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ORIGINAL ARTICLE

Removal of Zinc and Lead from Aqueous Solution using Low Cost Bioadsorbent *Pennisetum glaucum* (Bajara) Husk

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ABSTRACT
In this study Bajara husk was applied as an efficient bioadsorbent for the removal of two heavy metals lead (Pb) and zinc (Zn) from aqueous solution. For studying the surface morphology of bioadsorbent characterization was done by IR spectral and SEM analysis. The effect of different conditions including pH (3-8), adsorbent dose (0.5g-2.5g), contact time (30-150 min) and initial concentration of metal ions (5mg/L-100mg/L) were investigated. The maximum removal of lead and zinc of 86.0% and 88.0% were observed at optimized pH 5.0 and other optimized conditions like adsorbent dose and metal ion concentration. The adsorption data were investigated for adsorption isotherms and kinetic models and found to fit for the first order kinetics and best fitted to langumir and frendulich adsorption isotherm.
Keywords: *Bajra husk, Lead, Zinc, Bioadsorbents, Characterization, Adsorption isotherm.*

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INTRODUCTION

The human health and ecological systems are threatened to get worse because abundant and harmful heavy metals can be found in the water sources due to the rapid industrial and agricultural development together with the population growth. One of the most toxicological relevance presented by the industrial and agricultural effluents is the heavy metals. Their presence in streams and lakes has been responsible for several health problems in animals, plants, and human beings. Main sources of these heavy metal ions are from the discharge of waste from many industries such as metal plating, mining, textile and electric/electronic devices manufacturing. The waste effluents from these industrial operations, untreated or even treated, can have significant amounts of heavy metal ions [1-4]. Heavy metal ions in aquatic systems and ground water pose risks to the living organisms by accumulating in food chain due to their mobility, stability and non-biodegradability. The most important heavy metals include zinc (Zn), lead (Pb), mercury (Hg) and cadmium (Cd), which are considered to have dangerous environmental impacts according to their toxicological criteria. In fact, lead (Pb), zinc (Zn) mercury (Hg), cadmium (Cd), chromium (Cr) and arsenic (As) are commonly considered as the priority heavy metals due to their high toxicity, prevalent, existence and persistence in the environment [5-9]. Different physical, chemical and biological methods have been investigated like leaves of Araucaria cookie, Corn cobs mango peels, papaya seeds as a absorbent for zinc in aqueous medium [10-18]. Lead were removed by using chalk, rice husk, sesame, sun flower and tea waste with an efficiency of 85%, 90%, 100%, 86%, 98%, respectively. Fava beans, used paper mill sludge, banana and orange peel were also applied for the removal of lead from water [19-24]. In the present study, Bajra Husk columns were prepared in the laboratory to study the removal efficiency of Zn and Pb. Zinc is an essential mineral perceived by the public today as being of "exceptional biologic and public health importance however, excess concentration may cause nausea and vomiting, epigastric pain, abdominal cramps, and diarrhea, skin irritation, bronchiolar leukocytes and anemia. Similarly Lead (Pb) has been cited as one of the three most toxic heavy metals that have latent long-term negative impacts on health, causing anemia, encephalopathy, hepatitis and nephritic syndrome.

Limited studies are existing in the scientific literature to remove Zn and Pb by using Bajra husk (Pennisetum glaucum). Pearl millet (Pennisetum typhoides) belongs to family Poaceae, also known as Bajra is a cereal of tropical and subtropical areas of world and is consumed in Asia and Africa as a staple crop. India ranks the list at top in pearl millet production with 8.59 million tonnes usually requires relatively low rainfall and can stand and endure under continuous or intermittent drought. The presence of hydrolysates and peptides with bioactive peptide-rich protein in Pearl millet is an indication that this crop could be used as a future bioremediation plant. The good amount of hydrophobic amino acids including Gly, Leu, and Pro and the presence of hydrophobic amino acids may improve the interaction between peptide and metal species [25-29]. The peptide chain with repeating amino acids component in the peptide sequence that constitute the same amino acid residuals such as Leu–Leu; and Asn–Asn may also be helpful in the bonding of heavy metals. In the present study, bajra husk columns were prepared in the laboratory to study the removal efficiency of Zn and Pb.

