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Factors affecting the efficiency of rye husk as a potential biosorbent for the removal of metallic pollutants from aqueous solutions

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ABSTRACT

Biosorbents have maintained their high rank for the removal of toxic substances from water. In this study, the rye husk was used to remove the toxic lead (Pb) and zinc (Zn) ions from water using batch mode of adsorption. The rye husk was characterized by scanning electron microscopy and Fourier transform infra-red spectroscopy. The concentration of metals was determined using atomic absorption spectroscopy. The maximum uptake of Pb^{2+} from the water was found to be 97.2% at 3 g of adsorbent dose, 96.64% at 240 min of contact time, and 95.44% for 100 ppm initial metal ion concentration. On the other hand, the Zn^{2+} uptake was comparatively low at optimized conditions, that is, 3 g adsorbent dose, 150 min contact time, and 125 ppm of initial metal ion concentration. The data was well fitted in both Langmuir and Freundlich adsorption isotherms. It is concluded that the efficiency of rye husk for Pb and Zn removal is dependent on adsorbent dose, contact time, and metal ion concentration. The rye husk is probably one of the efficient adsorbents for the removal of metallic pollutants.

Keywords: Adsorbent isotherms; Metallic pollutants; Rye husk, Environmental remediation; Industrial effluents

1. Introduction

Water is not essential for life on the planet and has an extensive industrial application. Most of the population living in major cities are lacking pure water. More than 40% of deaths are linked with waterborne diseases. The only reason for this wastewater contamination is attributed to the mixing from sewage and industrial sources water in drinking water distributary systems. Human activities have brutally damaged the natural environment with respect to water bodies. The industrial revolution has become a source for the production and usage of toxic metals [1–6]. These toxic metals, is the natural components of crust cannot be destroyed owing to their persistent nature. These metals are carcinogenic and mutagenic even at very low concentrations or they have the ability to produce such substances that can be carcinogenic. These heavy metal contaminants are mostly generated by industrial processes. It is recommended to lessened their amount to tolerable limits. So, the wastewater must be treated prior to discharging into water bodies otherwise this could be very lethal particularly for marine life [7–10].

Water pollution has remained a major environmental issue over many years. A lot of diseases are originated due to water pollution. Heavy metal discharge into our water bodies is increasing pollution and is a silent threat to our ecosystems [11–15]. The Pb and Zn are discharged into water systems from electroplating industries, battery manufacturing units [16], and paint industries which discharges Pb in huge amounts [17]. Moreover, all heavy metals

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are health hazards [18]. For example, Pb can cause serious kidney problems [19], mental retardation [20]. Similarly, Zn can cause liver damage [21] and lethargy [22]. Worst of all these problems, these metals are non-biodegradable [23], they can persist in water for a very long period of time causing the diseases in many generations.

The removal of these toxic pollutants becomes a dire necessity, especially of heavy metals that are ranked at high in Agency for Toxic Substances and Diseases Regulatory (ATSDR) [24]. Many methods, like chemical precipitation, ion exchange and membrane separation, electrochemical deposition, osmosis, evaporation, coagulation, etc. [25–31], were used for the removal of metals. However, these methods have some limitations due to their expensive nature and toxic by-products [32]. On the other hand, biosorption has been considered as economical, time saving, easy, and efficient method [33–36]. In this method, different adsorbents can be employed that have the ability to bind with specific material in order to remove it from wastewater. The adsorption process could be physical, chemical, and ionic based on the tensile strength between absorbing surface and dissolved particles. Moreover, the biosorbent material is easily available all over the world. Many types of biosorbents were utilized for uptake of heavy metals like fungi, yeast, sugarcane bagasse, leaves of many trees, peels of fruits, rice straw, and date pits [37–40].

The main objective was to evaluate the effects of biosorbent (rye husk) on removal of toxic metals from aqueous solution and to prepare eco-friendly and low-cost adsorbent. This was further assisted by optimizing adsorbent dose, time of contact, and initial metal ion concentration.

