

AN EFFICIENT TECHNIQUE OF REMOVING Pb^{2+} IONS FROM WATER USING LEFTOVER COCONUT SHELL

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Abstract

Each country's industrial, agricultural, and technical growth depends on metals and their compounds. With the advancements in contemporary science and technology, there are more and more uses for metals in industry. One of the heavy metals that are frequently found in industrial wastewater is lead, and because it is hazardous to both aquatic and terrestrial life, its release into the environment poses a severe risk. Lead is a hazardous pollutant that has negative effects on the health of people, animals, and plants. This research looked at the adsorption of lead (II) onto activated carbon made from used coconut shells and activated using potassium hydroxide. The starting lead (II) concentration used for the adsorption research was 10–50 mg/l, and the temperature range used was 10–50 °C. The difference in the concentration was studied by Ultrasonic studies.

Keywords: coconut shell, lead, activated carbon.

Introduction

Each country's industrial, agricultural, and technical growth depends on metals and their compounds. With the advancements in contemporary science and technology, there are ever more uses for metals in industry [1]. One of the heavy metals that is frequently found in industrial wastewater is lead, and because it is hazardous to both aquatic and terrestrial life, its release into the environment poses a severe risk. Lead is a hazardous pollutant that has negative effects on the health of people, animals, and plants. Lead negatively impacts the cardiovascular, neurological, gastrointestinal, reproductive, immunological, renal, skeletal, and muscular systems. Lead has a great affinity for and forms complexes with many bio molecules. In 1998, Johnson [2] reported that lead can cause cancer, birth defects, enzyme inhibition, and aberrations in DNA synthesis and mutation. Lead exposure to children has been associated with impaired cognitive skills [3], intellectual impairment [4], reduced mental IQ and quantitative skills [5], mild mental retardation and cardiovascular disease [6]. Chronic exposure of adults to lead can lead to neurological, reproductive system, and liver damage [7]; reduced cognitive function [8], and kidney disease [9]. Sadly, lead contamination from various sources is a global problem and represents a serious threat to soil, water, and air with a potential for propagation into the food chain. Thus, our global village is in need of innovative and cheap technology for the amelioration of lead contamination. Presently, several technologies exist for the remediation of lead contaminated soil [10-12] and they include a) excavation and bury in landfills; b) capping; c) subsurface barriers; d) *in-situ* and *ex-situ* precipitation, solidification stabilization; e) washing and f) biological treatment such as vermiremediation [13], phytostabilization, phytodegradation or transformation, Phytochelation, and phytoextraction [14-17]. Adsorption of metal ions by several functionalized polymers based on amines derivatives such as ethylenediamine, polyacrylamides, poly-4-vinylpyridine, polyethyleneimine and aniline formaldehyde condensate has been reported. Polypyrrole was used in the removal of fluoride ions from aqueous solution by conducting Polypyrrole. Conductive polymers such as polyaniline, polypyrrole, and polythiophene, have attracted so much research interest in wide range applications such as rechargeable batteries, electromagnetic interference (EMI) shielding, antistatic coatings, gas sensors, optical devices and removal of heavy metals (Reyad 2015) [18]. Activated carbon is one of the most popular adsorbents for the removal of metal ions from aqueous solutions. Currently, activated carbon is widely used as an adsorbent in wastewater treatments. It has highly developed porosity, a large internal surface area, and relatively high mechanical strength. Despite its widespread use in industries, activated carbon remains an expensive material. Therefore, it is necessary to investigate and develop low-cost effective carbons that can be applied to water pollution control. The properties such as surface charge, type of surface functional groups, specific surface area, and pore-size distribution affect the adsorption capabilities of metal ions on activated carbon. All above mentioned physical and chemical properties of activated carbon depend on the precursor materials and activation methods used.

