Removal of Zinc (II) Ions by Wheat Bran and Waste Coffee as Low-Cost Biosorbents

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ABSTRACT: *In this research, wheat bran and waste coffee without any chemical treatment are used as low-cost biosorbents for the removal of zinc ions from an aqueous solution. Parameters such as contact time, adsorbent dose, initial concentration, and pH were studied. To describe adsorption equilibrium, Langmuir and Freundlich isotherms were used. Experimental results confirm that the adsorption of zinc ions on waste coffee fits well with the Langmuir isotherm while Freundlich isotherm is a better fit for wheat bran. The maximum capacity of zinc ions adsorbed, with the Langmuir model for wheat bran is a bit higher (q_{max}= 9.01 mg/g) than waste coffee (q_{max}= 6.41 mg/g). The thermodynamic parameters, enthalpy (ΔH°), entropy (ΔS°), and Gibbs free energy (ΔG°), provide that the adsorption process is exothermic, spontaneous, and favorable for both used biosorbents. The structure of both biosorbents was analyzed by the pH of the point zero charge (pH_{PZC}) and FT-IR spectra.*

KEYWORDS: *Biosorbent; Thermodynamic parameters; Waste coffee; Wheat branl Zinc ion.*

INTRODUCTION

Our environment quality is deteriorating day by day with the largest cities reaching saturation points and unable to cope with the increasing pressure on their infrastructure. Industrial effluents, sewage, and farm wastes are the major pollutants contaminating the environment [1]. The heavy metals of most concern from various industries include lead, zinc, copper, arsenic, cadmium, chromium, nickel and mercury [2-4]. These heavy metal aqueous wastes have induced many problems for human beings and their environment [5]. Toxicity in water due to heavy metal pollution plays a crucial role in determining its effects on all organisms, living in water and land, including humans [6]. International bodies, such as the WHO, have been extensively studying and regularly reviewing the effects of heavy metals on human health. Heavy metals having the ability to accumulate in the living body, and cause different diseases, such as headaches, cancer, and kidney failure [7, 8]. Toxicity by heavy metals causes a great deal of health issues, damaging central nervous function, the cardiovascular and gastrointestinal (GI) systems, lungs, kidneys, liver, endocrine glands, and bones. Several degenerative diseases of these same systems have been implicated with chronic heavy metal exposure and may increase the risk of some cancers [1].

Sources of such exposures include metal complex dyes, pesticides, fertilizers, fixing agents (which are added

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to dyes to improve dye adsorption onto the fibers), mordant, pigments and bleaching agents, etc. [9]

Zinc is found almost everywhere: air, soil, water and almost all foods [10]. It is used in industry for galvanization of steel to the manufacture of the negative plate in electrical batteries, preparation of some alloys, as a pigment in plastics, cosmetics, photocopier paper, wallpaper, printing inks etc. [11]. In general, the wastewater is enriched with harmful complex ingredients such as organic matter, heavy metals and antibiotics, many of which affect the degradation of zinc, often requiring other treatments to meet the regulatory standards [12]. Zinc usually hinders the function of environmental microorganisms by destroying cell membranes and inhibiting enzyme activity [13, 14]. Zinc after entering the environment, it will not only cause harm to the environment but also threaten human health and survival because it has high toxicity, difficult degradation, migration and biological uptake. Therefore, it is urgent to study the pollution and related remediation mechanisms [15]. The World Health Organization recommended a maximum acceptable zinc concentration in drink water of 5.0 mg/dm^3 [16].

The uptake of heavy metals from wastewater is important not just to eliminate their toxic impact, but also to recover precious materials [17, 18]. Removing toxic heavy metals from industrial wastewater is of primary importance for the protection of public health and environment [19]. The growing problem of water pollution has led to a great deal of interest in the development of innovative and relatively cheap methods of neutralizing such compounds [20, 21]. Different methods have been applied by the scientific community in order to decontaminate water, free from any heavy metal ions [22]. These methods include adsorption, complexation, chemical oxidation or reduction, chemical precipitation, reverse osmosis, ion exchange, coagulation etc. [23]. Heavy metals adsorption by low cost biomass of sea weeds, molds, yeasts, and agricultural waste materials has attracted much attention since the 1990s [24]. Biosorption materials or agriculture wastes have several advantages over conventional treatment methods, such as their low cost, regeneration ability, high adsorption efficiency, lesser chemical or biological sludge, and the possibility of metal recovery [25, 26]. Adsorption, compared to other treatment alternatives, is one of the most cost-effective methods due to its ease of operation, high efficiency, and low maintenance cost [27, 28]. The advantage of the tendency of one or more components of a liquid or gas to collect on the surface of a solid is used by adsorption. The affinity of the component for a particular adsorbent depends on molecular characteristics such as size, shape, polarity, the partial pressure or concentration in the fluid and the system temperature. Although adsorption bonding energy is high enough for adsorption to occur, it is also low enough to allow the adsorbent to be regenerated by removing the adsorbed molecules [29]. Adsorbents of agricultural origin have high mechanical strength, rigidity and porosity, they have polymeric groups like cellulose, hemicellulose, pectin, lignin and proteins as active centers for metal uptake [30]. Some researchers have investigated wheat brain and coffee waste as a bioresource for various valuable compounds. Wheat brain is rich in proteins, carbohydrates, minerals and fats [31] while waste coffee contains large amounts of fatty acids, lignin, cellulose, hemicellulose, and other polysaccharides that justify its valorization [32].

