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# Adsorption study on porous carbon derived from pods of Prosopis Juliflora (Kikar) for removal of Pb(II) ions

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**ABSTRACT**

Adsorption is a powerful method for the removal of heavy metals even at low concentrations. Prosopis Juliflora (Kikar) trees are abundantly available in various states of India mainly in Haryana, U.P., M.P., and Maharashtra. These naturally occurring pods of kikar can potentially offer an economical solution for the removal of heavy metals from aqueous streams. Also, increasing demand of eco-friendly techniques promote the interest to natural and bio-degradable adsorbents. In the present experimental work, the adsorption of Pb (II) ions by biosorbents prepared from raw kikar pods and carbonized kikar pods have been investigated. To study the adsorption of Pb(II) ions, batch experiments were performed. The characterization of carbonized kikar pods was carried out using FTIR, SEM and proximate analysis. The effect of carbonization and adsorbent dose has been studied for finding out the maximum adsorption of Pb (II) ions. The results indicate that carbonized powder is an effective, eco-friendly and economical adsorbent for removal of Pb (II) ions from aqueous samples exhibiting maximum lead uptake capacity of 19.5 mg/g of adsorbent. Further, to understand the adsorption kinetics analysis three kinetic models were investigated and pseudo-second-order model showed superior fit with the experimentally generated data.

***KEYWORDS- Adsorption, carbonization, kinetics, Prosopis Juliflora, Pb(II)***

## 1. Introduction

There are various industries which discharge effluent contaminated with heavy metals. Some of those are electroplating industries, paint industries, chemical process industries, electronics equipment manufacturing industries and mining plants. Level of heavy metal ions have increased considerably due to rapid industrialization. These enter in food chain through the disposal of heavy metals in water system as they are highly soluble in water. Cadmium, chromium, lead, copper and zinc are super toxic and poisonous heavy metals are used in various industries. Due to release of these heavy metal pollutants there are various serious affects on the ecology. Hence, it is indispensable to withdraw heavy metals from drinking and waste water [1].

Lead (II) is one such metal which is of major concern due its toxicity. The main sources of lead pollution in wastewaters are discharge of waste streams from acid battery manufacturing, metal plating and finishing, printing, metallurgical alloying, lead mining, ceramics or glass industries [2]. The permissible levels of lead in drinking water surface water are 0.015 mg/l and 0.10 mg/l [3]. Lead can threaten human life due to its toxicity, accumulation in food chains and persistence in nature. It is a general metabolic poison and enzyme inhibitor and can accumulate in bones, brain, kidney and muscles [4]. Unlike organic contaminants, lead is non-biodegradable and therefore, must be removed from wastewater. Subsequently, the current studies focus on the preparation of porous carbons for removal of lead from aqueous solutions using low cost biodegradable precursors namely fruit wastes, husk of barley, almond shells, orange and banana peels etc [5-9].

Raman et al. [10] used kabuli kikar (Prosopis juliflora) pods as biosorbent for the removal of binary textile dye mixture (gold HE-R and green HE-4BD). The exhibited adsorption capacity was 50 mg/g and 62.5 mg/g for gold HE-R and green HE-4BD, respectively. Activation energy was reported to be 16.569 kJ/ mol and -20.710 kJ/ mol for gold HE-R and green HE-4BD respectively. Jena et al. [11] explained the removal of Pb (II) ions from aqueous solution by fruits peel as a low cost adsorbent material. Four different fruit peels lemon; banana, water melon and orange were used for adsorbent synthesis in order to investigate the removal of heavy metals from aqueous solutions. The effect of various adsorption process parameters like pH, contact time, initial metal ion concentration, adsorbent dose and temperature were explored. The maximum adsorption capacity for the removal of Pb (II) ions was of 91%, 94%, 92% and 96% for orange, lemon, banana, and watermelon peels respectively. Khan et al. [12] explored the water green algal biomass for the removal of for Pb (II) and Cd (II) ions from aqueous solution. The parameters like solution pH, temperature, contact time, dose, and initial metal ions concentration were optimized. The maximum uptake obtained for Pb (II) ions was reported to be 100.mg/g. The kinetic data was best fitted by pseudo-second order model.

