ADSORPTION OF Pb(II) FROM AQUEOUS SOLUTIONS BY ACTIVATED CARBON PREPARED FROM AGRICULTURAL WASTE: MAIZE LEAVES

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Adsorption of Pb(II) from the aqueous solutions was studied using activated carbon prepared by agricultural waste maize leaves. The influence of Pb(II) concentration (5-30 mg L^{-1}), pH (2-8) and contact time (0-120 min.) on adsorption have been reported. Adsorption of Pb(II) is pH dependent and the results indicate that, optimum pH for the removal was found to be 4 for maize leaves activated carbon (MLAC). The Freundlich and Langmuir isotherm models were also used to describe the adsorption of Pb(II) on MLAC. Results shows that both the isotherms were fitted well. Maximum adsorption of lead on MLAC attained was 96 %. The results suggest that MLAC can be used as adsorbent for the removal of Pb(II) from aqueous solutions as industrial wastewater.

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Introduction

Heavy metals present in drinking water sources and in agricultural crops can be harmful to human. Heavy metals can be toxic, e.g. they damage nerves, liver and bones and they block functional groups of vital enzymes.[1] Various chronic disorders in human beings caused by all heavy metals including lead.[2] Lead poisoning in humans causes severe damage to the kidneys, nervous system, reproductive system, liver and brain and can cause death. Severe exposure to lead has been associated with sterility, abortion, stillbirth and neonatal death.[3] Permissible limit for lead in drinking water given by U.S.Environmental Protection Agency (U.S. EPA) is 0.015 mg L^{-1} and for wastewaters is 0.1 mg L^{-1}, given by both the U.S. EPA and Bureau of Indian Standards (BIS).[4] The main anthropogenic pathway through which heavy metal enters the water bodies is via wastes from industrial processes such as metal plating, mining operations, tanneries, chloralkali, radiator manufacturing, smelting, alloy industries and storage batteries industries, etc.[5] Current treatment methods for the removal of metal ions from wastewater includes mainly reduction, ion exchange, electrodialysis, electrochemical precipitation, solvent extraction, reverse osmosis, chemical precipitation and adsorption.[6] Most of these methods suffer from drawbacks such as high capital and operational costs or the disposal of the residual metal sludge.[7] For example, precipitation processes cannot guarantee the metal concentration limits required by regulatory standards and produce wastes that are difficult to treat. On the other hand, ion exchange and adsorption processes are very effective but require expensive adsorbent materials for the removal of heavy metals from dilute aqueous streams. The use of low cost and waste materials of biological origins as adsorbents of dissolved metal ions has been shown to provide economic solutions to this global problem. Adsorption of heavy metal ions on to activated carbon has been applied widely as a unit operation in the treatment of industrial wastewater. The use of commercial activated carbon may not be suitable for developing countries because of its high cost; therefore there is a need to produce activated carbon from cheaper and readily available materials, which can be used economically on a large scale. Activated carbon prepared from the rice husks, ground nut husks, coconut husks, waste fertilizer slurry, peanuts hull, jute stick, *Moringa oleifera* seed husk, coconut husk and sawdust have been used for wastewater treatment and the potential of their ultimate usage are determined through by their adsorption capacity, regeneration characteristics and physical properties of the subsequent products.[8,9] Activated carbon with their large surface area , microporous character and chemical nature of their surface area have made them potential adsorbents for the removal of heavy metals from industrial wastewater.

In this study activated carbon prepared from agricultural waste *Zea mays* leaves was used for the adsorption of Pb(II) from aqueous solution on batch scale. The performances of adsorption of Pb(II) have been predicted using Freundlich and Langmuir equilibrium isotherms. The objective of present endeavor, therefore, is to study the adsorption behavior of Pb(II) onto maize leaves activated carbon (MLAC), an economic viable and easily available adsorbent.