MATERIALS AND METHODS

Bajra (*Pennisetum. glaucum*) husk collected from rural area of Gwalior, were used in the present work to develop low cost adsorbent and to evaluate its efficiency. These wastes were washed repeatedly with the tap water followed by double distilled water to remove dust soluble impurities. The washed biomass was sun dried for one day and then dried at 90^{o}C in oven and ground to powder by laboratory grinder. Powdered biomass was pretreated with acid and filtered. Then it was dried in oven at 90°C to a constant weight and then was sieved with meshes to obtain fine powder of 0.2 mm. The adsorbents were preserved in desiccators until the time of use.

Reagents and solution

The entire chemicals used were of analytical grade obtained from sigma aldrich and solutions were prepared in distilled water. A stock solution of Zn (II) (1000 ppm) and Pb (II) (1000 ppm) were prepared by dissolving $ZnCl_2$ and $Pb(NO_3)_2$ in deionized water. Working solutions of 5, 10, 20, 50 and 100 mg/L were prepared by dilution. Britton-Robinson Buffers in the pH range 3 to 8 were prepared.

Instrumentation

pH metric measurements were made on decibel DB 1011 digital pH meter fitted with a glass electrode, which was previously standardized with buffers of known pH in acidic and alkaline medium. The reaction kinetics was studied with the help of spectrophotometer over the wavelength range of (180 to 990 nm).

RESULT AND DISCUSSION

Adsorbent characterization

The physiochemical characteristics of the adsorbents are important in order to evaluate their adsorption capacities. The brief outlines of the characterization techniques employed in the present investigation are given below:

Infrared spectra

The infrared spectral assignment of leaves of bajra (*Pennisetum glaucum*) husk was obtained by KBr disc method using Fourier Transform Infrared Spectroscopy, 4100 JASCO, Japan (Fig.1). The absorption bands identified in the spectra and their assignment to the corresponding functional groups were listed in Table 1.

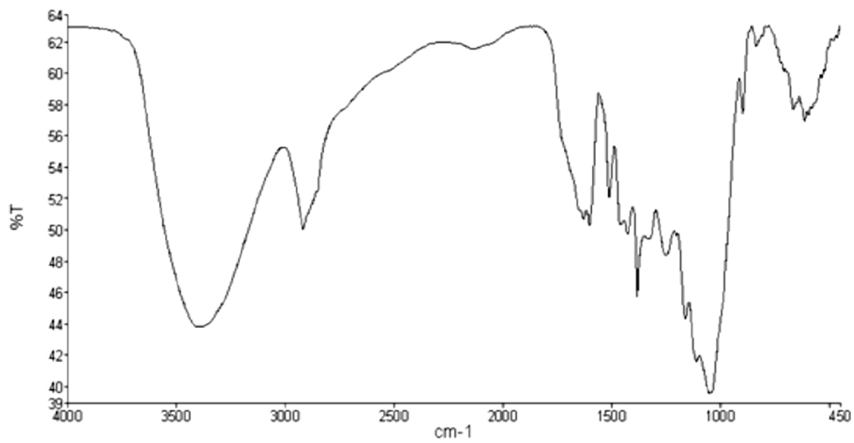


Figure 1: IR Spectra of bajra husk

Table 1: IR bands of bajra husk

Band position (cm^{-1})	Assignment
3399 b	O-H stretch
2920 sh	C-H stretch
1631 s	C=O stretch
1604 m	N-H bend
1513 s	N-O stretch
1250 m	C-H wag

m=medium, w=weak, s=strong, n=narrow, b=broad, sh=sharp

Surface Topography

The surface morphology of bioadsorbent was studied by scanning electron microscopy (SEM). The surface of *P. glaucum* was observed by SEM JSM- electron microscope Jeol: JSM-6510LV. The samples for SEM were prepared by spreading the powder on a double adhesive tape bound to an aluminium stab. A layer of gold which was about thickness of about 300 A^0 was mounted to the stubs in an inert argon atmosphere using a gold sputter module in a high-vacuum evaporator. Finally these coated samples were then observed under a scanning electron microscope ZEISS: SEM and photomicrographs were taken using different magnification Fig. 2.