In this work, wheat bran and waste coffee were used as low-cost biosorbents to remove zinc ions from aqueous solution. Optimal conditions as contact time, adsorbent dose, initial concentration and pH, were determined.

EXPERIMENTAL SECTION

Materials

The adsorbents wheat bran and coffee waste were obtained commercially from Kosovo. They were washed thoroughly to remove dust using distilled water then dried at 80 ºC for 20 hours [33]. The dried samples were grinded and fractions of >0.2 mm were used for experiments.

Methodology

The sorption of Zn (II) ions on used adsorbents (wheat bran and coffee waste) were studied using a batch technique. The method used for this study was carried out as follows. The stock solution of zinc at different concentrations (47.5, 23.75, 11.81 and 4.71 mg/dm^3) was used in experimental runs. A known weight of adsorbent (0.10, 0.25 and 0.50 g) was equilibrated with 50 cm^3 Zn (II) solutions in a stopper Pyrex glass flask for a known period of time (5, 10, 20, 30, 60, 90, and 120 min), at different pH (3, 5, 7, 9, and 11) and different temperature (25, 35, 45, 55 ºC) values in a thermostatic shaker bath

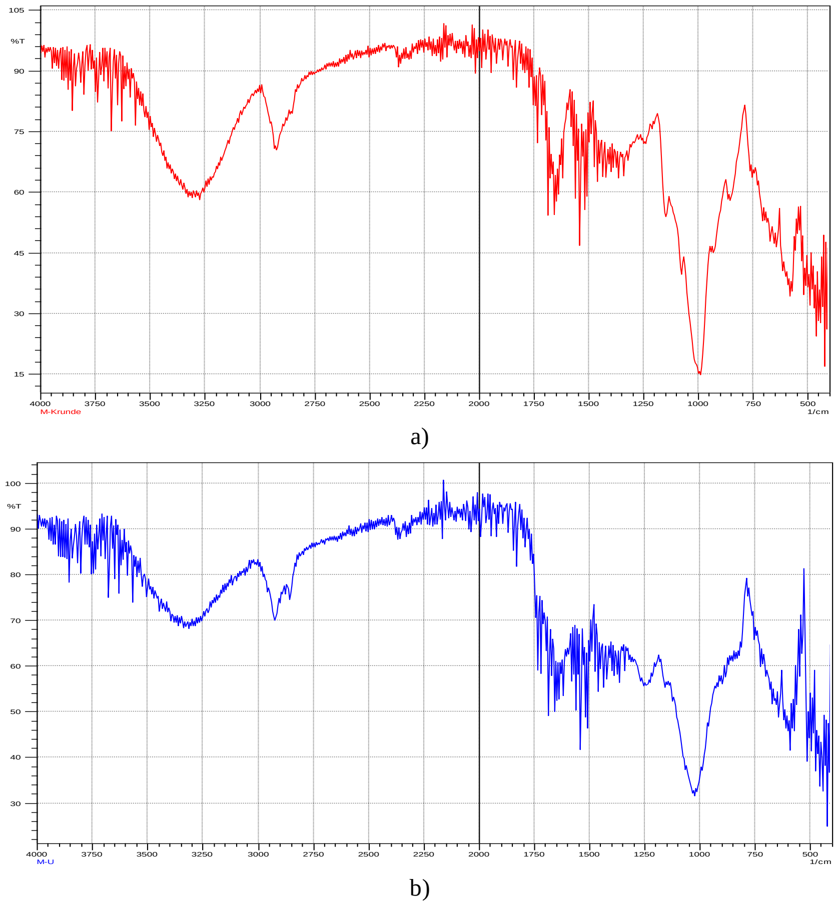

Fig. 1: IR Spectrum of a) wheat bran and b) waste coffee.

(200 rpm). The solutions were adjusted to final desired pH using 0.1 M HCl or 0.1 M NaOH (pH-meter HANA Model, HI 98130). To observe the effect of certain parameters, one selected parameter has been changed progressively keeping the others constant. After equilibration, the suspensions were filtered and analyzed by AAS (Atomic Adsorption Spectrometer, flame Contra AA 300, Analytik Jena).

The amount of adsorbed zinc ions per gram wheat bran at equilibrium q_e (mg/g), and the removal percentage (% A), were calculated using the following equations:

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

$$\%(A) = \frac{C_o - C_e}{C_0} \times 100 \quad (2)$$

Where C_0 and C_e are the initial and equilibrium concentrations of zinc (mg/dm^3), respectively; V is the volume of zinc solution (dm^3); and m is the weight of used wheat bran or waste coffee (g).