Experimental

Adsorbent preparation

The maize leaves used in this study was harvested from the agricultural farm in the Kaushambi, near by 60-70 km away from Allahabad, was washed several times with deionized water and left to dry. The activated carbon was prepared by treating maize leaves with concentrated sulphuric acid (1:1 w/v). The resulted black material was activated in an air-free oven at 160 ± 5 °C for 6 h, followed by washing with deionized water until free of excess acid and MLAC was dried at 160 ± 5 °C.[10] The activated carbon prepared from agricultural waste maize leaves was ground and sieved to 100 mesh and then stored in air tight container.

Reagents

Analytical grade of Pb $(NO_3)_2$(Qualigens) was used for making stock solution of Pb(II) (1000 mg L^{-1}) in deionized water. The stock solution was diluted by serial dilution method as per requirement. The initial pH of the solution was adjusted by using either 0.1 N NaOH or 0.1 N H_2SO_4.

Batch adsorption experiments

Batch experiments with maize leaves activated carbon (MLAC) were conducted to investigate using a certain amount of adsorbent and 50 mL solution of Pb(II) ion solution in a conical flasks. The mixture was shaken in an orbital shaker (Shivam, ISO, 900/2000) at 120 rpm at 30°C for 24 h. The following operation conditions such as pH, contact time and metal concentration were investigated. Then the solution was centrifuged and the residual concentration of Pb(II) ion in supernatant was determined by atomic absorption spectrophotometer (ECIL-4141, Hyderabad).

The effect of pH on the biosorption of Pb(II) by MLAC was determined at pH values of 2, 3, 4, 5, 6, 7and 8. For the adsorption 0.5 g of MLAC was added to 50 mL solution of Pb(II) ion (at 30 mg L^{-1}) in seven different flasks at pH ranging from 2-8 .The mixture was shaken in an orbital shaker at 120 rpm at 30°C for 24 h. The supernatant was analyzed for residual lead after contact period.

For the determination of rate of the metal adsorption by MLAC (0.5 g) were mixed with 50 mL Pb(II) ion solution at concentration of 30 mg L^{-1}, The mixture was shaken in an orbital shaker at 120 rpm at 30°C .The supernatant was analyzed for residual lead concentration after the contact period of 0, 5, 10, 20, 25, 30, 40, 60, 80, 100, and 120 min.

In order to investigate the effect of different initial metal concentration on the uptake of lead from aqueous solution, 0.5 g MLAC were mixed with 50 mL Pb(II) ion solution at concentration of 5, 10, 15, 20, 25, 30 mg L^{-1}. , The mixture was shaken in an orbital shaker at 120 rpm at 30°C for 24 h.The supernatant was analyzed for residual lead concentration after the contact period.

Calculations

The percent removal of Pb(II) ion by MLAC was calculated by using the Eqn. 1.

$$R(\%) = \frac{C_i\text{-}C_f}{C_i} \times 100 \qquad (1)$$

where, R is the removal, C_i is the initial metal concentration and C_f is the final concentration of the metal ion in mg L^{-1}.

The sorption capacity was calculated from Eqn. 2

$$Q_e = \frac{V(C_i - C_e)}{1000W} \qquad (2)$$

where, Q_e is the adsorption capacity (mg g^{-1}), C_i is the initial metal concentration (mg L^{-1}), C_e is the equilibrium concentration of metal (mg L^{-1}), W is the adsorbent dose (g) and V is the solution volume (mL).

Fourier Transform Infrared Spectroscopy

FT-IR spectroscopy was used to determine the vibration frequency groups in the adsorbent. The spectra was collected using a model (ABB, Canada; FTLA; 2000,) with in the wave-number range 500-4000 cm^{-1}. Specimens of adsorbents were first mixed with KBr and then grounded in an agate mortar (Merck,) at an approximate ratio of 1/100 for the preparation of pellets. The resulting mixture was pressed at 10 tons for 5 min. These pellets are used in the recording of spectra.