Gopal et al. [13] used activated carbon prepared from seeds of prosopis juliflora for the removal of direct red 23 (dye) from its aqueous solution. Surface area of activated carbon was 1028 $m^2$/g. Maximum lead uptake capacity was 109.89 mg/g at pH 3.0. Saygili et al. [14] obtained high surface area porous carbon by phosphoric acid activation from citrus fruits wastes comprising mainly of mandarin, orange, lemon and grapefruit wastes. The optimal sample was investigated for adsorption of Pb (II). The sample displayed maximum Pb (II) adsorption capacity of ~164 mg/g. Pseudo-second-order kinetic model exhibited good fitness to the experimental data. Sutirman et al. [15] developed an adsorbent by grafting PMMA on chitosan for removal of lead ions from aqueous solutions. The modified chitosan adsorbent samples were investigated in laboratory batch experiments to assess the removal of Pb(II) ions from water samples and remarkable results were produced.

In present study adsorption of Pb (II) ions have been studied on pods of Prosopis Juliflora (kiker), abundantly available in dry deciduous regions of India. Further, to understand the adsorption kinetics analysis two kinetic models were investigated.

## 2. Materials

Pods of kikar tree (Prosopis Juliflora) in their raw as well as in carbonized form were used as precursors for adsorbent synthesis. AR grade $Pb(NO_3)_2$ procured from MERCK, India was used for preparation of stock solutions. Double distilled water was used for preparation of solutions.

2.1 Adsorbent synthesis and characterisation

The pods were washed thoroughly with distilled water to remove adhering soil and clay and then dried in an oven at 105 $^oC$ for 24 hours. The pods were milled and then passed through different sieves. The powder of mesh size between150-200 was collected and packed in air tight packing for use with proper labeling.

Muffle furnace (temperature range 0-1100 $^oC$) was used for the carbonization of pods of Prosopis Juliflora. Hot air oven (temperature range 0-200 $^oC$) was used to dry the pods. The surface properties and functional groups were determined by SEM and FTIR analysis respectively Scanning electron microscope operating at 20 kV Model JSM6100 (Jeol) was to obtain the micrographs of the samples. FTIR spectra were collected on Perkin Elmer - Spectrum (RX-IFTIR) operating over a scan range of 4000 $cm^{-1}$ to 400 $cm^{-1}$ and resolution of 1 $cm^{-1}$.

2.2 Preparation of stock solution

Stock solution was prepared by mixing 159.8 mg of $Pb(NO_3)_2$ in 1000 ml distilled water. All experimental solutions were prepared by diluting the stock solution with distilled water. For maintaining the pH of solutions, KOH and $H_2SO_4$ were used.

## 3. Experimental procedure

The batch adsorption experiments were conducted to determine the metal uptake capacity at varied doses of adsorbent. To determine the effect of dose on adsorption, the amount of adsorbent was altered and other process parameter like contact time, temperature and volume were kept constant. 100 ml volume of Pb II) aqueous solution with 50 ppm concentration was prepared at pH 7. Adsorbent dose was altered from 0.1 to 0.6 g/100 ml at temperature 25 ± $2^0$C and was stirred for 120 minutes at 200 rpm. Graph between percent recovery and adsorbent dose of metal ions was plotted for analyzing the effects.

## 4. Results and discussion

Adsorption being a surface phenomenon depends upon surface topology and chemical nature of adsorbent. Under different conditions same adsorbent behave differently and hence we observed the effect of carbonization and then optimized the adsorbent dose for maximum metal uptake.

4.1 Characterization

The pods were characterized by proximate analysis. The volatile matter, ash content and fixed carbon were calculated. Pods of Kikar (Prosopis Juliflora) have considerable amount of fixed carbon that is mainly required for adsorption. Results are summarized in Table 1.

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Table 1. Proximate analysis of Kikar Pods

| Name of material | Moisture % | Volatile matter % | Ash content % | Fixed carbon % |
|---|---|---|---|---|
| Pods of Kikar | 21.27 | 56.46 | 5.97 | 16.30 |

4.1.1 Scanning Electron Microscope (SEM) analysis

SEM analysis was carried to understand the surface morphology of the adsorbent material. The SEM images of Prosopis Juliflora pods powder before and after carbonization are shown in the Figure 1 (a & b). Figure 1 shows that porosity increases after carbonization due to removal of volatile matter from the raw adsorbent. The surface of the carbonized material appears more porous with distorted layers as compared to raw adsorbent powder. The main advantages of carbonized form of biomaterial are its environmental stability and increase in adsorption capacity towards heavy metals because of increase in available surface area.