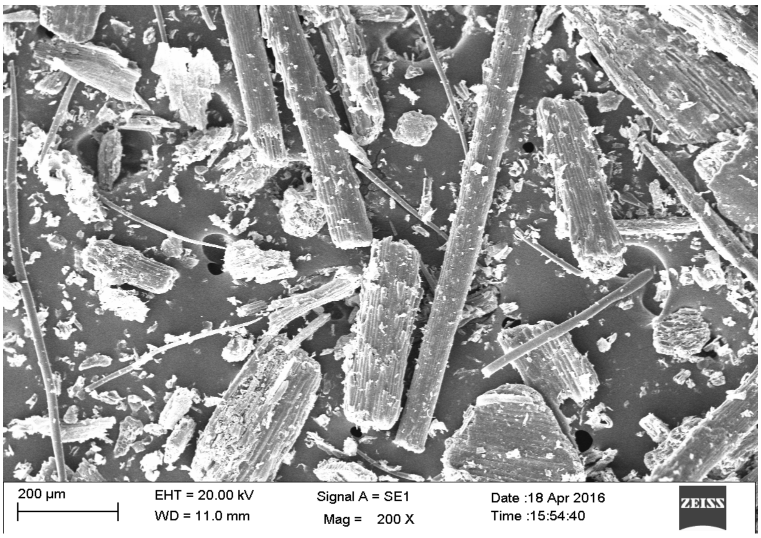


Fig. 2: SEM image of powdered bajra husk

Removal of Zn and Pb by using bajara (*P. glaucum*) husk bioadsorbent

By optimizing different parameters *viz*., pH, contact time, dosage the ability of the bioadsorbent to remove Zn and Pb from water has been investigated under different condition.

Effect of contact time

The effect of contact time was investigated at a room temperature of 30°C, at constant intervals of 30 min and the observed results showed that the rate of adsorption of metal increases with the increase in contact time and remains almost constant for 90 min to120 min for bajra powder, in case of Zn and Pb as shown in Fig.3. So 90 min chosen optimum one for further study. The maximum percentage of zinc and lead removed by bajra husk at different contact time during the study was up to 83 and 85%, respectively (Table 2).

Table 2: Effect of contact time on the removal of zinc and lead by bajra husk.

S.No.	Initial metal concentration (ppm)	Contact time (min)	Dose of adsorbent (gm)	Percentage removal of metal	
				Zinc	Lead
1.	10	30	1.0	47	53
2.	10	60	1.0	72	75
3.	10	90	1.0	83	85
4.	10	120	1.0	81	82
5.	10	150	1.0	77	79

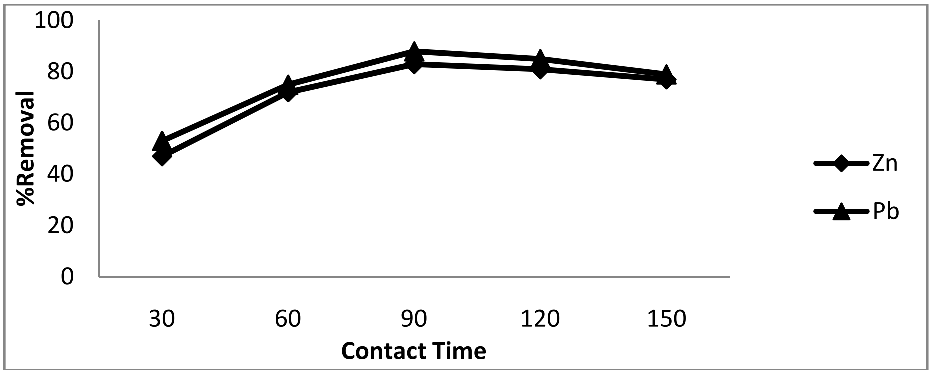


Figure 3.Percentage removal of zinc and lead by bajara husk with contact time

Effect of metal ion concentration

The removal of Zn and Pb by bajra husk under batch adsorption experiments carried out at optimum pH, contact time at room temperature using different initial metal ion concentration viz, (05, 10, 20, 50 and 100 mg/L) is shown in Fig.4. It was observed that the percentage removal increases with the increase in initial metal ion concentration up to 10 mg/L after this due to saturation of adsorption sites on the adsorption surface of the bajra husk removal % decreases. 85 and 87 % removal of Zn and Pb were observed at 10 mg/L for bajra under similar conditions, respectively, the linear trend was observed as the concentration increased from 5 to 10 ppm(Table.3).