Results and Discussion

Effect of pH

The adsorptive behavior of Pb(II) ion was studied from the aqueous solution at different pH values are the principle factor influencing the adsorptive capacities of Pb(II) ion on MLAC. The removal of lead from the solutions presents several difficulties, mainly due to the fact that a precipitation process is not possibly by simple pH regulation of the solution as in the case of polyvalent metallic cations.[11] The result obtained are shown in figure-1, which shows the effect of pH on the adsorption of Pb(II) ion from the aqueous solution on MLAC. It is clear that Pb(II) ion was effectively adsorbed in the pH range of 4-7 and the maximum adsorption of ion MLAC occurred at pH 4 thus, pH 4 is chosen for all experiments. The decrease in adsorption at pH greater than 7 is probably due to the formation of hydroxide. This is in agreements with the results obtained by Khalid *et al*.[12] for adsorption of lead on rice husk. The hydrolysis of cations occurs by the replacement of metal ligands in the inner coordination sphere with the hydroxyl groups.[13] This replacement occurs after the removal of the outer hydration sphere of metal cations. Adsorption may not be related directly to the hydrolysis of the metal ion, but instead of the outer hydration sphere that precede hydrolysis.
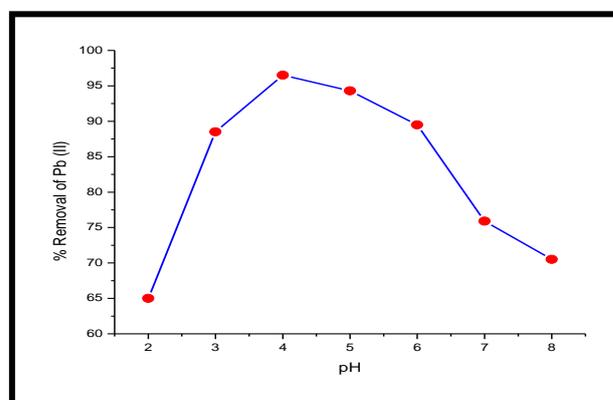

Figure 1: Effect of pH on Pb(II) removal

Most probably, the removal of lead from the aqueous solution by activated carbon involves a complex mechanism which is partly controlled by adsorption and partly by the chemical precipitation at the solid solution interface and also partly by the pore filling mechanism.[14]

Effect of contact time

The effect of contact time on the adsorption of lead is shown in Fig. 2. The results indicated that increase in the contact time increased the metal uptake but remained constant after an equilibrium time. The uptake of lead was rapid and the equilibrium was attained in 30 min of contact between the biosorbent and metal solution.
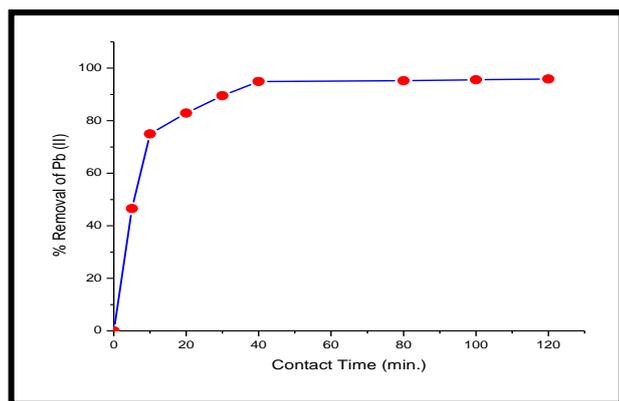

Figure 2. Effect of contact time on Pb(II) removal

Adsorption models

Modeling of equilibrium data is fundamental for the industrial application of adsorption since it gives information for comparison among different adsorbent under different operational conditions, designing and optimizing operation.[15]

The adsorption data were applied to the isotherm models.[16,17] The adsorption isotherms generally used for the design of adsorption system. The Langmuir and Fruendlich equations are commonly used for describing the adsorption isotherm.
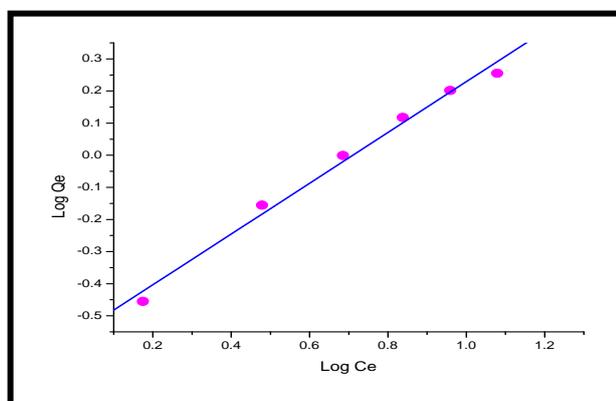