Materials and methods

All the chemicals and equipments used were of standard quality. Essential materials and equipments required for given analysis in the laboratory were as follow:

1. Selection of Granular Activated Carbon Treatment of adsorbents and its characterization.
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2. Preparation of solution of lead ion and its estimation.
3. Construction of Calibration curve.
4. Selection of surfactant and preparation of solution.
5. Experimental set up for the study of adsorption isotherm on Granular Activated Carbon (GAC).
6. Study of adsorption of lead ion on Granular Activated Carbon (GAC).
7. Study of adsorption of lead ion on surfactant loaded Granular Activated Carbon (GAC).

i) Selection of Granular Activated Carbon

a) Collection of Samples and materials

Coconut fruits were bringing in large quantity from temple. The fruits were transported to the laboratory for immediate use. The coconut fruits were sorted out to obtain coconut shells (endocarps) which were thoroughly washed with water to remove dirt/ unwanted parts and dried very well in an oven at 105°C for one hour

b) Carbonization/Activation of Samples

The coconut shells samples were carbonized in the muffle furnace at optimum DE volatilization temperature of 300°C for 1hour according to the method reported elsewhere. They were ground into powder; pass through 0.22mm mesh size. The chemical activated was carried out on the carbonized samples. A weighed quantity of 10g each of the activating agents of CaCO₃, KOH, H₃PO₄ and ZnCl₂ were used.

ii) Treatment of adsorbent and its characterization.

After size fractionation the selected carbon was first washed by hot distilled water several times until a clear visible liquid was obtained. Then distilled water was drained off and GAC was transferred to a Petridish. Carbon was air dried properly to remove all the moisture on the surface of carbon and from pores of carbon. It was kept in an oven at temperature range 100-110°C for 6 hours and then cooled GAC was placed in desiccators containing CaCO₃. To ensure it the carbon sample was in equilibrium with the surroundings, 0.5gm of the carbon sample which was kept in a weighing bottle in the same desiccators and its weight was monitored over a period of one week until it shows constant weight.

iii) Preparation of Solution of Lead ion and its estimation. Preparation of solution

The preparation of lead ion solution needed extensive care. Distilled water used for the preparation of lead ion solution was obtained a fresh to avoid even slight traces of metal ions that could interfere in subsequent work. Standard solution of Lead nitrate (Loba make) was prepared by dissolving 1.656 gm in distilled water. It was then standardized with EDTA.

a) Estimation of Lead ion (Pb²⁺)

A standard solution of the lead solution was taken for estimation. In 10 ml of the solution, 2-3 drops of Xylenol Orange indicator were added. At this stage the color of solution was changed to yellow. Then powdered Hexamine was added with continuous shaking until the deep red color was restored (pH =6). Such an addition improved the end point. The solution was titrated with standard EDTA solution until the color changed from red to yellow orange at the end point.

iv) Construction of calibration curve.

Calibration Curve using Beer's law is a general method for estimating the concentration of a metal in an unknown sample by comparing the unknown with standard samples of known concentration at constant temperature. For the construction of calibration curve ten systems of known concentration of metal ion were prepared and their respective absorbance values were determined by UV-Visible Spectrophotometer. Calibration curve was obtained by plotting concentrations versus the absorbance which gave an equation of straight line, from which concentrations of lead were estimated. For calibration curve ten systems containing different concentration of Pb²⁺were prepared 1ml NaOH (2 N) and 2 ml alizarin red solution were added in each system. These solutions were diluted to 50 ml and absorbance measured at 475 nm wavelength against a blank taken carefully in 1 cm path length matched glass cuvette using UV-Visible Spectrophotometer. The Beer's law data are given in (Table .2) and regression analysis of the data of absorbance verses amount of lead in solution gave a working equation which was used in all experimental work subsequently. The equation given in Table 2 was used for the measurement of initial and final concentrations of Pb²⁺ ions.

v) Selection of surfactant and preparation of solution.

The GAC surface was modified by surfactant namely Sodium Dodecyl Sulphate.