2. Materials and methods

2.1. Biosorbent preparation

Rye husk was obtained from the local area of district Kasur, Punjab, Pakistan. Husk was washed thoroughly with water to remove dirt. It was dried in air and then dried in oven at 55°C for 24 h. The husk was grinded to fine particle size and passed through sieve to obtain uniform particle size of 1 mm. The stock solution of Pb ions was prepared by dissolving 1.98 g of Lead nitrate $Pb(NO_3)_2$ in de-ionized water. Zinc sulfate hepta hydrate ($ZnSO_4·7H_2O$) was used to prepare stock solution of Zn ions by dissolving 4.1 g of the salt in water.

2.2. Characterization of biosorbent

Biosorption is a surface phenomenon. Prior to biosorption studies, the knowledge about the surface texture and morphology is necessary. Biosorbent was characterized by using Fourier transform infra-red (FTIR) spectroscope from Genesis Pharmaceutical Pvt., Ltd., Lahore, Pakistan and scanning electron microscopy (SEM), VEGA TESCAN LMU 300 (Brno, Czech Republic), from COMSATS University of Information and Technology, Lahore campus, Pakistan. FTIR was carried out to check the available functional groups for the adsorption of heavy metals while SEM was used to see the surface texture, porosity, and roughness. SEM was performed at power of 6.0 kV and 1.0 and 5.0 kx magnification.

2.3. Adsorption studies

The adsorption was studied using batch mode of adsorption in which biosorbent was stirred with a metal ion solution, in Erlenmeyer flasks, under different adsorbent dose, time of contact, and initial metal ion concentration. After this treatment, the biosorbent was separated from the solution by filtration. The concentration of Pb^{2+} and Zn^{2+} was determined before and after this treatment with the help of the atomic absorption spectrometer (AAS) of Hitachi (Tokyo, Japan). The difference in concentration was used to calculate the percentage adsorption and thus adsorption efficiency of rye husk. The quantity of heavy metal ion adsorbed per gram of adsorbent (*A*) can be obtained using the following equation:

$$A = \frac{V\left(C_0 - C_e\right)}{m} \tag{1}$$

The percentage adsorption and thus percentage efficiency (%*E*) was measured using the following equation:

$$\%E = \frac{C_0 - C_e}{C_0} \times 100 \tag{2}$$

In these equations C_0 is initial metal ion concentration, C_e is metal ion concentration at equilibrium, V is the volume of solution while m is the mass of adsorbent utilized. Moreover, kinetic studies were also performed to study the effects of variables on adsorption percentage and equilibrium phenomenon [41–44]. For this purpose, Langmuir and Freundlich adsorption isotherms were used:

$$Q_e = \frac{q_{\max} b C_e}{1 + b C_e} \tag{3}$$

While the exponential and logarithmic form of Freundlich adsorption isotherm is as following:

$$Q_e = K_d C_e^{\frac{1}{n}} \tag{4}$$

$$\log Q_e = \log K + \left(\frac{1}{n}\right) \log C_e \tag{5}$$

where C_e is metal ion concentration at equilibrium, Q is the amount of adsorbate per gram of adsorbent, $q_{\max}$ maximum amount of adsorbate per gram of adsorbent, while b and K_d are equilibrium constants of Langmuir and Freundlich adsorption isotherm, respectively.

3. Results and discussion

Previous studies report that heavy metals are one of the major class of pollutants found in water reservoirs due to their non-biodegradable nature. Their presence is extremely dangerous for marine life as these are highly soluble. So, it is needed to treat the water for metal removal before introducing it to water channels. In this study, the Rye husk, *Secale cereale*, has been turned into an efficient biosorbent for the Pb and Zn ions removal. The batch mode of adsorption studies was utilized for research. The equilibrium studies were performed by Langmuir and Freundlich adsorption isotherms. Aqueous solution of metals was prepared and experiments were performed on the solution to optimize adsorbent dose, time of contact, and metal ion concentration.

3.1. Characterization of adsorbent

FTIR spectroscopy is a powerful tool with many applications and is used to identify organic, inorganic, and polymeric materials through functional group analysis. It is a quantitative and qualitative technique as well. Fig. 1 shows the FTIR spectrum of rye husk indicating the presence of different functional groups. The prominent peaks are at 1,000 cm^{-1} due to C–O bond stretching in C–OH group, 1,720 cm^{-1} for carbonyl group stretching, sp^3 C–H stretch at 2,900 cm^{-1}, and a broadband at 3,200–3,400 cm^{-1} for O–H stretch of carboxylic acid group. The broadband of O–H indicates the presence of hydrogen bonding. Free O–H stretch (absence of hydrogen bonding) appears at about 3,600 cm^{-1}. The spectrum showed that adsorbent has functional groups, required for binding the metal ions; especially the carbonyl group is responsible for this binding.