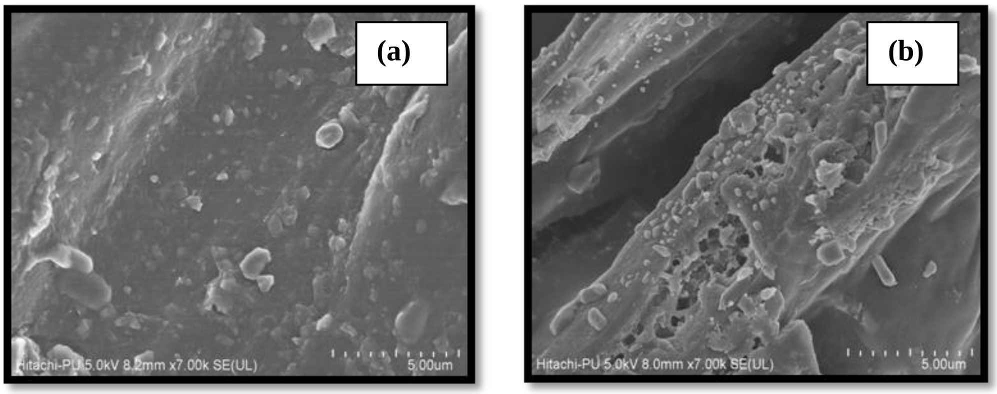


Figure 1(a): SEM images of Prosopis Juliflora powder before carbonization and (b) after carbonisation

4.1.2 Fourier Transform Infrared Spectroscopy

To identify the metal ions responsible for the adsorption FTIR study was performed. The FTIR spectra of carbonized Prosopis Juliflora pods powder in the range of 400–4000 $cm^{-1}$ was recorded to obtain information regarding vibrational frequency changes of the functional groups present in the adsorbent. FTIR spectra of carbonized Prosopis Juliflora pods powder before and after metal ion adsorption are shown in Figure 2 (a & b) by plotting graph between transmittance % and wave number ($cm^{-1}$). FTIR study revealed that functional groups like amide, alkanes, methyl, methylene and organohalogens were present in significant proportion and responsible for adsorption of Pb (II).