The pH of the point zero charge (pH_{PZC}) of adsorbents was determined by following the salt addition method [34].

RESULTS AND DISCUSSION

Characterization of adsorbents

The spectra of adsorbents (wheat bran, and waste coffee) which were analyzed by FT-IR spectrophotometer (Shimadzu, FT-IR 8400 S with KBr disc) over a scan range of 500–4000 cm^{-1} with an average 16 scans, are shown in Fig. 1a and 1b. From the FT-IR spectra it could be seen that there is a number of functional groups characteristic for adsorbents used. For wheat bran, the broad band at 3320 cm^{-1} was dominated by the stretching vibration of aromatic and aliphatic O-H groups. The peaks at 2925 and 2850 cm^{-1} from C-H stretching in the methyl and methylene groups of side chains and aromatic methoxyl groups. Three next peaks, at about 1740, 1690 and 1650 cm^{-1}, based from

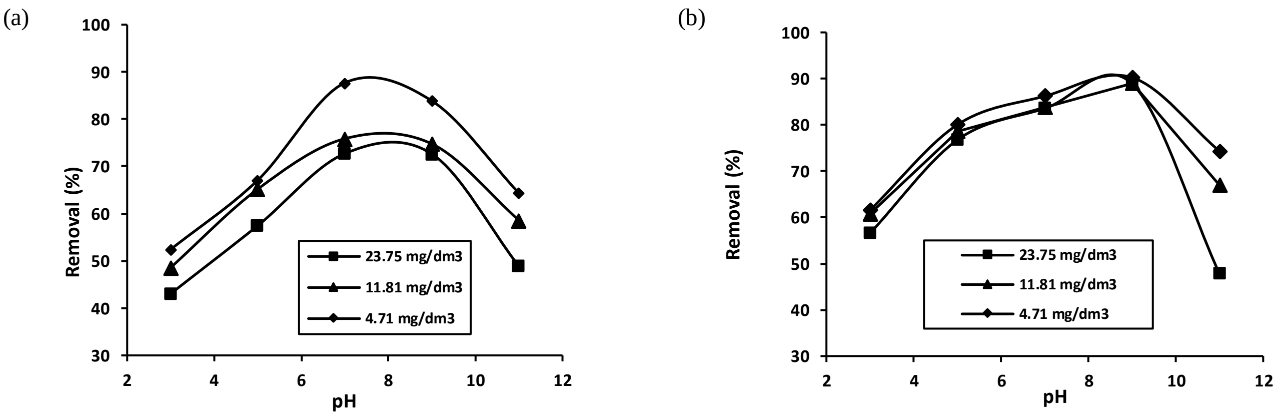

Fig. 2: Removal of Zn (II) ions by a) wheat bran and b) waste coffee vs pH, at different initial concentration levels.

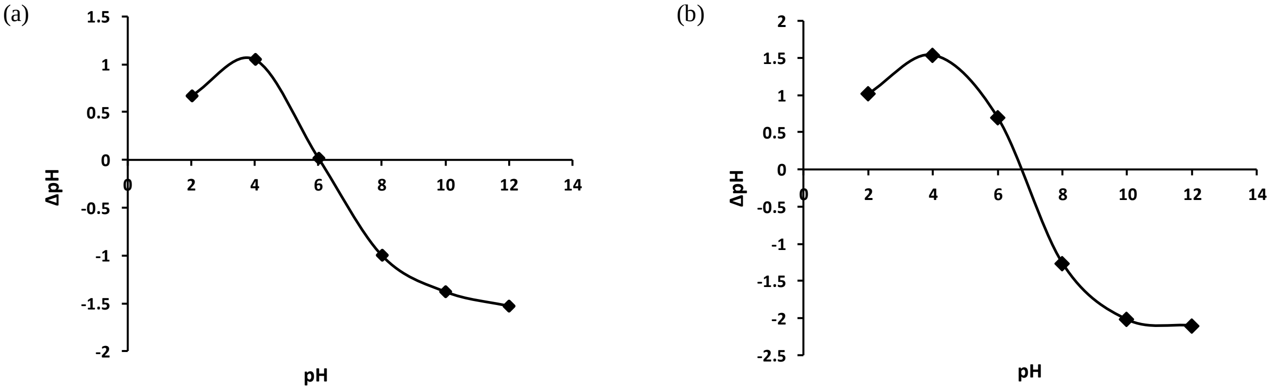

Fig. 3: Determination of the pH_{PZC} for a) wheat bran and b) waste coffee.

conjugated carboxyl and carbonyl stretching. Moreover, two peaks at 1520 and 1550 cm^{-1} originated from aromatic vibrations and at around 1000 cm^{-1} vibration of C-O-C group [35]. IR spectrum of waste coffee is approximately the same as the wheat bran, but the intensity of peaks is lower.