SEM is a versatile tool used to characterize a variety of materials. It is a high-resolution surface imaging technique and provides information regarding the surface of materials. Surface structure of rye husk (Fig. 2) showed that this adsorbent has a porous structure and rough texture. Both of which are helpful in the removal of heavy metal ions. Adsorption is a surface phenomenon thus knowledge about the surface of adsorbent is a must for evaluating the adsorption process. The SEM images and FTIR spectrum of adsorbent reveal that adsorbent is good enough for the adsorption of heavy metal ions.

3.2. Effect of adsorbent dose

The ability of adsorbent to remove the heavy metal ions from water depends upon the number of adsorption sites available. The adsorption site means the functional groups present on the surface of the adsorbent, which is involved in capturing of heavy metal ions. So, by increasing the adsorbent dose, we actually increase the number of adsorption sites, which increases the adsorption percentage. An increase in rye husk dose increases the uptake of both Pb and Zn ions (Tables 1 and 2). Fig. 3 shows the effects of adsorbent dose, contact time, metal ion concentration on to the adsorption, and depicts the increment in percentage adsorption and attainment of equilibrium at the optimum value of 3 g biosorbent dose.

3.3. Effect of time of contact

By increasing the time of contact, the immersion time increases, and thus the interaction between adsorbent and heavy metal ions increases. This increase in interaction results in an increase in adsorption percentage. A fixed amount of adsorbent and fixed initial metal ion, 3 g and 125 ppm, respectively, was stirred with a solution in Erlenmeyer flask for varying time periods. It was seen that adsorption percentage was increased by increasing the time of contact, but only up to an optimum value, after that, it does not increase. Because after optimum value all the adsorption sites are saturated. The maximum adsorption percentage 96.64%, is obtained at 240 min of contact time for Pb (Table 1) and 91.48% at 150 min for Zn removal (Table 2).

3.4. Effect of initial metal ion concentration

Three grams of adsorbent was stirred, for 150 min of contact time with Pb and Zn metal ions solutions separately. The initial metal ion concentration was varied from 25 to 200 ppm. Similar results were obtained, as were for adsorbent dose and time of contact. The adsorption Percentage came to equilibrium at 100 and 125 ppm of Pb and Zn ion concentration giving 95.44% adsorption percentage of Pb and 92.04% of Zn removal, respectively. The reason for equilibrium at these optimum values is again due to the saturation of adsorption sites.

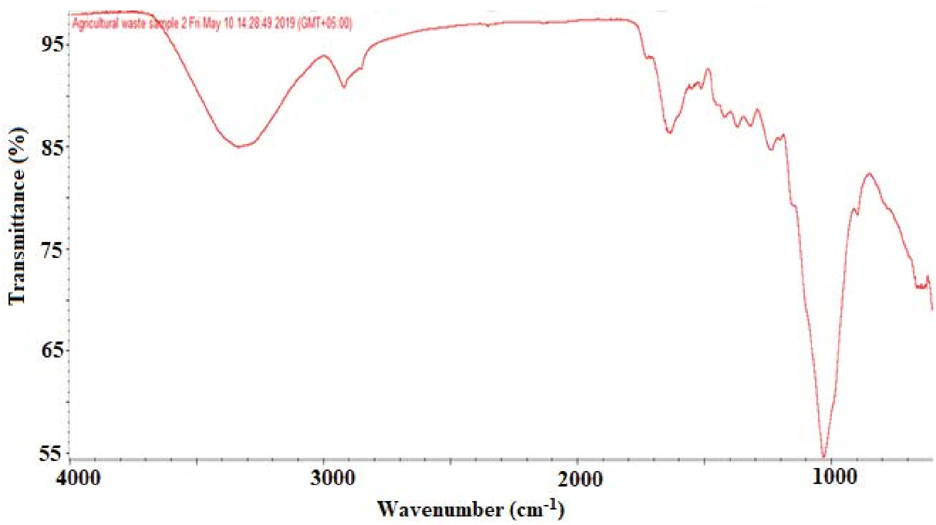

Fig. 1. FTIR spectrum of rye husk.

