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Adsorption of Zn(II) from aqueous solution by using different adsorbents

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Abstract

The removal of Zn(II) from aqueous solution by different adsorbents was investigated. Clarified sludge (a steel industry waste material), rice husk ash, neem bark and a chemical adsorbent activated alumina were used for the adsorption studies. The influence of pH, contact time, initial metal concentration, adsorbent nature and concentration on the selectivity and sensitivity of the removal process was investigated. The adsorption of Zn(II) increased with increased concentration of the adsorbents and reached maximum uptake at 10 g/L and pH between 5 and 7. The equilibrium time was achieved after 1 h for clarified sludge, 3 h for rice husk ash and 4 h for activated alumina and neem bark, respectively. The adsorption process was found to follow a first-order rate mechanism and rate constant was evaluated at 30 °C. The rate constant was highest in case of clarified sludge (6.90×10^{-2} min^{-1}) and the activated alumina gave the lowest value (1.86×10^{-2} min^{-1}). Langmuir and Freundlich adsorption isotherms fit well in the experimental data and their constants were evaluated. The thermodynamic equilibrium constant and the Gibbs free energy were calculated for each system. The adsorption capacity (q_{max}) calculated from Langmuir isotherm and the values of Gibbs free energy obtained showed that clarified sludge has the largest capacity and affinity for the removal of Zn(II) compared to the other adsorbents used in the study.

Keywords: Zn(II) removal; Clarified sludge; Rice husk ash; Neem bark; Activated alumina; Batch adsorption; Adsorption capacity

1. Introduction

Ecotoxicological effects of heavy metals are well understood and have been a global concern for environmentalists. Due to their accumulation through food chain and persistent in nature, it is necessary to remove toxic heavy metals from wastewater. Metals are non-biodegradable and have great environmental, public health and economic impacts [1,2]. Beyond the permissible limits, they are generally toxic and some are even hazardous [3].

Zinc is considered as an essential element for life and act as a micronutrient when present in trace amounts. But too much zinc can be harmful to health. Zn(II) is reported to be toxic beyond permissible limits. Symptoms of zinc toxicity include irritability, muscular stiffness, loss of appetite and nausea [4]. The metal is further reported to be bioaccumulated into flora and fauna creating ecological problems. Canadian Water Quality Guidelines [5], Indian Standard [6] and WHO [7] recommended level of zinc in drinking water are 5 mg/L. The inland surface water discharge limit of zinc for effluent is 5 mg/L [8]. Most zinc enters the environment as the result of human activities such as mining, purifying zinc, lead and cadmium ores, steel production and coal burning and burning of wastes. Zinc is present in high concentration in wastewater of pharmaceuticals, galvanizing, paints, pigments, insecticides, cosmetics, etc. that causes serious problem to the environment.

Conventional technologies for the removal of heavy metal such as chemical precipitation, adsorption, electrolysis, ion exchange and reverse osmosis are often neither effective nor economical [9–16]. Among the physico-chemical treatment process adsorption is found to be highly effective, cheap and easy to adapt. Activated carbon in most cases has been used as an adsorbent for reclamation of municipal and industrial wastewater for almost last few decades [17–20]. But the high cost of activated carbon has inspired the investigators especially in developing countries like India to search for suitable low-cost adsorbents.

As a result, recent research has focused on the development of cost effective alternatives using various natural sources and industrial wastes [21–23]. Industrial wastes are potential low-cost adsorbents for metal removal since some of them displayed high ion exchange capability. Pretreatment of adsorbent is also commonly used to increase the adsorption capacity of these materials. Several researches have been made significant

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contributions in this area, utilizing a number of materials including fly ash [24,25], sugar beat pulp [26], clay [27,28], chitosan [29], coconut coirpitch carbon [30], biomass [31,32], zeolites [33,34], rice bran, soybeans and cotton seed hulls [35], sunflower stalks [36], calcined phosphate [37], low-grade phosphate [16], red mud [38,39], tea leaves [40], natural zeolite [41], almond shells, olive stones and peach [42], sediments of rivers [43], peanut hull [44], bentonite [45], saw dust [46,47], baggage fly ash [48], banana and orange peels [49], carrot residue [50], etc.