(a) Surfactant (Sodium Dodecyl Sulphate)

A sample of sodium Dodecyl Sulphate (S .D. F. C. Ltd., India) of purity greater than 99% was purified by routine method. Its melting point was determined (205.5°C) and compared with the literature value (206°C).

(b) Preparation of Surfactant solution.

SDS is sparingly soluble in water [5]. For the preparation of the 0.001 M solution 0.5767 g of SDS compound was transferred to 2000 ml round bottom flask and volume was made up to the mark by warm distilled water. The entire solution was stirred to get a clear and homogeneous solution. This solution was used as a complexing agent in the process of loading of GAC.

vi) Experimental set up for the study of adsorption isotherms on Synthesized Activated Carbon.

To get appropriate results of adsorption isotherms proper arrangement of experimental set up was essential. All the adsorption isotherms were carried out at a fixed temperature of $25^{\circ}\text{C} \pm 1^{\circ}\text{C}$ and as far as possible over at fixed intervals of time. For this, a water bath was used to maintain constant temperature of solution. Mechanical shaker (Etek Motor, Type M 56. Elektrocrats India, Pvt. Ltd. Mumbai) was used as a stirrer. An acrylic rod 10 cm long with a paddle (2 cm x 1 cm) attached to the stirrer was used to agitate the experimental solution. For agitating the solution reagent bottles of 300 ml capacity were used.

vii) Study of adsorption of Lead ion on Synthesized Activated Carbon.

For batch experiments ten stirring arrangements were operated at a time. Each system was operated at a fixed temperature i.e. $25^{\circ}\text{C} \pm 1^{\circ}\text{C}$ and for a fixed time. It consisted of clean and similar shaped reagent bottles of 300 ml capacity. As described above the stirring rods of 10 cm length attached to the stirrer were used. Complete adsorption study was dependent on GAC. Hence all types of carbon were weighed carefully. 0.5 g GAC was transferred to each of the ten reagent bottles. 200 ml of experimental lead solution pH =6 was carefully introduced in to the each reagent bottle. All the ten reagent bottles and stirrer were kept in the water bath. The whole arrangement was stirred at a desired bath temperature for 5 hours. After achieving the equilibrium final concentration of solution was estimated spectrophotometrically. Ten such systems of different concentrations were arranged. The equilibrium concentration of the lead on the carbon was obtained from the expression.

q_e = Concentration of lead ion on GAC in mg/g;

C_o = Initial concentration lead ion in solution in mg/L,

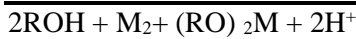
C_e = Final concentration of lead ion in solution in mg/L; V = Volume of solution in liters; W = Weight of GAC in gm. (0.5 gm)

Plots of q_e verses C_e then represented a typical adsorption isotherm for the lead ion on GAC. These adsorption isotherm data are given in the table.

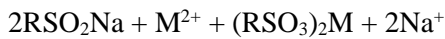
Results and Discussion

Mechanism of Pb^{2+} adsorption

Acidic functional groups hide heavy metals ions mainly by adsorption For this reason attempt was made to increase the total quantity of surface functional groups and to make the surface charge more favourable for adsorption of cationic heavy metals In this study, impregnation of GAC with anionic surfactants (SDS) reduced its total acidity and increased its total basicity. This result means that these anionic surfactants successfully covered the surface of the GAC. Specifically, total acidity of the activated carbon was decreased because the surfactants covered surface acidic groups, especially carboxylic groups. Meanwhile, the hydrophilic head(s) of the surfactants can act as basic functional groups. In aqueous solutions, the bound anionic surfactants can be dissociated, and then the protons bind to the hydrophilic head(s), resulting in the increase of the GAC's total basicity. Anionic surfactant is bound to activated carbon by a hydrophobic reaction in which hydrophobic alkyl chain(s) of the surfactant interact with the non-polar portion(s) of the activated carbon's surface. The investigations on the surface functional groups of the SDS revealed that their enhanced adsorptive capacity was due to the negatively charged groups in the hydrophilic head of the anionic surfactant. These groups made the surface charge of the activated carbon more negative, resulting in more favourable conditions for $\text{Pb}(\text{II})$ adsorption. Therefore, we conclude that surface modification method using anionic surfactants can be used to enhance the capacity of activated carbon to adsorb cationic heavy metal ions. The surface charges of activated carbons impregnated with anionic surfactants were negative because the hydrophilic negatively charged head groups of the surfactants are arranged toward the aqueous phase. Therefore lead ions can easily bind to negatively dissociated forms of the surfactant's active groups and can form complexes with its surface groups, as indicated in following equation