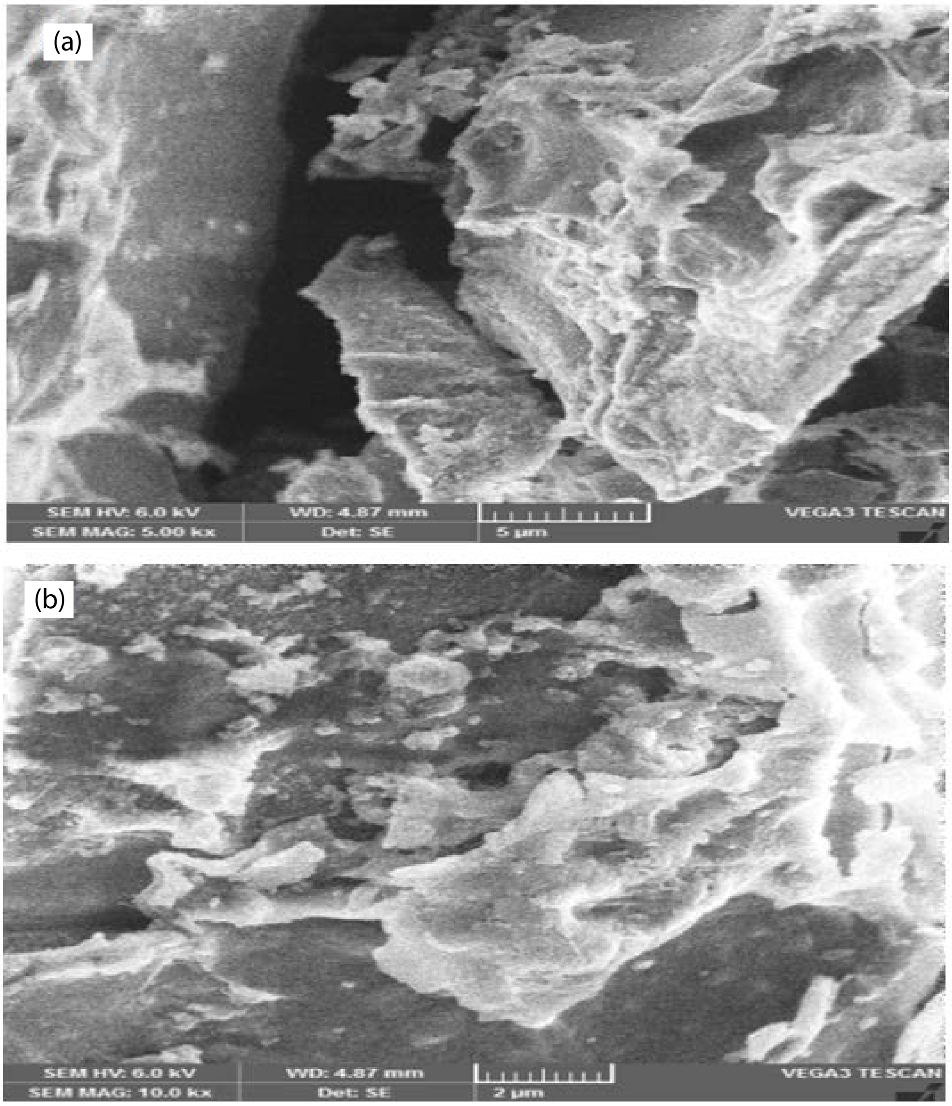

Fig. 2. SEM images of rye husk (a) 5 kx magnification and (b) 1 kx magnification both at 6.0 kV showing porous nature of adsorbent.

3.5. Equilibrium studies

Adsorptions isotherms have importance in evaluating the adsorption system, mechanism of adsorption, adsorption capacity, and interaction between adsorbent and adsorbate. The data was characterized using Langmuir and Freundlich adsorption isotherms.

The Langmuir equation is normally applied to uniform adsorption systems. Particularly, the system where the adsorption of adsorbate on to the surface has identical sorption activation energy. This model is based on the assumption that the adsorbent surface is uniform and all active sites have the same attraction to adsorbate. The adsorption is a monolayer deposition of adsorbate molecules onto the adsorbent surface with a fixed number of capable binding centers [5,45–48].