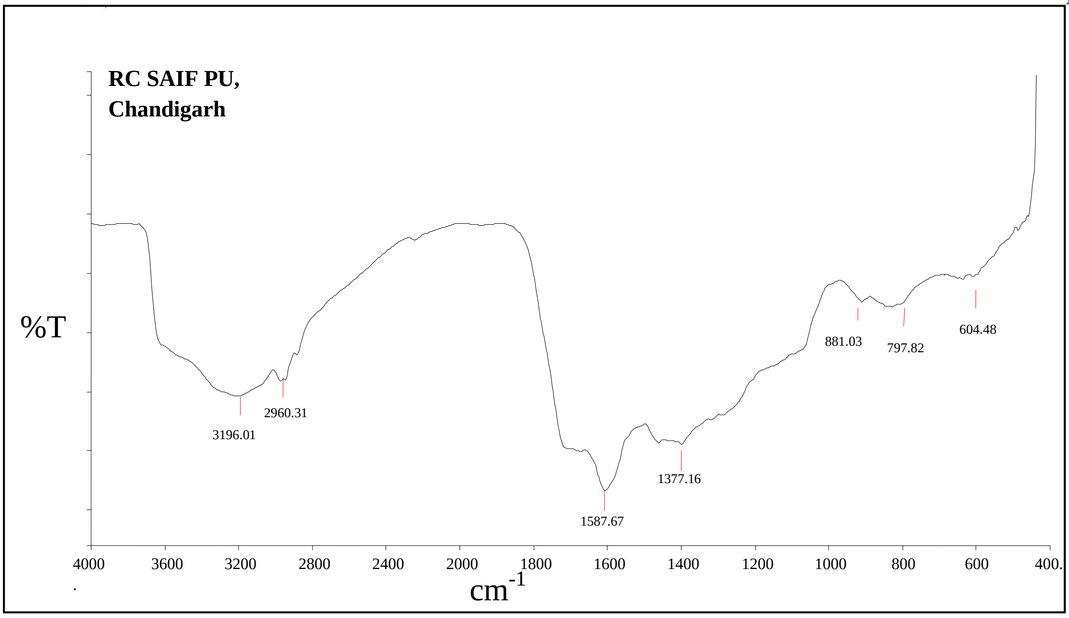


Figure 2 (a) FTIR spectra of unloaded carbonized powder of Kikar pods

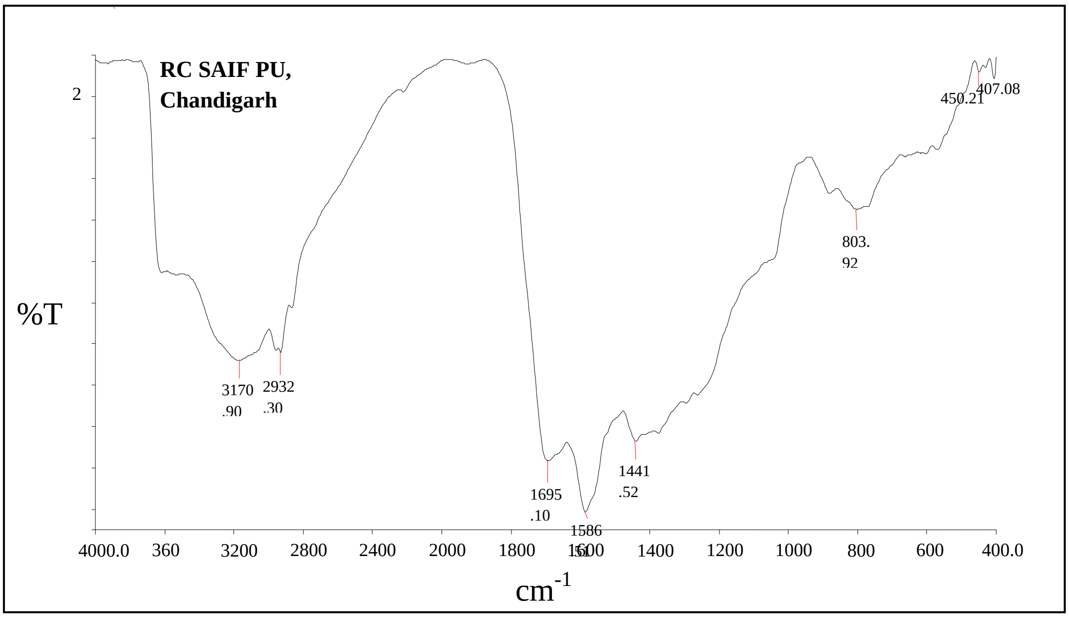


Figure 2 (b): FTIR spectra of Pb(II) loaded carbonized powder of Kikar pods

4.2 Effect of Carbonisation

SEM results indicate increase in porosity in carbonized adsorbent. So the adsorption is expected to be more in case of carbonized powder. The Table 2 clearly shows that the uptake of lead ions on the prepared adsorbent. The effect of carbonization was studied at following conditions: pH 7; Adsorbent dose 0.2 g/100ml; Stirring speed 200 rpm; time 2 hr, temperature 25 ± 2 $^{0}$C and initial metal concentration of 50 ppm.

Table 2. Uptake of Pb(II) by pods of Kikar tree in various forms

| Sr. No. | Name of adsorbent | Final concentration of adsorbate (ppm) | Removal (%) | Pb(II) uptake,q (mg/g) |
|---|---|---|---|---|
| 1 | Kikar pods raw powder | 16 | 68 | 17 |
| 2 | Carbonized Kikar pods powder | 11 | 78 | 19.5 |

4.3 Effect of Adsorbent dose

Variation in adsorption dose has considerable effect on metal uptake capacity and percentage removal as indicated in Figure 3. Effect of adsordent dose on percentage removal of lead from water sample was investigated at constant pH 7, stirring speed 200 rpm, time 120 minutes, temp. 25 ± 20 $^{o}$C, and initial metal concentration of 50 ppm. Percent removal of metal ions increased gradually with increase in adsorbent dose and attained equilibrium between 0.5 to 0.6 gram/100ml. The availability of vacant sites for binding the metal ions may be responsible for enhancement in lead ions removal. Graph shows that best economical dose weight for 50ppm initial concentration is 0.5 gm per 100 ml of solution resulting in removal of 96 % of Pb(II) ions. Wheras, adsorbent dose of is 0.2 gm per 100 ml of solution could achieve only 68 % removal of metal.