Effect of pH solution

The pH of the aqueous solution is an important control parameter in the heavy metal adsorption process because the surface charge density of the adsorbent and the metallic species depend on the hydrogen ion concentration [36]. This can also affect the degree of ionization of the adsorbate molecules and is accountable for the higher/lower sorption capacity of the adsorbent [37]. The batch studies were carried out to obtain optimum pH for the removal of zinc ions, using both adsorbents (wheat bran and waste coffee) by varying the range of pH from 3 to 11, under specific conditions (adsorbent dose 0.25g, contact time 30min and temperature 25 °C).

The results for both adsorbents are presented in Fig. 2a wheat bran, 2b waste coffee.

It was observed that the removal of Zn (II) was increased by increasing the pH of the liquid phase and reaching the optimum value at pH 7 for wheat bran and pH 9 for waste coffee. The removal of zinc ions by the wheat bran at pH 3 was only 52.44%, but at pH 7 it was 87.69 %. While the removal of zinc ions by waste coffee at pH 3 was 60.80% and at pH 9 was 88.99 %. This substantial increase in zinc ions removal by the two adsorbents can be well described based on pH of the point of zero charge (pH_{PZC}), which depends on the chemical structure and electronic properties of the functional groups on the adsorbent surface [38]. These results are presented in Fig. 3a and 3b.

From Fig. 3, the pH_{PZC} values are about 6 for wheat bran and 6.8 for waste coffee respectively. There was a negatively charged surface of adsorbent at pH above these values, while there was a positively charged surface

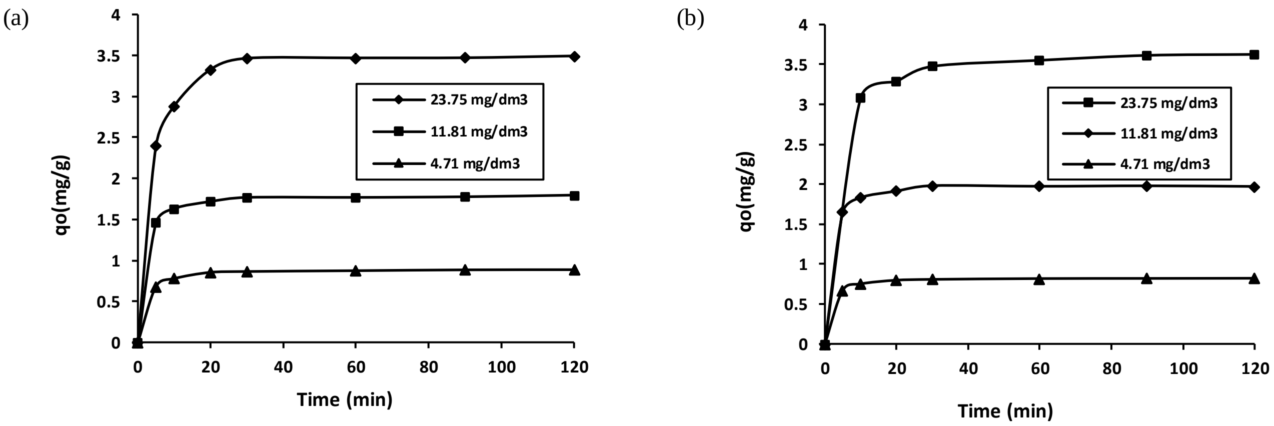

Fig. 4: Effect of different contact times on adsorption of Zn(II), by a) wheat bran and b) waste coffee, for different initial concentrations.

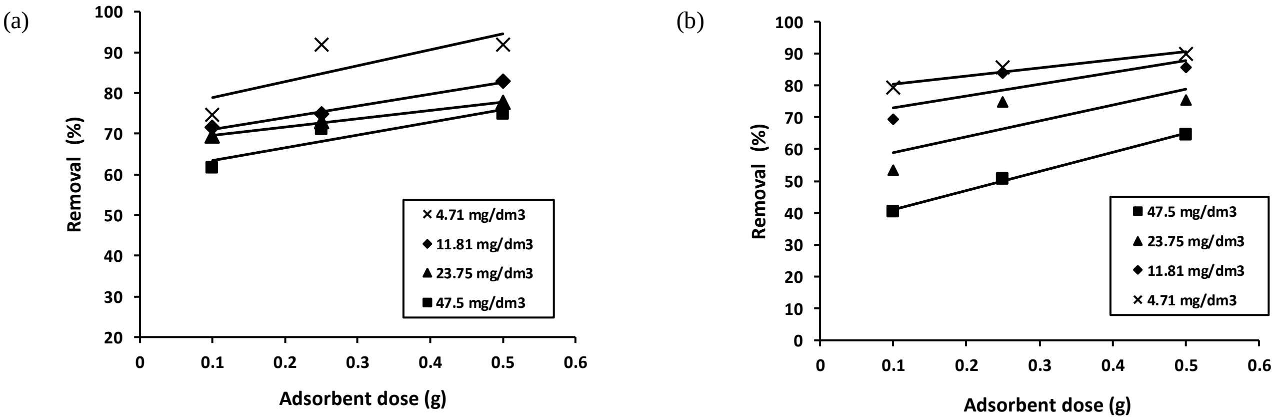

Fig. 5: Effect of adsorbent dose on the adsorption of Zn(II) ions by a) wheat bran and b) waste coffee, for different initial concentration.