Freundlich adsorption isotherm is for heterogenous surface and was used to study the concentration effect on adsorption at constant temperature and explained the mechanisms of adsorption. The adsorption is a multilayered process with unequal distribution of heat of adsorption [49].

Langmuir adsorption isotherm is a plot between C_0 vs. C_e, while the Freundlich adsorption isotherm is a plot between $\log C_0$ vs. $\log C_e$. Linear plots of C_e vs. Q_e (Fig. 2) show that adsorption process for Zn ($R^2 = 0.9507$) seemed to follow the Langmuir model (Fig. 4) compared to the Freundlich model (Fig. 5). On the other hand, the adsorption process for Pb seemed to follow the Freundlich isotherm ($R^2 = 0.9822$) vs. Langmuir model.

The adsorption efficiency of rye husk was calculated at different adsorbent dose, time of contact, and initial metal ion concentration. The maximum adsorption percentage was obtained at 3 g of biosorbent dose, 125 min of contact time, and 150 ppm of initial metal ion concentration. So, the rye husk biomaterial is very effective adsorbent, eco-friendly, easily accessible, and economical for Pb and Zn removal from aqueous solution and could possibly be used

Table 1
Adsorption parameters for Pb^{+2} using rye husk as biosorbent

Adsorbent dose (g)	Volume	mass	V/m	C_0	C_e	$C_0 - C_e$	Percentage adsorption	Q_e	LogQ_e	LogC_e
0.5	0.1	0.5	0.2	25	3.5	21.5	86	4.3	0.6335	0.5441
1	0.1	1	0.1	25	3.34	21.66	86.64	2.16	0.3357	0.5237
1.5	0.1	1.5	0.066	25	2.35	22.65	90.6	1.51	0.179	0.3711
2	0.1	2	0.05	25	1.34	23.66	94.64	1.18	0.073	0.1271
2.5	0.1	2.5	0.04	25	1.12	23.88	95.52	0.95	–0.02	0.0492
3	0.1	3	0.033	25	0.7	24.3	97.2	0.81	–0.092	–0.155
3.5	0.1	3.5	0.028	25	1.03	23.97	95.88	0.68	–0.164	0.0128
Contact time (min)										
30	0.1	3	0.033	25	5.43	19.57	78.28	0.65	–0.186	0.7348
60	0.1	3	0.033	25	3.42	21.58	86.32	0.71	–0.143	0.534
120	0.1	3	0.033	25	2.12	22.88	91.52	0.76	–0.118	0.3263
150	0.1	3	0.033	25	1.11	23.89	95.56	0.79	–0.099	0.0453
180	0.1	3	0.033	25	0.78	24.22	96.24	0.80	–0.093	–0.108
210	0.1	3	0.033	25	0.94	24.06	96.44	0.80	–0.096	–0.027
240	0.1	3	0.033	25	0.84	24.16	96.64	0.80	–0.094	–0.076
C_0 (ppm)										
25	0.1	3	0.033	25	2.74	22.26	89.04	0.74	–0.13	0.4378
50	0.1	3	0.033	50	3.42	46.58	93.16	1.55	0.1911	0.534
75	0.1	3	0.033	75	3.45	71.55	95.40	2.38	0.3775	0.5378
100	0.1	3	0.033	100	4.56	95.44	95.44	3.18	0.5026	0.659
125	0.1	3	0.033	125	8.76	116.24	92.992	3.87	0.5882	0.9425
150	0.1	3	0.033	150	13.45	136.55	91.033	4.55	0.6582	1.1287
200	0.1	3	0.033	200	13.65	186.35	93.175	6.21	0.7932	1.1351

Volume: volume of solution (L); mass: mass of adsorbent (g); C_0: initial metal ion concentration (ppm); C_e: metal ion concentration at equilibrium (ppm); Q_e: adsorbate per gram of adsorbent (mg/g).

