intercept	R^2	n	q_o	K	R_L
Langmuir	-2.17391	8.954501	0.2472		0.1117	0.46	0.3030
Freundlich	-2	-0.0023	0.9051	-0.5		434.78	

IV. CONCLUSIONS

Application of naturally defatted neem seed cake as bio-sorbents is a viable, friendly, cheap and efficient approach. Iodine number strongly reveals that the material is suitable for sorption processes.

Freundlich model strongly supported the adsorption mechanism of this material which means that, the adsorption process is a relationship between the sorbent material and the lead nitrate solution.

Langmuir isotherm did not support the interaction between these two phases (neem cake and lead nitrate solution).This approach declares that the process is potentially profitable. The wasted and defatted cake form the oil extraction processes seem to have limited applications only to animal feeds and with the challenge of disposal. In order to minimize these limitations, the development of economical and cheap technologies that can reuse these residues should be encouraged.

V. RECOMMENDATION

Further works are necessary to study the kinetics, the sorption capacities, factors that control the adsorption processes and other models of adsorption should be exploited.

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