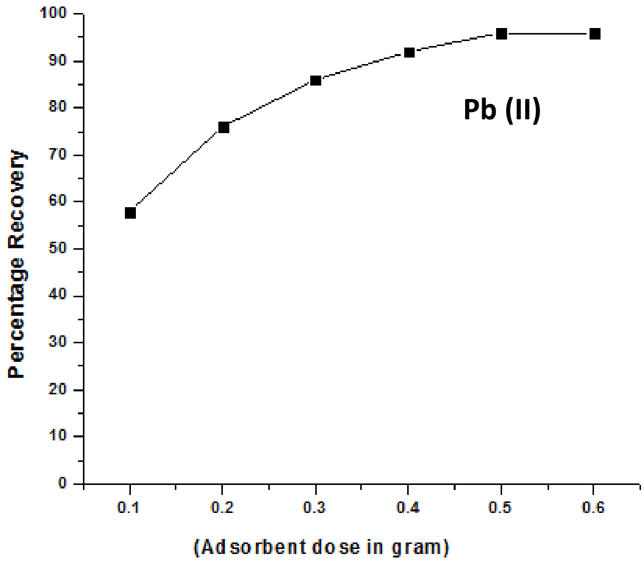


Figure 3: Effect of adsordent dose on percentage removal of lead from water sample

The above results show that the optimum adsorption of metal ions found at pH 7 using adsorbent dose of 0.5 g/100ml, stirring speed 200 rpm, time 2 hr, temperature 25± 2 $^{o}$C and initial metal concentration of 50 ppm by carbonised kikar pods was 19.5 mg/g. The maximum percentage removal was found to be 96% for Pb(II).

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**5. Kinetic study of Pb(II) adsorption**

For the purpose of determining the kinetic mechanism of adsorption, the behavior of Pb(II) adsorption process has been analyzed using the pseudo-first order and pseudo-second order kinetics models. By using above found results for adsorption of Pb(II) from aqueous solutions by carbonized pods of kikar tree, the graphs have been plotted as $\ln(q_e-q_t)$ versus time and t/q versus time for pseudo-first order and pseudo-second order kinetics models respectively as indicated in Figure 4 and 5. Subsequently the experimentally obtained uptakes were regressed over the predicted uptakes. Regression analysis shows that pseudo-second order model fits better with the experimental data than the pseudo-first order kinetics model for Pb(II) adsorption by carbonized pods of kikar tree as observed from much higher $R^2$ values and least value of standard error as depicted in Table 3.

Table 3: Pseudo 1st and 2nd order kinetics model parameters

| **Pseudo 1st order kinetics model** | | | | | |
|---|---|---|---|---|---|
| Metal ions | $q_e$, experimental | $q_e$, calculated | K1 | $R^2$ | Standard error |
| Pb(II) | 19.5 | 5.0028 | 0.33 | 0.58 | 0.4817 |
| **Pseudo 2nd order kinetics model** | | | | | |
| Metal ions | $q_e$, experimental | $q_e$, calculated | k1 | $R^2$ | Standard error |
| Pb(II) | 19.5 | 19.24 | 0.0219 | 0.99 | 0.0222 |