Because activated carbon is highly hydrophobic, exterior molecules with hydrophobic groups can be strongly bound to its surface by the Vander wall interaction and then can influence the characteristics of activated carbon's surface. In anionic surfactant long (hydrophobic) alkyl chain binds to the surface of the activated carbon while its negatively charge (hydrophilic) head group is arranged toward the surrounding water. As a result of this the hydrophilic part of the surfactant contributes a large quantity of anionic functional group to the SDS. For this reason, the capacity of activated carbon to adsorb positive ion increases.



Adsorption Isotherm of Pb^{2+} on Surfactant Loaded GAC.

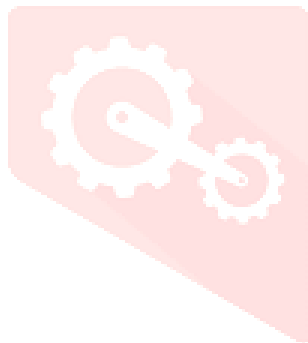
The process of adsorption is usually studied through an adsorption isotherm. It is the plot between the amounts of adsorbate adsorbed on the surface of adsorbent at constant pressure and temperature. The adsorption isotherms of Lead on plain GAC and loaded with surfactant namely, SDS on the grades of carbon i.e F-100, N - 1240 were obtained as described in the previous chapter. Keeping in view the objectives of the present work the apparent adsorption isotherms were determined at constant temperature. The reproducibility of each experimental point on the adsorption isotherm was checked in a few cases in order to ensure reliability of the experimental values. At the stage of equilibrium between the solute in the solution and solute on the carbon, there is the definite distribution of the adsorbate between the solution and the solid phase which is a measure of the position of equilibrium in the adsorption process. A relation between these two quantities at constant temperature is called an adsorption isotherm. Several types of isothermal adsorption relations may occur and the most common being where adsorption leads to the accumulation of an apparent single layer of Lead atoms on the surface of the adsorbent. The Langmuir adsorption model is valid for such types of adsorption while for multi-molecular adsorption more complex adsorption models are considered. Figures indicate equilibrium adsorption isotherms i.e. the plots of q_e vs C_e were plotted for different grades of Granular Activated Carbon. The amount of lead on the surfactant adsorbed GAC was determined using the equation 1.

q_e = Concentration of lead ion on the surfactant loaded GAC in mg/millimoles
 C_o = Initial concentration lead ion in solution in mg/L.