Table 3: Effect of metal ion concentration on the removal of zinc and lead by bajra husk.

S.No.	Initial metal concentration (ppm)	Contact time (min)	Dose of adsorbent (gm)	Percentage removal of metal	
				Zinc	Lead
1.	5	90	1.0	67	76
2.	10	90	1.0	85	87
3.	20	90	1.0	80	83
4.	50	90	1.0	77	79
5.	100	90	1.0	71	72

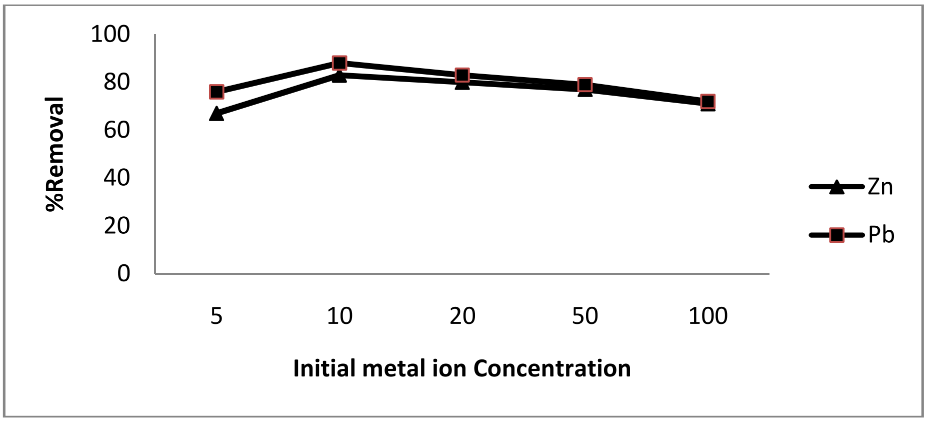


Figure 4: Percentage removal of zinc and lead by bajara husk with metal ion concentration.

Effect of adsorbent dose

The effect of adsorbent dosage on the removal of Zn (II) and Pb (II) ion at 10mg/L were studied at optimum pH and contact time, at room temperature, and results are represented in Fig (5). The dosages varied from 0.5, 1.0, 1.5, 2.0 and 2.5 gm/100 mL. The removal of Zn and Pb metal ions were found to increase with an increase in adsorbent dosage upto dosage of 1.0 gm/100 mL. The removal percentage of Zn increases with increase in adsorbent dose varied from 68 to 82% and in the case of Pb removal percentage varies from 73 to 87 % by bajra powder. The maximum removal was observed of 82% and 87% for Zn and Pb, respectively at the adsorbent dose of 1.0gm under the same condition (Table 4).

Table 4: Effect of adsorbent dose on the removal of zinc and lead by bajra husk

S.No.	Initial metal concentration (ppm)	Contact time (min)	Dose of adsorbent (gm)	Percentage removal of metal	
				Zinc	Lead
1.	10	90	0.5	68	73
2.	10	90	1.0	82	87
3.	10	90	1.5	78	81
4.	10	90	2.0	74	75
5.	10	90	2.5	71	71