Figure 3. The linearized Freundlich adsorption isotherm of Pb(II) using maize leaves carbon

The adsorption data have been fitted to the Freundlich isotherm. Its linearised form is represented by equation.

$$\lg Q_e = \lg K + \frac{1}{n} \lg C_e \tag{3}$$

where, C_e is the equilibrium concentration (mg L^{-1}), Q_e is the amount adsorbed (mg g^{-1}) K is adsorption capacity and $1/n$ is adsorption intensity. A plot of log Q_e versus log C_e gives a straight line of slope $1/n$ and intercept K is shown in Fig. 3.

The linear equation of Langmuir represented as equation.

$$\frac{C_e}{Q_e} = \frac{1}{Q_{max}b} + \frac{C_e}{Q_{max}} \tag{4}$$

where, C_e is the metal concentration in the solution at equilibrium (mg L^{-1}), Q_{max} (adsorption capacity) and b (energy of adsorption) are the Langmuir constants.
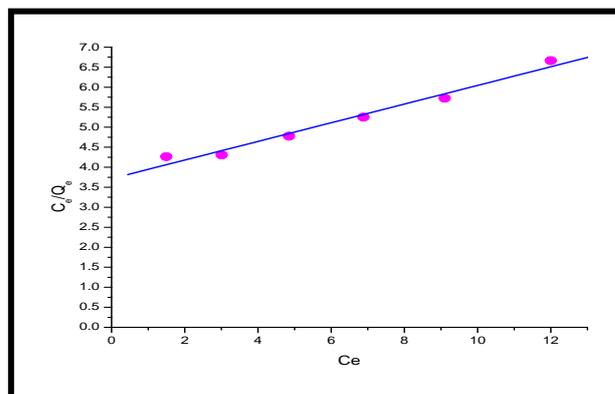

Figure 4: The linearized Langmuir adsorption isotherm of Pb(II) using maize leaves carbon

Adsorption of Pb(II) on MLAC was studied in the concentration range 5-30 mg L^{-1} with 0.5 g of adsorbent in 50 mL for 24 h of equilibrium time. The plots of C_e/Q_e against C_e for adsorption of lead gave a straight line are shown in Fig. 4. It has seen that the linear fit is fairly good and enables the applicability of the Langmuir model to the Pb(II) adsorption on the maize leaf activated carbon.

The values of both Langmuir and Freundlich isotherm parameters were given in Table 1. Examination of data suggests that Freundlich isotherm is a good model for the sorption of Pb(II). The values of $1/n$ that vary between 0.1 and 1.0 indicate the favorable adsorption of heavy metals.[18]

Table-1: Langmuir and Freundlich adsorption parameters for the adsorption of Pb(II) ions at 30 °C.

Langmuir Parameters		Freundlich Parameters	
Q_{max}, mg g^{-1}	3.7136	K	0.2744
b L, mg^{-1}	0.6277	1/n	0.7907
R^2	0.9989	R^2	0.9893

The essential characteristics of Langmuir equation can be described by dimensionless equilibrium parameter,[19] R_L which is defined as;

$$R_L = \frac{1}{1+bC_0}\ b \qquad (5)$$

where, b is the Langmuir constant, C_0 is the initial metal concentration of lead. The R_L values indicate the shape of isotherm as shown in Table 2. The R_L values between 0 and 1 indicate favorable adsorption.[20]

Table 2. Relationship between R_L and type of isotherm

R_L	Type of isotherm
$R_L > 1$	Unfavourable
$R_L = 1$	Linear
$R_L < 1$	Favourable
$R_L = 0$	Irreversible