of adsorbents at pH below these values. Therefore, below pH_{PZC}, there were competition between the hydrogen and zinc ions to reach the surface. These repulsive forces hinder the contact of positively charged zinc ions to the surface of adsorbents and contribute to the small amount of Zn adsorbed on adsorbents until pH < 5, but a large increase in the amount of adsorption is observed at pH > 5. From the graphs (Fig. 3a and 3b) it may be concluded that the amount of zinc ions adsorbed is increased at pH $>pH_{PZC}$ in both adsorbents.

Effect of contact time

The effect of contact time on the zinc removal for two different materials (wheat bran and waste coffee), at pH solution of 5.1, adsorbent dose 0.25g, and 25°C are shown in Fig. 4a and 4b.

The zinc adsorption increases with time until equilibrium is attained between the amounts of zinc adsorbed on the biosorbents and the remaining zinc in the solution [39]. Figs. 4a and 4b show that, the adsorption of zinc increases with time from 0 to 30 min and then becomes constant, so the equilibrium was reached after 30 min. The rate of Zn(II) uptake was quite rapid, at the beginning. At equilibrium removal of zinc was 72.97 % with wheat brain, and 74.78 % with waste coffee (initial conc. 23.75 mg/dm^3). The rate behavior of two different materials is similar.

Effect of adsorbent dose

The effect of adsorbent dose on the uptake of Zn(II) ions by wheat bran and waste coffee is studied by changing the adsorbent dose: 0.10, 0.25, and 0.50 g for 50 cm^3 zinc solution, while other parameters are kept unchanged. These results are represented in Fig. 5a and 5b.

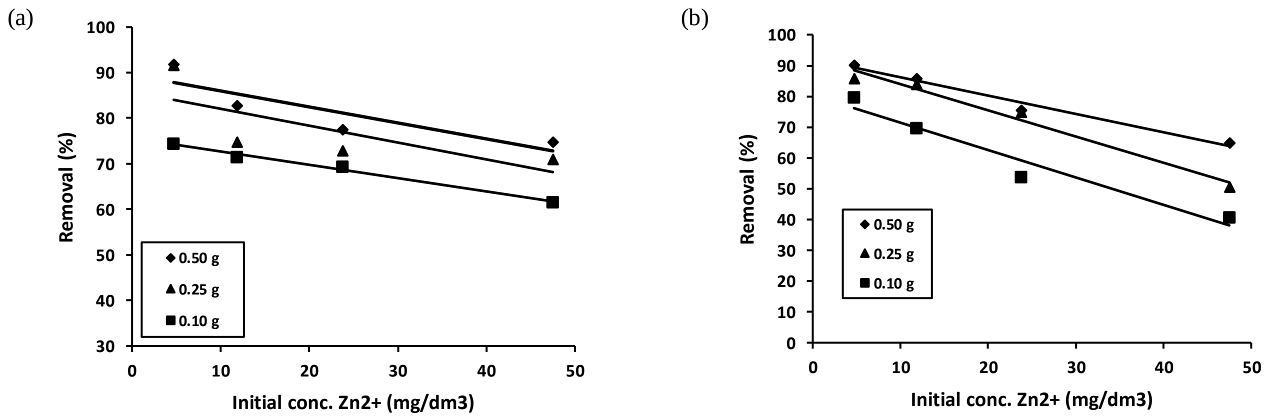

Fig. 6: Effect of initial concentrations on the adsorption of Zn(II) by a) wheat bran and b) waste coffee for different adsorbent doses.

As it can be seen from the Figs. 5a and 5b, percentage removal increases with increasing the adsorbent dose for both adsorbents. While, the adsorbent dose increased from 0.10 to 0.50 g, removal of zinc increased from 74.52 to 91.93 % by wheat bran and from 79.41 to 90.02 % by waste coffee, respectively. A similar trend was found for all used initial concentrations (47.5, 23.75, 11.81 and 4.71 mg/dm^3). This trend is expected because as the adsorbent dose increases the number of adsorbent particles increases and thus more zinc is attached to their surfaces [40-42].

Effect of initial concentration

The effect of initial concentration on zinc removal was studied by varying the concentration of zinc solution: 4.71, 11.81, 23.75, and 47.5 mg/dm^3, adsorbent dose 0.10, 0.25 and 0.50 g, at contact time 30 min, pH 5.1 and temperature 25 ^{o}C. The graph was plotted between different zinc ion concentration and percentage of removal, as shown in Fig. 6a for wheat bran and 6b for waste coffee.