The objective of the study is to investigate comparative adsorption characteristics for removal of Zn(II) from aqueous solution by the use of low-cost abundantly available non-conventional adsorbents like clarified sludge, rice husk ash, neem bark and a chemical adsorbent activated alumina. The effects of pH, contact time, adsorbent dosage level and initial metal concentration on the adsorption capacity are studied. During the work program, adsorption kinetics, isotherm models and thermodynamic parameters are also investigated.

2. Materials and methods

2.1. Adsorbents used

Rice husk ash, clarified sludge, neem bark and activated alumina.

The rice husk ash was collected from a local rice mill. The clarified sludge was collected from sludge thickener of Basic Oxygen Furnace of Steel Industry, Steel Authority of India Limited, Rourkela, India. Neem bark was collected from neem tree. After collection it was washed thoroughly with double distilled water to remove muddy materials and then sun dried. Then it was cut into small pieces. After screening it was again washed with double distilled water several times to remove dust and color. Finally it was dried in an oven at 80 °C for 6 h and then used as adsorbent. Activated alumina was procured from Titan Biotech, New Delhi, India. The entire samples were dried and then cooled, homogenized and ground to pass through a −44 + 52 mesh screen.

The above adsorbents were examined by scanning electron microscopy (SEM, Hitachi S 415 A). The micrographs of the adsorbents obtained from SEM study are shown in Fig. 1(a–d). These figures showed that the adsorbents had an irregular and porous surface texture.

2.2. Reagents and equipments

All the necessary chemicals obtained from E. Merck India Limited, Mumbai, India. HACH-DR-4000 UV Visible Spectrophotometer was used for determination of Zn(II) content in standard and treated solution. The pH of the solution was measured with a 5500 EUTECH pH Meter using FET solid electrode calibrated with standard buffer solutions. The stock solution containing 1000 mg/L of Zn(II) was prepared by dissolving pure zinc metal in 1:1 hydrochloric acid solution and then diluting the same up to 1000 ml in a volumetric flask with double distilled water.

2.3. Batch adsorption studies

Using the necessary adsorbents in a 250 ml stoppered conical flask containing 100 ml of test solution batch adsorption studies were carried out at the desired pH value, contact time and

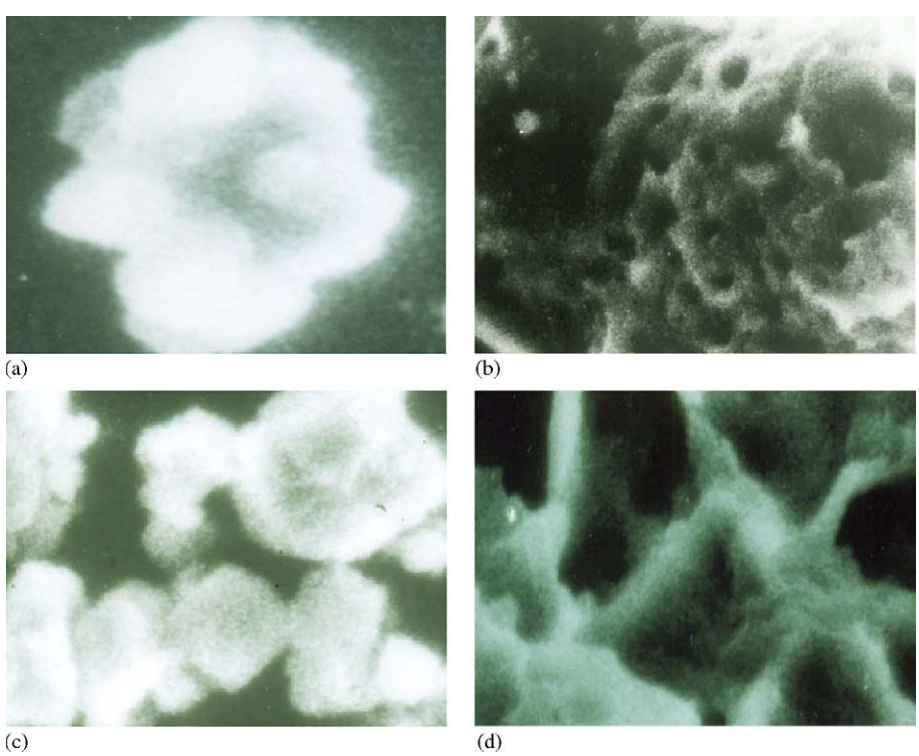

Fig. 1. SEM micrographs of (a) clarified sludge (500×), (b) rice husk ash (500×), (c) activated alumina (500×) and (d) neem bark (750×).