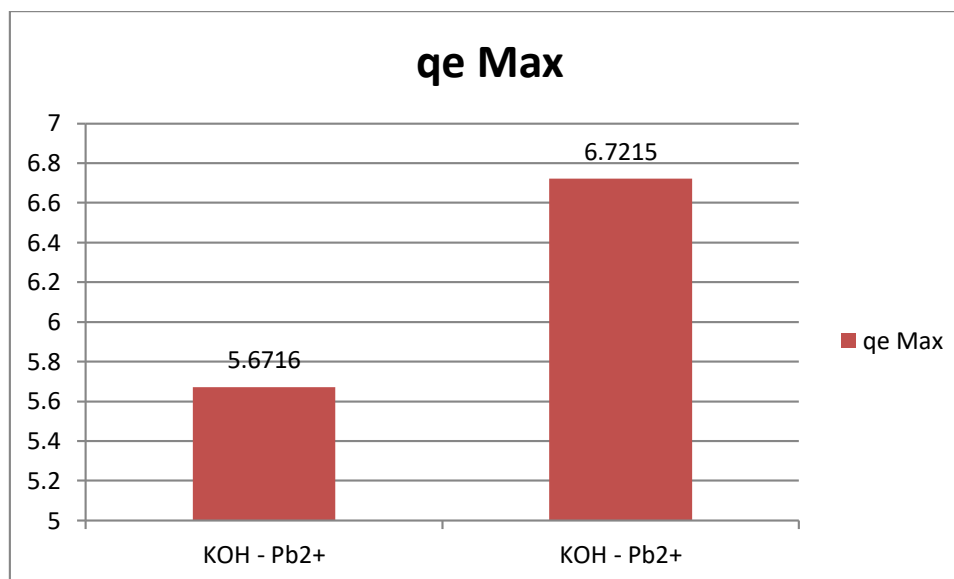
C_e = Final concentration of lead ion in solution in mg/L.

V = Volume of solution in litres.

W = Millimoles of the surfactant actually present on GAC (0.5 g).



The comparative adsorption capacities (saturation values of q_e) of lead on loaded and unloaded grades of granular activated carbon used in the present investigation and are reported in the following:



From this, q_e max values for the systems show the following trend.

N-1240 > KOH

The Langmuir treatment is based on the assumption that maximum adsorption corresponds to a standard monolayer of adsorbate molecules on the adsorbent surface, that the energy of adsorption is constant and there is no transmigration of adsorbate in the plane of surface. Langmuir equation in terms q_e and C_e could be expressed as follows

Where,

Q_0 = Amount adsorbed per unit weight of the adsorbent forming a complex monolayer on the adsorbent surface in mole/gm.

C_e = Equilibrium concentration of adsorbate solution in mole/L.

q_e = Amount of adsorbate adsorbed per unit weight of adsorbent in mole/gm.

b = Langmuir constant.

Rearranging the above equation

The linearity in the plot of $\frac{q_e}{C_e}$ versus $\frac{1}{C_e}$ shows the validity of Langmuir model. The surface area of the adsorbent can be determined using values of Q_0 . However it must be cautioned that the Langmuir equation may not always be strictly valid over the range of concentration used in the present study and only a mathematical analysis of the experimental data would validate this point. The above equation is helpful in determining the surface area occupied by the Lead ion under the present experimental conditions. This is done by using the isothermal equilibrium data by determining the monolayer capacity of the adsorbent expressed in mole/gm of GAC and related to the monolayer capacity factor by the following equation.

Where,

S_1 = Surface area, m^2/gm .

N_a = Avogadro number.

A = Cross sectional area of the adsorbate ion, m^2 .

Since the value of Q_0 can be obtained from Langmuir plots, the value of S_1 for any particular GAC sample can easily be calculated. The parameters Q_0 and b are Langmuir constants relating to the sorption capacity and adsorption energy respectively. The intercept and slope of the linear plots of $\log q_e$ vs $\log C_e$ and of $1/q_e$ vs $1/C_e$ under given set of experimental conditions provide values of k , $1/n$, Q_0 and b respectively. The high value of regression correlation coefficient (R^2) as observed which indicates a good agreement between the experimental values and isotherm parameters and also confirms the monolayer adsorption of Pb^{2+} ion on the surface of Granular Activated Carbon. The corresponding Freundlich, Langmuir constants and regression correlation coefficient (R^2) obtained are listed in Table 5.