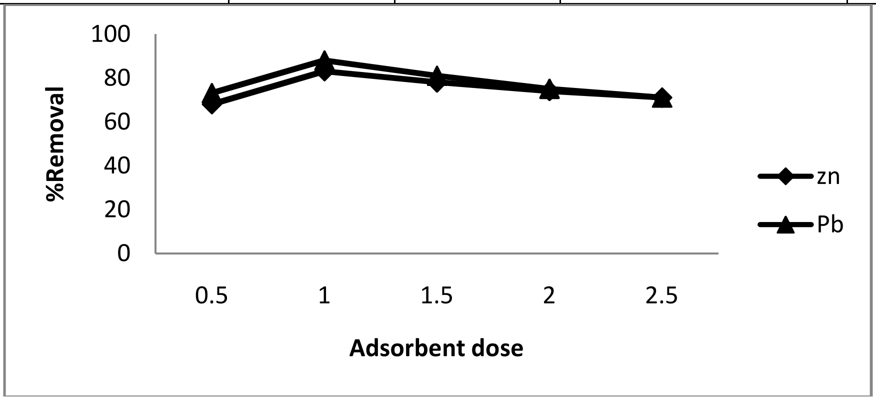


Figure 5: Percentage removal of zinc and lead by bajara husk with different adsorbent dosage

Effect of pH

In order to evaluate the influence of pH on the adsorption, the experiments were carried out at different pH values. The pH was varied from 3 to 8. The data revealed that adsorption increased with increase in pH up to 5 above which it shows slightly decrease in removal up to pH of 8. The removal percentage increases from 68 to 86% for Zn and 58 to 88% for Pb respectively on increasing in pH from 3 to 5 for bajra husk (Table 5). The maximum percentage of Zinc and Lead were removed by bajra husk at pH 5.0 which were found to be 86 and 88 %. In case of both the metals removal percentage increases with increase in pH up to 5 and afterwards decreases the results may be due to weakening of electrostatic force of attraction between the adsorbate and the adsorbent and it ultimately led to the reduction in sorption capacity (Fig.6).

Table 5: Effect of pH on the removal of zinc and lead by bajra husk

S.No.	Initial metal concentration (ppm)	Contact time (min)	Dose of adsorbent (gm)	pH	Percentage removal of metal	
					Zinc	Lead
1.	10	90	1.0	3	68	58
2.	10	90	1.0	4	75	78
3.	10	90	1.0	5	86	88
4.	10	90	1.0	6	81	85
5.	10	90	1.0	7	78	79
6.	10	90	1.0	8	67	75

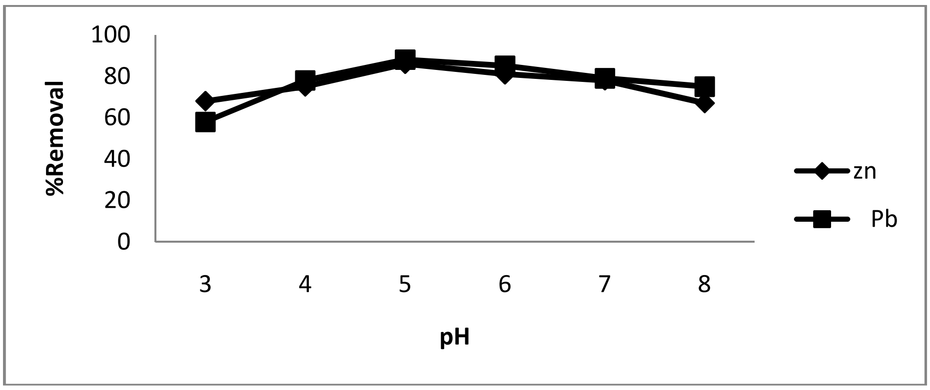


Figure 6: Percentage removal of zinc and lead by bajara husk with pH

Adsorption Isotherms

The adsorption isotherms for Zn and Pb were investigated using initial concentrations of 10 ppm at pH = 5 and 30°C temperature and amount of biomass dosage was 1.0 g. The data obtained were fitted to the Langmuir and Freundlich isotherms. These models were tested to determine the maximal capacity of Zn and Pb removal using bajara husk powder. The quality of the isotherm fit to the langmuir equation, in the linear form is written as:

$$C_e/Q_e=1/bq_{max} + Ce/q_{max}$$

$.\frac{Ce}{Qe} = \frac{1}{bqmax}$ Where C_e is the equilibrium concentration of metal ions (mg/L), q_e is the amount of metal ions adsorbed per unit weight of adsorbent (mg/g bentonite), q_{max} is the maximum adsorption capacity (mg/g), and b is the adsorption equilibrium constant (L/mg).