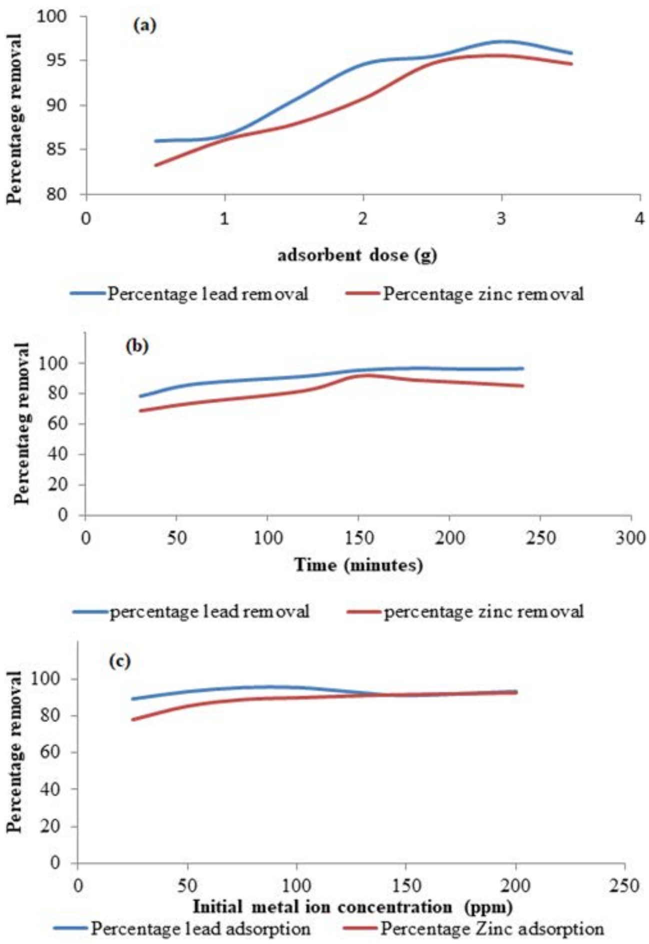

Fig. 3. Effect of (a) adsorbent dose, (b) contact time, and (c) initial metal ion concentration on removal of Pb and Zn.

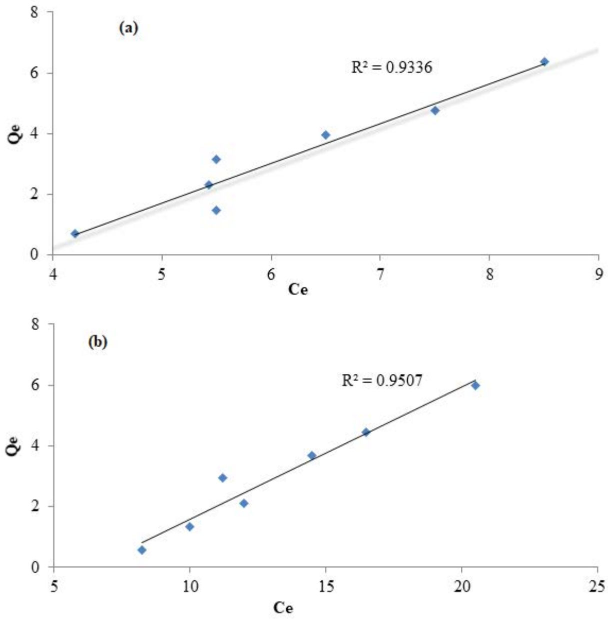

Fig. 4. Langmuir adsorption isotherm with rye husk for (a) Pb and (b) Zn uptake.

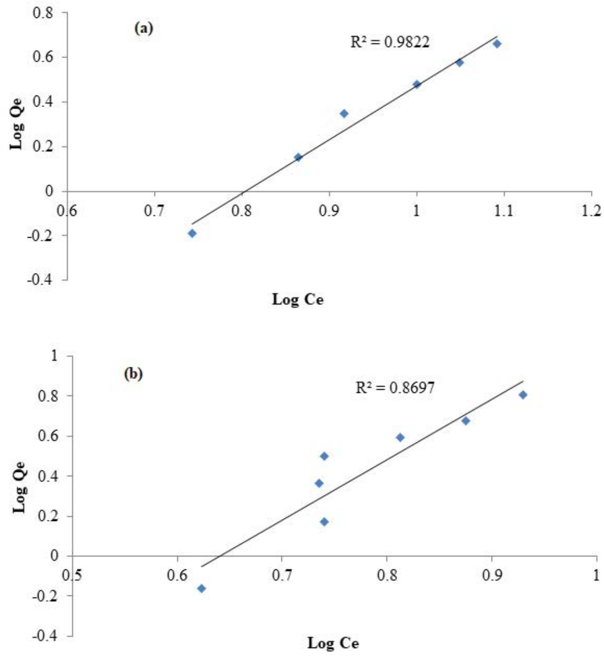

Fig. 5. Freundlich adsorption isotherm with rye husk for (a) Pb and (b) Zn uptake.

for the removal of heavy metals from industrial effluents at large scale [4,7,8,50–52].