The Figs. 6a and 6b, indicated that, the removal percentage decreases with the increase in initial zinc concentration. The removal is higher with lower initial concentration, and higher concentration is due to the availability of more adsorption binding sites at the initial stage [43, 44]. The maximum removal of zinc using wheat bran as adsorbent was 91.93% and for waste coffee 90.02% respectively (adsorbent dose 0.50 g and initial concentration 4.71 mg/dm^3).

Adsorption Isotherms

Adsorption equilibrium is a fundamental property in adsorption studies, considering that fact, numerous studies have been conducted in order to determine the amount of species adsorbed under a given set of conditions [45]. Adsorption isotherms are used to express the surface properties and affinity of the adsorbent and can also be used to compare the adsorption capacities of the adsorbents for pollutants in aqueous solutions. Langmuir and Freundlich isotherms are most used to describe the equilibrium sorption of metal ions [46].

Langmuir's isotherm model is based on a theory of monolayer adsorption. The quantity of particles adsorbed corresponds to the number of active centers, on the surface of the adsorbent [6].The model is expressed by:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{1}{q_m} C_e \quad (3)$$

q_m is the monolayer adsorption capacity of the adsorbent (mg/g); K_L (dm^3/mg) is the Langmuir adsorption constant and it is an affinity parameter related to the energy of biosorption; C_e is the equilibrium metal ion concentration in the solution (mg/dm^3), and q_e is the equilibrium metal ion concentration on the adsorbent (mg/g). Plotting C_e/q_e versus C_e results in a straight line of slope $1/q_m$ and intercepts $1/K_L q_m$. Langmuir isotherms for wheat bran and waste coffee are presented in Fig.7a and 7b.

The essential characteristics of the Langmuir isotherm can be expressed by a dimensionless constant called the separation factor R_L [47]:

$$R_L = \frac{1}{1 + K_L C_0} \quad (4)$$

K_L is Langmuir constant (dm^3/mg) and C_o is initial concentration of adsorbate (mg/g). R_L values indicate

Table 1: Separation factor R_L of wheat bran and waste coffee in different concentrations.

	Wheat bran			Waste coffee		
C_o (mg/dm^3)	23.75	11.81	4.71	23.75	11.81	4.71
R_L	0.336	0.505	0.719	0.185	0.314	0.534

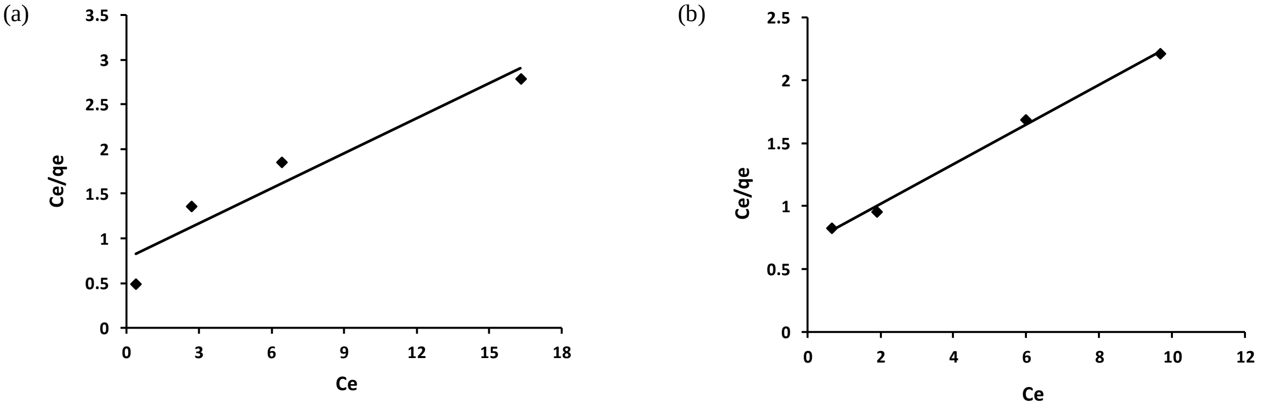

Fig. 7: Langmuir isotherms for adsorption of Zn (II) ions by a) wheat bran and b) waste coffee.