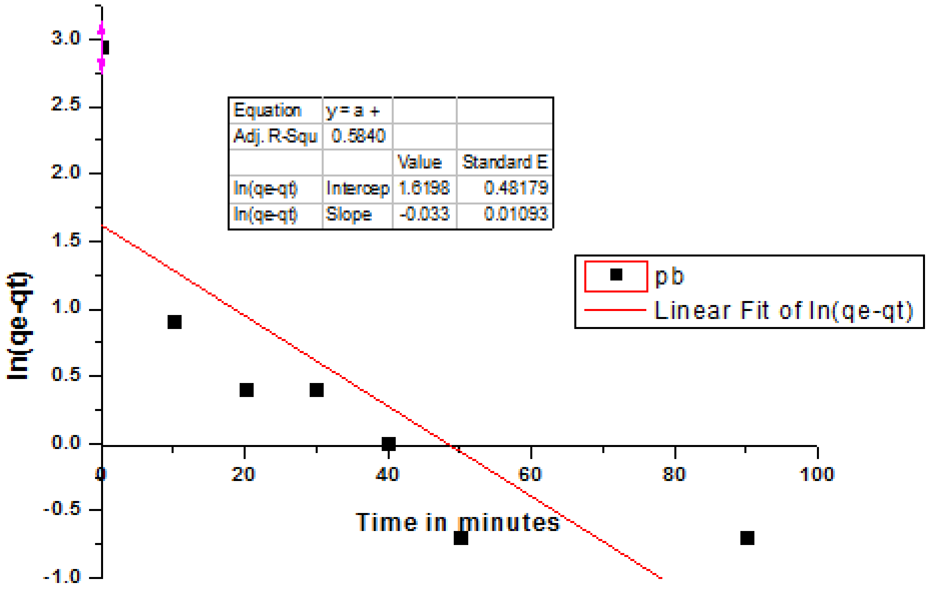


Figure 4. Pseudo-first-order plot for adsorption of Pb(II) using adsorbent dose = 0.5gm/100ml solution, initial metal concentration = 50 ppm; temperature = 25 ± 2$^0$C, pH = 7, stirring speed and time of 200rpm and 2hr respectively

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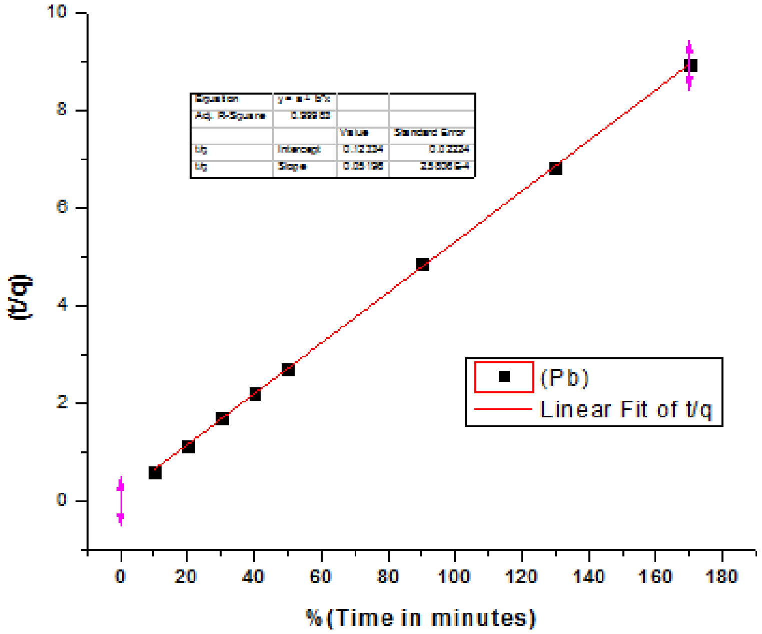


Figure 5. Pseudo-second-order plot for adsorption of Pb(II) using adsorbent dose = 0.5gm/100ml solution, initial metal concentration = 50 ppm; temperature = 25 ± 2$^{0}$C, pH = 7, stirring speed and time of 200rpm and 2hr respectively

## 6. Conclusion

This work shows that adsorbent based on kiker pods can be an excellent biosorbent for removal of toxic lead metal from aqueous solutions under specified experimental conditions. 0.5 gm of carbonized adsorbent is found to be enough to adsorb 96% of Pb(II) from 100ml solution consisting of 50ppm of metal concentration at room temperature. Carbonized pods powder possesses better adsorption capacity than uncarbonised powder of pods due to generation of well developed pores. Batch studies of Pb(II) adsorption from aqueous solution with 2hr contact time, temperature 25$^{0}$C, and adsorbent dose 0.5 gram/100 ml resulted in 96% removal of Pb(II) ions and produced metal uptake capacity of 19.5 mg/g for Pb(II) ions. Besides, pseudo-second order kinetics model best explained the kinetics of adsorption. On the whole, we can say that the biosorbent prepared from kikar pods is inexpensive and easily available and is potent to remove undesirable heavy metals from industrial effluents.

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