In the present study the R_L is shown in Fig. 5, for the initial concentration of Pb(II) ion of 5 - 30mg L^{-1} indicating that the adsorption of Pb(II) is favorable.
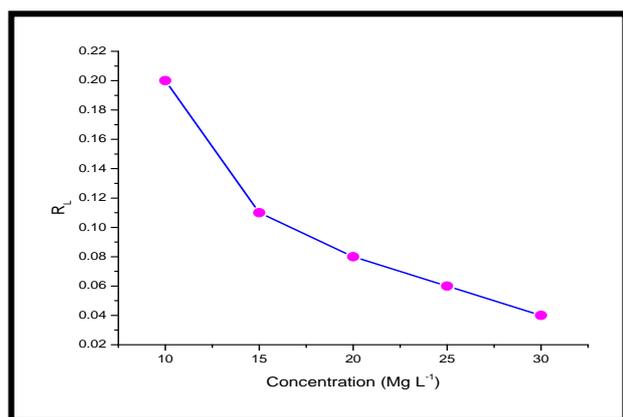

Figure 5. Plot of R_L vs initial Pb(II) concentration

The Langmuir model deals with monolayer coverage and constant adsorption energy while Freundlich equation deals with physicochemical adsorption on heterogeneous surfaces.[21] The applicability of both these isotherms to the activated carbon, in the present study, implies that monolayer adsorption and heterogeneous surfaces conditions exist under the experimental conditions used. The adsorption properties of the adsorbent are thus likely to be complex, involve more than one mechanism.

Fourier Transform Infrared Spectroscopy

The absorption spectra of MLAC are represented in Fig. 6, reveals the functional groups that are responsible for binding the heavy metal ion. Table 3 gives the wave number with the corresponding groups. The hydroxyl and carboxyl functional groups provide the major biosorption sites for the metal binding.

Table-3. Infrared absorption bands and their corresponding groups of MLAC

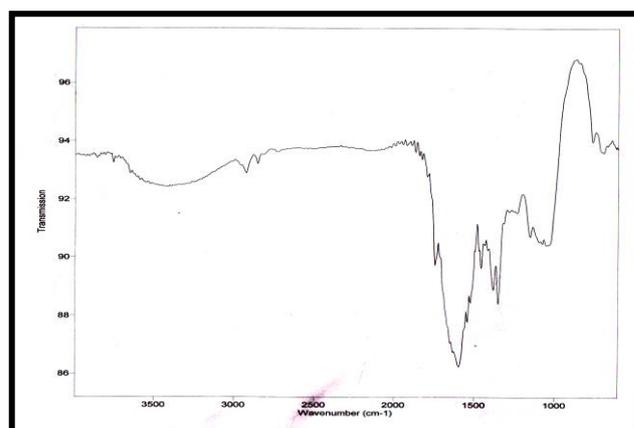| Wave numbers (cm^{-1})	Functional groups
3435.935	-OH, -NH
2923.2	-CH
1515.79	-CH
1709	C=O
1630.36	C=O, -COO
1384.54	-CH
1118.84	-C-O,C-N

Figure 6. FTIR Spectra of activated carbon prepared from maize leaf

Conclusions

The maize leaves activated carbon is adsorbent of great potential and has proven appropriate for lead removal from aqueous solution, percentage of lead removal reach 96 %. The sorption isotherm of both Langmuir and Freundlich are obtained and they well described the sorption process indicating favorable adsorption of lead (II) onto MLAC as a monomolecular type. Removal of lead is highly pH dependent, the best results being obtained at pH 4. The sorption capacity was found to decreases lightly with increase in the adsorbate pH. The adsorption mechanism of lead(II) ion on MLAC involves either cation exchange or complexation between the metal cation and the hydroxide ion in the solution. The FT-IR of maize leaves carbon indicates the presence of several –OH and –COOH groups. Hydrogen of these groups is capable of ion exchange with metal cation. Based on the experimental conditions, it is concluded that the removal of lead ion from their aqueous solution could 96 %. This shows a new trend for using agricultural wastes for the benefit of environmental pollution control.

Acknowledgement

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