An empirical equation given by Freundlich is often useful and generally agrees well with the Langmuir equation and experimental data over moderate range of adsorbate concentrations. The equation is-

Where, q_e and C_e have same importance, K and β are constant. Rearranging, it can be written as:

Where a plot of $\log q_e$ versus $\log C_e$ should be linear bring out the validity of the Freundlich equation over range of concentrations. The data for both the Freundlich and Langmuir equation are given in Table. For adsorption of Pb^{2+}

linear plots were obtained over the range of concentrations used for adsorbate. It can be concluded that both the Langmuir and Freundlich adsorption equation are applicable in almost entire range of concentrations used in the present work. Langmuir and Freundlich isotherms are given in bring out this aspect. In the calculation of specific area occupied by lead on the surfactant loaded GAC, values of A were obtained using the relation suggested by Brunauer and Emmett

M = Atomic weight of the Lead

N_a = The Avagadro number

D = the density of the Lead

The value of A was calculated i.e. $1.0613 \times 10^{-15} \text{ cm}^2$.

When the surface of adsorbent is saturated with monolayer of lead ion, the values of the surface area occupied by lead on the GAC could be roughly assessed by utilizing the values of $q_e \text{ max}$ using the relation.

On substituting the value of $q_e \text{ max}$ (6.7215) for a system, N- 1240 - SDS - Pb^{2+} , in equation 8, the value of S calculated as $S=8.2940 \times 10^3$. Similarly by plotting $1/q_e$ versus $1/C_e$ which gave a linear plot the value of q_e when a monolayer of Lead ion is formed on the surface one could also assess the surface area S_1 from the Langmuir model. On Substituting q_e (6.9013) obtained from linear plot of $1/q_e$ versus $1/C_e$ for system N- 1240 the value of S_1 calculated as $S_1= 8.5159 \times 10^3$

These values are given in Table B and both S and S_1 are found to be comparable. The Table B also clearly shows the fact that surface area of the GAC samples S and S_1 obtained from $q_e \text{ max}$ and Q^0 respectively is much smaller compared to area of the GAC samples supplied by the manufacturer. This is obviously clear that the lead ion is inaccessible to the inner pore in view surface groups hindering the diffusion of the Lead ion to the inner pores.

Table 2: Values of $q_e \text{ max}$, S, Q^0 and S_1 for GAC

S.no	System	$q_e \text{ max}$	S (cm^2/gm)	Q^0	$S_1(\text{cm}^2/\text{gm})$
1	F-100 - SDS - Pb^{2+}	5.6716	6.9985×10^3	8.1300	10.0320×10^3
2	N-1240 - SDS- Pb^{2+}	6.7215	8.2940×10^3	6.9013	8.5159×10^3

Table 3: Weight of Carbon F-100

S.No	Time	Weight of carbon
1	0 min	0.5004 g
2	15 min	0.4956 g
3	30 min	0.4885 g
4	45 min	0.4756 g
5	60 min	0.4771 g
6	75 min	0.4771 g
7	90 min	0.4771 g

Conclusion

Adsorption by granular activated carbon is a very effective technique for the removal of these toxic metals from wastewater as seen from literature studies in recent years. The following are some of the important aspects of the present investigation.

1. The surfactant selected in the present investigation are adsorbed favourably on the grades of GAC namely F and N- 1240.
2. The adsorption study clearly showed that the SDS adsorbed strongly on the GAC surface.
3. The result indicates that most of the acidic groups on the GAC surface were not active ones capable of interacting with $\text{Pb}(\text{II})$ ions. The impregnation with SDS can provide the activated carbon with active functional group.
4. The capacity of GAC to absorb $\text{Pb}(\text{II})$ was significantly increase due to impregnation with SDS.
5. The investigation on the surface functional groups of GAC revealed that the enhanced adsorptive capacity was due to the negatively charge groups in the hydrophilic head of the anionic surfactant.
6. The adsorption of Pb^{2+} ion from aqueous solution on to Granular Activated Carbon confirms to a Langmuir equation based on a monomolecular layer.

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