Heavy metals are considered the most abundant pollutants from industrial wastewater and are highly dangerous in disturbing the ecosystems. Biosorption is the most economical and green technology that can be used for the removal of metallic elements. Under the current environmental scenario, the rye husk can be applied for the removal of metals (particularly Pb and Zn) from the industrial wastewater streams. This could possibly be used for the other pollutants as well [11,15,50,53–58].

4. Conclusions

The study was conducted to exploit the potential of rye husk for the removal of Pb and Zn from aqueous solution. Rye husk exhibited high efficiency for adsorption of both metals and could probably be utilized for the adsorption at a large scale. The effect of different variables including adsorbent dose, time of contact, and initial metal ion concentration was evaluated. The optimum values for adsorbent dose (3 g), contact time (125 min), and metal ion concentration (150 ppm) were observed. The R^2 value showed the dependence of adsorption on factors and fitness of data in Langmuir and Freundlich adsorption isotherm. It is concluded that this kind of biosorbents could be used to remove these poisonous heavy metals from industrial effluents. Ultimately, the biosorbents could lead to a green and safe

Table 2
Adsorption statistics for Zn^{+2} using rye husk as biosorbent

Adsorbent dose (g)	Volume	mass	V/m	C_0	C_e	$C_0 - C_e$	Percentage adsorption	Q_e	LogQ_e	LogC_e
0.5	0.1	0.5	0.2	25	4.2	20.8	83.2	4.16	0.6191	0.6232
1	0.1	1	0.1	25	3.48	21.52	86.08	2.152	0.3328	0.5416
1.5	0.1	1.5	0.066	25	3.04	21.96	87.84	1.464	0.1655	0.4829
2	0.1	2	0.05	25	2.32	22.68	90.72	1.134	0.0546	0.3655
2.5	0.1	2.5	0.04	25	1.32	23.68	94.72	0.947	–0.024	0.1206
3	0.1	3	0.033	25	1.11	23.89	95.56	0.79	–0.099	0.0453
3.5	0.1	3.5	0.028	25	1.34	23.66	94.64	0.676	–0.17	0.1271
Contact time (min)										
30	0.1	3	0.033	25	7.87	17.13	68.52	0.571	–0.243	0.896
60	0.1	3	0.033	25	6.56	18.44	73.76	0.614	–0.211	0.8169
120	0.1	3	0.033	25	4.56	20.44	81.76	0.681	–0.167	0.659
150	0.1	3	0.033	25	2.13	22.87	91.48	0.762	–0.118	0.3284
180	0.1	3	0.033	25	2.78	22.22	88.88	0.740	–0.13	0.444
210	0.1	3	0.033	25	3.25	21.75	87	0.725	–0.14	0.5119
240	0.1	3	0.033	25	3.75	21.25	85	0.708	–0.15	0.574
C_0 (ppm)										
25	0.1	3	0.033	25	5.54	19.46	77.84	0.648	–0.188	0.7435
50	0.1	3	0.033	50	7.32	42.68	85.36	1.422	0.1531	0.8645
75	0.1	3	0.033	75	8.25	66.75	89	2.225	0.3473	0.9165
100	0.1	3	0.033	100	10	90	90	3	0.4771	1
125	0.1	3	0.033	125	11.2	113.8	92.04	3.793	0.579	1.0492
150	0.1	3	0.033	150	12.34	137.66	91.77	4.588	0.6617	1.0913
200	0.1	3	0.033	200	14.5	185.5	91.75	6.183	0.7912	1.1614

Volume: volume of solution (L); mass: mass of adsorbent (g); C_0: initial metal ion concentration (ppm); C_e: metal ion concentration at equilibrium (ppm); Q_e: adsorbate per gram of adsorbent (mg/g).

environment by the removal of toxic substances through the process of biosorption.

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