adsorbent dosage level. Different initial concentration of Zn(II) solutions was prepared by proper dilution from stock 1000 mg/L Zn(II) standard. pH of the solution monitored by adding 0.1 M HCl and 0.1 M NaOH solution as per required pH value. Necessary amount of adsorbent material was then added and contents in the flask were shaken for the desired contact time in an electrically thermostated reciprocating shaker at 110 strokes/min at ambient temperature, i.e. 30 ± 2 °C. The time required for reaching the equilibrium condition estimated by drawing samples at regular intervals of time till equilibrium was reached. The contents of the flask were filtered through filter paper and the filtrate was analyzed for Zn(II) concentration using HACH-DR-4000 UV Visible Spectrophotometer following standard methods for examination of water and wastewater, APHA, AWWA 20th edition [51].

The percent removal of Zn(II) was calculated as follows:

$$\%\text{Removal of Zn(II)} = \left(\frac{C_{\text{initial}} - C_{\text{final}}}{C_{\text{initial}}} \times 100\right) \quad (1)$$

where C_{initial} and C_{final} are the initial and final Zn(II) concentrations, respectively.

Adsorption experiments for the effect of pH were conducted by using a solution having 25 mg/L of Zn(II) concentration with an adsorbent dosage of 10 g/L and stirring the same for a contact time of 4 h. The effect of adsorbent dosage level on percent removal of Zn(II) was studied using Zn(II) concentration of 25 mg/L having pH adjusted to 5. Throughout the study, the contact time was varied from 15 to 300 min, the pH of the solution from 3 to 11, the initial zinc concentration from 3 to 50 mg/L and the amount of adsorbent from 2.5 to 30 g/L.

2.4. Adsorption kinetics

The kinetic parameters for the adsorption process were studies on the batch adsorption of 25 mg/L of Zn(II) at pH 5. The contact time was varied from 15 to 300 min and the percent removal of Zn(II) was monitored during the study. The data was fitted to Lagergren equation [52].

$$\log(q_e - q) = \log q_e - \frac{K_{ad} t}{2.303} \quad (2)$$

where q is the amount of Zn(II) (mg/g of adsorbent) removed at time t (min), q_e the amount of Zn(II) removed at equilibrium and K_{ad} is the rate constant of adsorption (min^{-1}).

2.5. Adsorption isotherms

The adsorption isotherms for the Zn(II) removed were studied using initial concentration of Zn(II) between 10 and 100 mg/L at an adsorbent dosage level of 10 g/L. The data obtained were then fitted to the Langmuir adsorption isotherm [52] applied to equilibrium adsorption assuming monolayer adsorption onto a surface with a finite number of identical sites and is represented as follows:

$$\frac{C_e}{q_e} = \frac{1}{q_{max} b} + \frac{C_e}{q_{max}} \quad (3)$$

where C_e is the equilibrium concentration of adsorbate (mg/L), q_e the amount adsorbed at equilibrium (mg/g adsorbent), and q_{max} (mg/g) and b (L/mg) are the Langmuir constant related to the adsorption capacity and energy of adsorption, respectively.

The adsorption data obtained were then fitted to the Freundlich adsorption isotherm [52], which is the earliest relationship known describing the adsorption equilibrium and is expressed by the following equation:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (4)$$

where q_e is the amount of adsorbate adsorbed per unit weight (mg/g of adsorbent), C_e the equilibrium concentration (mg/L) of the adsorbate and K_f is the Freundlich constant.