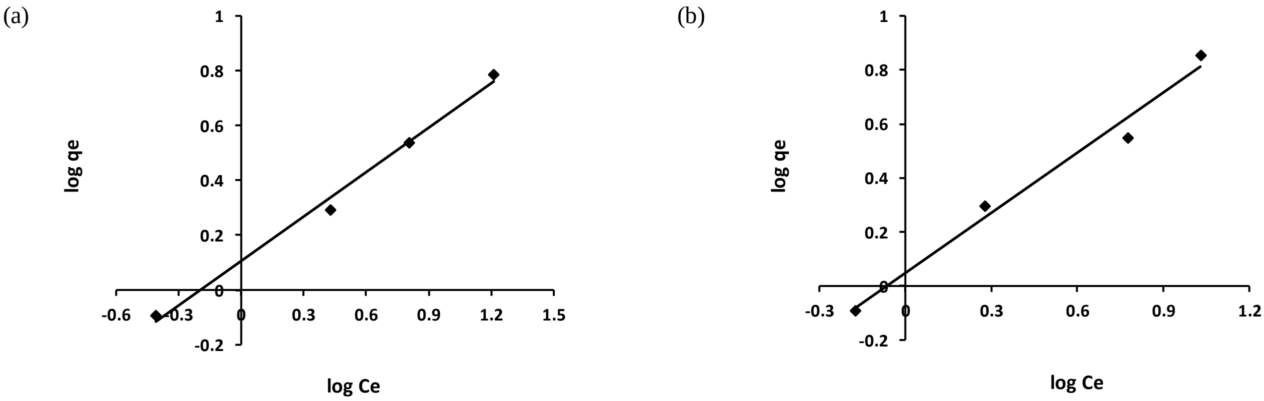

Fig. 8: Freundlich isotherms for adsorption of Zn (II) ions by a) wheat bran and b) waste coffee.

the adsorption to be unfavorable when R_L> 1, linear when R_L = 1, favorable when R_L<1, and irreversible when R_L=0 [47]. The R_L at different concentrations are between 0 and 1 for wheat bran and waste coffee which indicates a favorable adsorption of Zn(II) ions. The data of separation factorsr for wheat bran and waste coffee are presented in Table 1.

The Freundlich model isotherm proposes a heterogeneous energetic distribution of active sites and gives an expression that defines the surface heterogeneity and the exponential distribution of active sites and their energies. This isotherm describes reversible adsorption and is not restricted to the formation of a monolayer [48]. The Freundlich equation is given by [6]:

$$\log q_e = \log K_F + 1/n \log C_e \quad (5)$$

K_F and *1/n* are Freundlich constants, K_F (mg/g) is related to adsorption capacity and *1/n* is an empirical parameter related to the adsorption intensity, which varies with the heterogeneity of the material. The constants *1/n* and $\log K_F$ were calculated from the slope and intercept, respectively. Freundlich isotherms for wheat bran and waste coffee are presented in Fig.8a and 8b.

Langmuir and Freundlich isotherm data are presented in Table 2.

From these results, it is shown that the adsorption of Zn(II) ions on waste coffee fits well with the Langmuir

Table 2: Langmuir and Freundlich isotherm data.

Adsorbents	Langmuir model			Freundlich model		
	q_{max}(mg/g)	K_L(dm^3/mg)	R^2	1/n	K_F(mg/g)	R^2
Wheat bran	9.01	0.083	0.914	0.511	1.273	0.993
Waste coffee	6.41	0.185	0.993	0.672	1.132	0.980

Table 3: Data of the Zn(II) ion adsorption capacityof the various adsorbents.

Adsorbents	Adsorption capacity (mg/g)	References
Lig800	37.3	35
MISCBA	28.6	7
Lig	18.8	35
Lignocellulosic substrate	16.02	50
Lignin	11.18	51
Cork biomass	6.80	52
Activated Palm midrib	5.72	5
Kraft lignin	1.77	53
Wheat bran	9.01	This study
Waste coffee	6.41	This study

(R^2 0.993) more than Freundlich isotherms (R^2 0.980), confirming that, Zn(II) adsorption occurs on a homogeneous adsorbent surface, forming a monolayer, in which each adsorption site can take a single molecule of adsorbate with the same adsorption energy [33, 49]. Another situation is by wheat bran, from the data, it is obvious that, the adsorption process better fits with Freundlich (R^2 0.993) than Langmuir isotherms (R^2 0.914). Freundlich isotherm suggests that the adsorption occurred at the multilayer surface of the wheat bran. The maximum adsorption capacity of the adsorbent was found to be 9.01 mg/g by wheat bran and 6.41 mg/g by waste coffee.

Comparison of the zinc ions adsorption capacity of some adsorbents is presented in Table 3.

According to Table 3, adsorption capacity of used biosorbents is about in the medium in comparison with other adsorbent.

Thermodynamic parameters

The effect of temperature on the adsorption of Zn(II) ions was studied in interval 298 – 328 K. Thermodynamic parameters were calculated to determine which process would occur spontaneously [54]. The variation of the thermodynamic parameters (ΔH°, ΔS°, and ΔG°) should provide insight into the mechanism and adsorption of an isolated system [55]. Thermodynamic parameters were calculated from the following equation:

$$k_e = \frac{q_e}{C_e} \tag{6}$$

k_e equilibrium constant, it's calculated at different temperatures.

$$\Delta G^o = -RT\ln k_e \tag{7}$$

ΔG°- Gibss free energy change, R- universal gas constant, T- absolute temperature.

$$\Delta G^o = \Delta H^o - \Delta S^o \tag{8}$$

From Eq. (7) and (8) equation (9) is obtained:

$$\ln k_e = -\frac{\Delta H^o}{RT} + \frac{\Delta S^o}{R} \tag{9}$$

ΔH° and ΔS° are standard enthalpy and entropy changes. According to Equation (9), the enthalpy and the entropy values can be calculated from the slope and intercept of the plot of *$\ln k_e$vs 1/T* [56]. These data are shown in Fig. 9a and 9b.