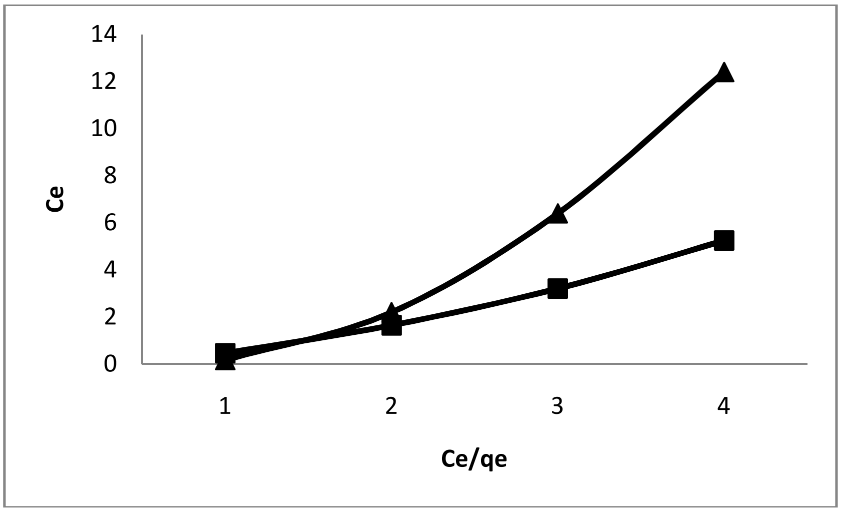
For the Freundlich equation the linear form is written as:

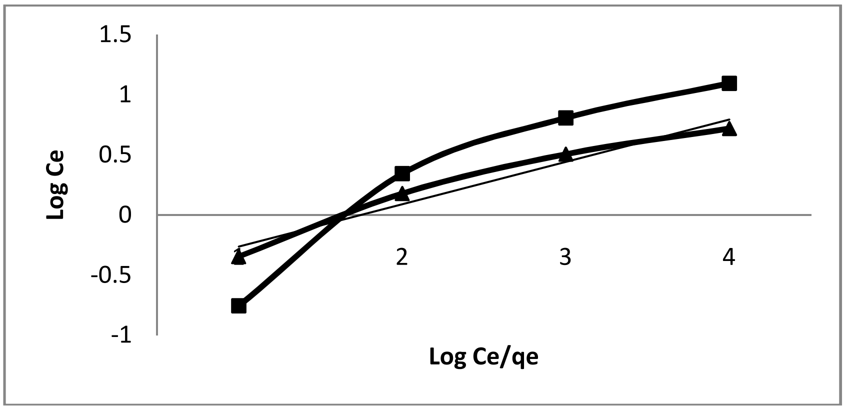
$$\text{Log } q_e = \log K + 1/n \log C_e$$

$\frac{1}{n}\log Ce$ The best estimated values of all the equation parameters are summarized in Table.6 The adsorption isotherm data are well fitted with both the linear Langmuir and Freundlich equations for Pb and Zn (Fig.7) & (Fig.8) gives the R^2 close to 1. In the case of both the metals value of R^2 was higher for Langmuir isotherm than the Freundlich isotherm; that means Langmuir equation represented the adsorption process very well. In the Table-6 the values of K_f, n, Q_0 and b were given.

Table 6: The values of Langmuir and Freundlich sorption constants for biosorption of zinc and lead ions on bajara husk powder.

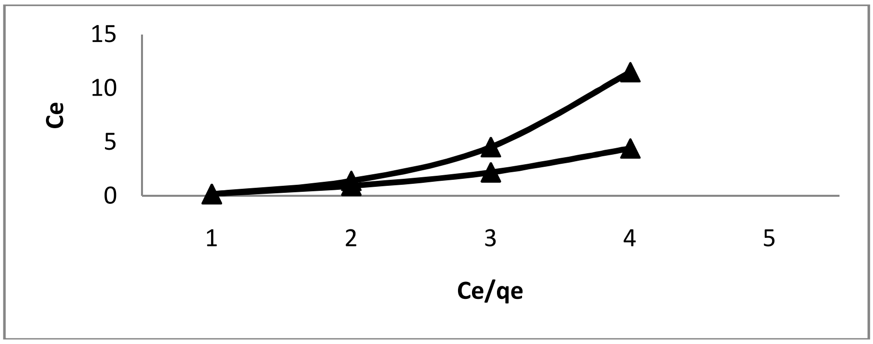
Metal ions	Langmuir Constants			Freundlich constants		
	Q^0_e (mg g^{-1})	b (L mg^{-1})	R^2	K_F	N	R^2
Pb	1.95	0. 287	0.976	0.6545	1.987	0.975
Zn	1.45	0.998	0.986	0.8763	3.89	0.923