2.6. Thermodynamic parameters

The thermodynamic equilibrium constant (K_C°) for each system was obtained at 30 ± 2 °C by calculating the apparent equilibrium constant K'_C at different initial concentration of Zn(II) and extrapolating to zero.

$$K'_C = \frac{C_a}{C_e} \quad (5)$$

where C_a is the concentration of Zn(II) on the adsorbent at equilibrium in mg/L and C_e is the equilibrium concentration of Zn(II) in solution in mg/L.

The Gibbs free energy (ΔG°) for the adsorption process was obtained at 30 ± 2 °C using the formula

$$\Delta G^\circ = -RT \ln K_C^\circ \quad (6)$$

where R is the ideal gas constant (8.314 J mol^{-1} K^{-1}) and T is the temperature in K.

All the experiments are repeated with the reproducibility and the relative deviation of the order of ±0.5% and ±2%, respectively.

3. Results and discussion

3.1. Effect of pH

The uptake of Zn(II) as a function of hydrogen ion concentration was examined over a pH range of 3–11. The removal efficiency was found to be highly dependent on hydrogen ion concentration present in solution. The effect of pH on adsorption efficiency is shown in Fig. 2. Maximum Zn(II) removal was obtained in the pH range of 5–7. For rice husk ash with an initial concentration of 25 mg/L of Zn(II), maximum 96.8% removal was obtain at a pH value of 5. For clarified sludge, optimum pH for adsorption of Zn(II) was found to be 5. In case of activated alumina and neem bark also, maximum sorption of Zn(II) from aqueous solution occurred at a pH value around 5. Hence, pH 5 was considered to be the optimum pH for further studies. The effect of pH can be explained considering the surface charge on the adsorbent material. At low pH, due to high positive charge density due to protons on the surface sites, electrostatic repulsion will be high during uptake of metal ions resulting in lower

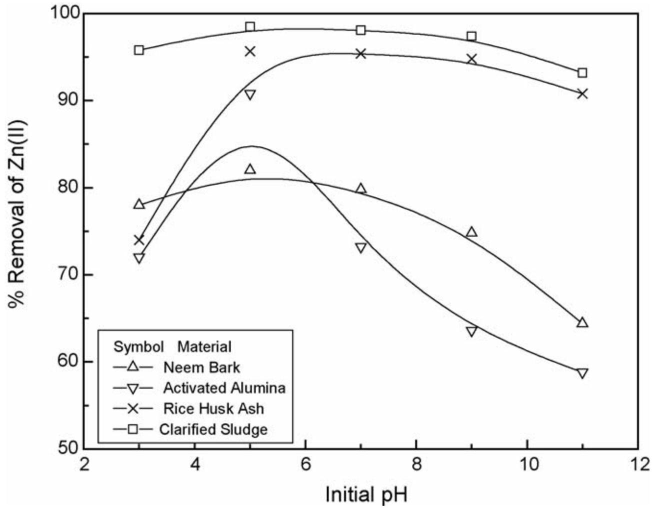

Fig. 2. Effect of pH on the adsorption of Zn(II) by selected adsorbents, initial Zn(II) concentration 25 ppm, adsorbent dosage 10 g/L, contact time 4 h and temperature 30 °C.

removal efficiency. With increasing pH, electrostatic repulsion decreases due to reduction of positive charge density on the sorption sites thus resulting in an enhancement of metal adsorption. The above fact related to the effect of pH on adsorption also supported by several earlier workers [53,37]. At higher pH values OH ions compete for Zn(II) with the active sites on the surface of the adsorbents [54].

3.2. *Effect of initial Zn(II) concentration*

The efficiency of Zn(II) removal is affected by the initial metal ion concentration, with decreasing removal percentages as concentration increases from 3 to 50 mg/L at constant pH of 5 (Fig. 3). Adsorbent dosage level maintained at 10 g/L for all the adsorbents considered for study. This effect can be explained as follows: at low metal ion/adsorbent ratios, metal ion adsorption involves higher energy sites. As the metal ion/adsorbent ratio increases, the higher energy sites are saturated and adsorption begins on lower energy sites, resulting in decreases in the adsorption efficiency [30,55].