The results in Table 4 confirmed that, the temperature has a negative effect on the adsorption of Zn(II) ions onto wheat bran and waste coffee, which means that the temperature favors the desorption process. The negative value of ΔG° (except for wheat bran at 318, 328 K) indicates the spontaneous and feasibility of Zn(II) ions adsorption [54]. Consequently, the increased value of ΔG° with increased temperature indicates that the adsorption was more favorable at low temperature. It was found that Zn(II) adsorption on wheat bran and waste coffee has negative values of the enthalpy change, which means that adsorption is an exothermic process [33]. Additionally, in this study the enthalpy change was -34.87 kJ/mol and -3.655 kJ/mol for wheat bran and waste coffee, respectively.

Table 4: Thermodynamics parameters for wheat bran and waste coffee adsorbents.

Adsorbents	Temperature (K)	lnk_e	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (kJ/mol K)
Wheat bran	298	0.726	-1.798	-34.87	-0.1107
	308	0.414	-1.060		
	318	-0.285	0.753		
	328	-0.468	1.276		
Waste coffee	298	0.187	-0.463	-3.655	-0.0106
	308	0.153	-0.391		
	318	0.102	-0.269		
	328	0.054	-0.147		

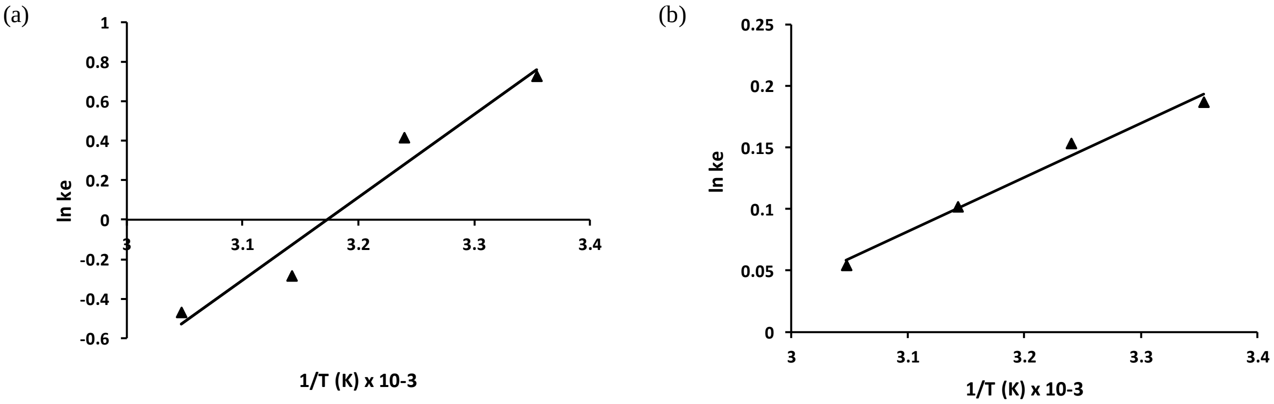

Fig. 9: Plot of lnk$_e$ vs 1/T for Zn (II) ions adsorption by a) wheat bran and b) waste coffee.

This suggests that the adsorption of Zn(II) ions is characterized with physical-chemical adsorption by wheat bran and physical adsorption by waste coffee [57]. Negative value of entropy change for two adsorbents suggested that randomness of the adsorption process decrease at the solid-solution interface [58].

CONCLUSIONS

In the present work, wheat bran and waste coffee have proven to be very good biosorbents. Wheat bran and waste coffee appear as effective and cheap biosorbents for the removal of zinc ions from aqueous solution. These two biosorbents are used without any chemical treatment. Furthermore, zinc ions were adsorbed onto the adsorbents very rapidly at the beginning, after 30 minute the equilibrium was reached and adsorption was constant. The maximum adsorption capacity of zinc ions by wheat bran and waste coffee were 9.01 mg/g and 6.41 mg/g respectively, using the optimal conditions of adsorbent dose: 0.25g/50cm^{3}solution, at 298 K. The equilibrium process was studied using Langmuir and Freundlich isotherms. Freundlich model was a better fit for zinc ion adsorption using wheat bran, while Langmuir model was a better fit for zinc ion adsorption using waste coffee. Thermodynamic parameters indicated that, the adsorption of zinc ions, using biosorbents (wheat bran and waste coffee) are exothermic in nature, favorable and spontaneous. These materials could be used for purification of waste water. The results are not only important for the industrial processes but also to the planet earth in general due to the resultant social and environmental benefits.

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