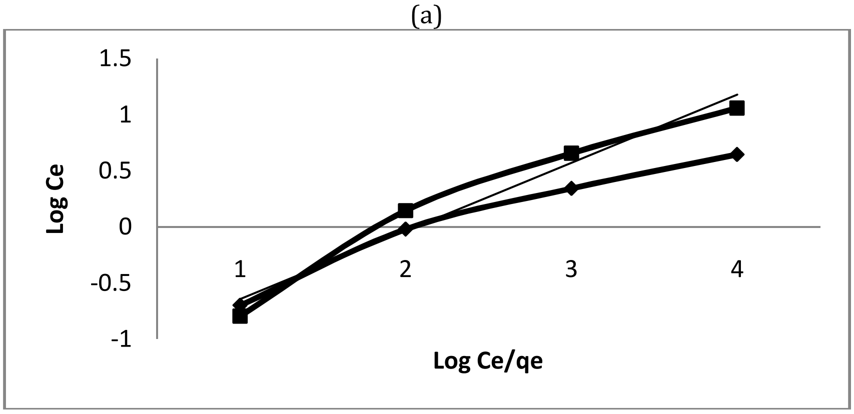


(b)

Figure 7: (a) Langmuir isotherms plot for adsorption of Pb onto adsorbent bajra husk
(b) Freundlich isotherms plot for adsorption of Pb onto adsorbent bajara husk.



(a)



(b)

Figure 8: (a) Langmuir isotherms plot for adsorption of zinc onto adsorbent bajra husk
(b) Freundlich isotherms plot for adsorption of zinc onto adsorbent bajara husk.

Rate kinetics

The kinetic parameters for the adsorption process were studied on the batch adsorption condition (temp=30^{0}C, initial Pb and Zn concentration = 10 ppm, adsorbent dosage =1.0 g and pH= 5). In order to examine the controlling mechanism of adsorption processes such as mass transfer and chemical reaction, the first- and second-order equations were used to test the experimental data. The first order equation was plotted for ln (qe-qt) against t (Fig.9) the values of ln (qe-qt) were observed given in Table.7. The k_1 were calculated from the slope. The value of k_1 was shown in Table.7. The second order equation was obtained for t/qt against t (Fig.10) . The values of q_e and k_2 were calculated from the slope and intercept of this plot. The values of q_e and $k_2$were calculated Table.7. The comparison of experimental sorption capacities (qexp) and the predicted values (q_{cal}, k_1, k_2, k_d, R_2) from pseudo first order, pseudo second order and intra particle diffusion constants are given in Table. The pseudo Second order could not satisfactorily explain the experiment results but sorption of metal ions were very close to the experimental (q_{exp}) values. The first order equation appeared to be the better fitting model than second order as equations has higher R^2 value.

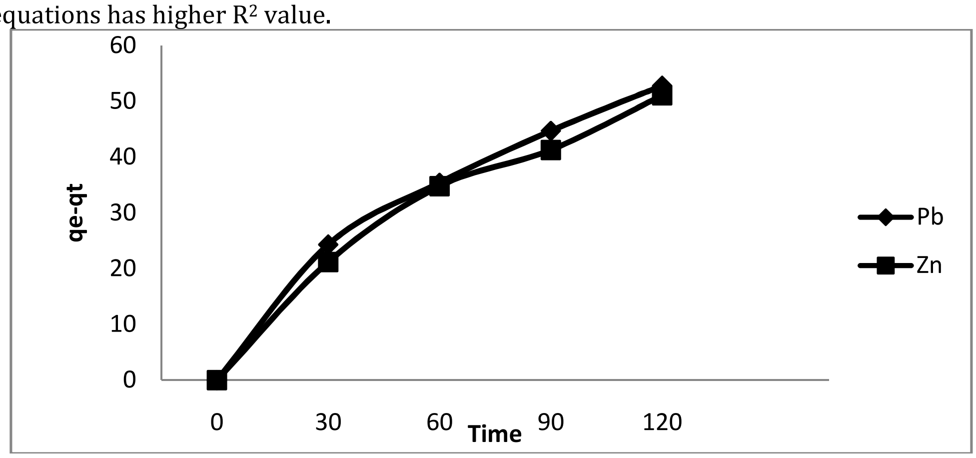


Figure 9: First order plots adsorption kinetics of Pb and Zn on adsorbent bajara husk

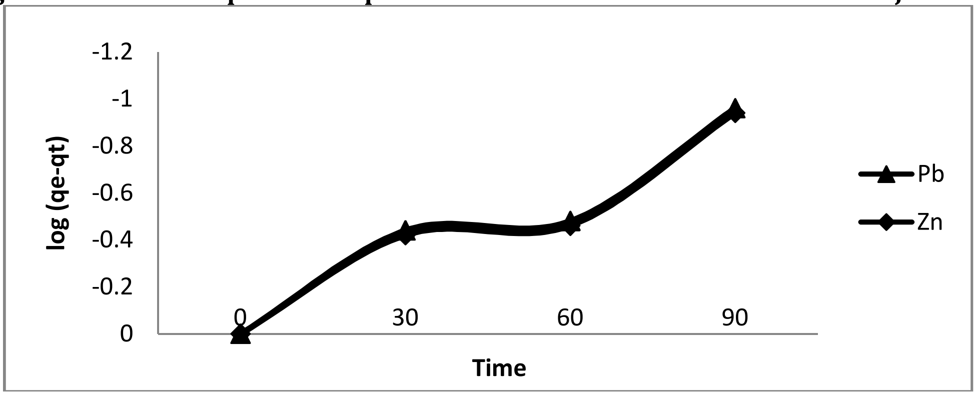


Figure 10: Second order plots adsorption kinetics of Pb and Zn on bajara husk.

Table 7: Values of q_e and K for adsorption plots kinetics

Metal ions	Conc. (mg/L)	Pseudo-first-order				Pseudo-second order		
		q_e (cal.) (mg g-1)	K_1 (min-1)	R^2	q_e (cal.) (mg g-1)	K_2 (g mg-1) min-1)	H (mg g^{-1}) min^{-1})	R^2
Pb	10ppm	1.523	0.022	0.978	1.998	0.0399	0.1456	0.824
	20 ppm	1.048	0.033	0.978	0.998	0.0721	0.1987	0.909
	50 ppm	0.9234	0.038	0.994	0.987	0.1423	0.198	0.954
	100 ppm	0.2678	0.030	0.959	0.546	0.3800	0.123	0.964
Zn	10ppm	1.220	0.029	0.989	1.287	0.0696	0.1965	0.912
	20 ppm	1.213	0.042	0.886	1.434	0.0466	0.1234	0.819
	50 ppm	1.985	0.033	0.976	1.00	0.1020	0.1123	0.923
	100 ppm	0.356	0.028	0.987	0.6123	0.2756	0.0986	0.942

CONCLUSION

The present study revealed that the Bajra (*P. glaucum*) husk is a low-cost adsorbent for removing the heavy metals viz. Zn and Pb from waste water. The results demonstrated that adsorption of Zn and Pb by Bajra husk adsorbents depends on pH, initial Zn and Pb concentration, contact time and temperature. On the other, kinetics and isotherms assays were performed in order to monitor the sorption dynamic behavior of each sorbents and to estimate their respective sorption capacities. It may be concluded that easy availability and suitability for production of bioadsorbent from bajra husk makes it one of the materials that can be used for removal of Zn and Pb from waste water. The removal efficiency of 86 and 88% of Zn and Pb by using bajra husk has been achieved in this study. However, it fluctuates with respect to different absorbant constants.

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