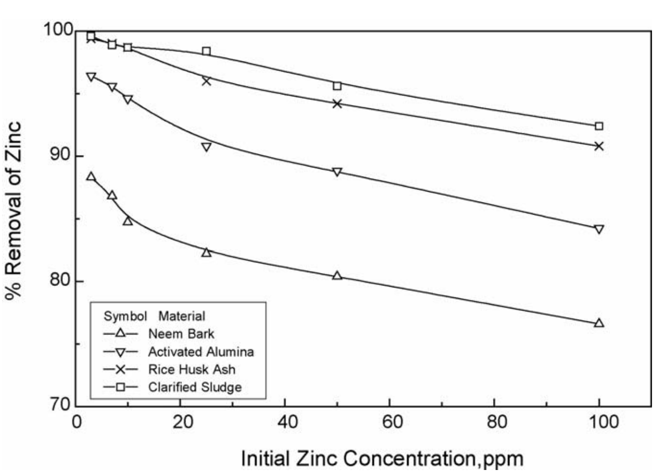

Fig. 3. Effect of initial concentration on the adsorption of Zn(II) by selected adsorbents: pH 5, adsorbent concentration 10 g/L, contact time 4 h and temperature 30 °C.

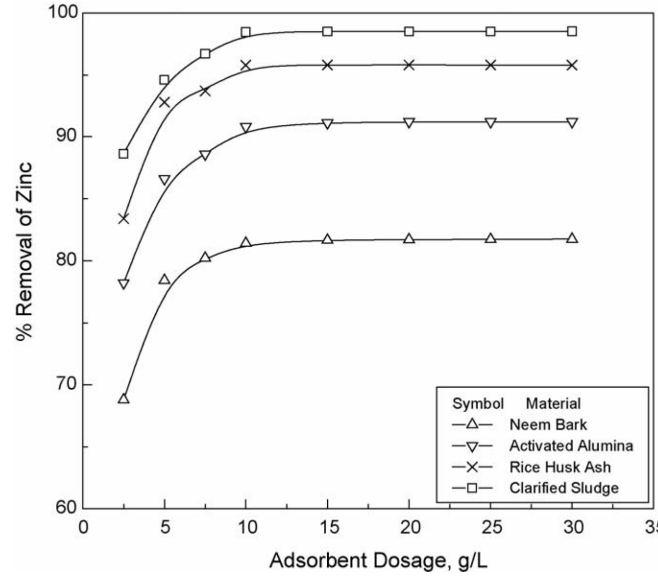

Fig. 4. Effect of adsorbent concentration on adsorption of Zn(II) by selected adsorbents: pH 5, initial Zn(II) concentration 25 ppm, contact time 4 h and temperature 30 °C.

3.3. *Effect of adsorbent type and concentration*

The effect of adsorbent type and its concentration is depicted in Fig. 4. The selected adsorbents (clarified sludge, rice husk ash, activated alumina and neem bark) were used at concentration ranging from 2.5 to 30 g/L in a batch adsorption technique. In each case increase in adsorbent concentration resulted in an increase in percent removal of Zn(II). After certain adsorbent dosage the removal efficiency is not increased so significantly. At 5 g/L of adsorbent dosage level the removal of Zn(II) was found to be between 94.6% (clarified sludge) and 78.4% (neem bark). At 10 g/L of clarified sludge the removal of Zn(II) from solution was found to be 98.7%. In case of rice husk ash, Zn(II) removal efficiency of 95.8% was achieved at an adsorbent dosage level of 10 g/L and for activated alumina under same condition the removal efficiency was 90.8%. It is evident that for all the adsorbents maximum removal efficiency was achieved at an adsorbent dosage level of 10 g/L. Therefore, the following experiments were carried out at adsorbent concentration of 10 g/L. The variation in sorption capacities between the various adsorbents could be related to the type and concentration of surface group responsible for adsorption of metal ions from solution [56]. With increasing adsorbent dosage more surface area is available for adsorption due to increase in active sites on the adsorbent. Rice husk ash contains carbon and silica based material that binds the metal ion from aqueous solution. Activate alumina is an alumina based material with trace amounts of metal oxides and silica which act as an adsorbent sites. Adsorption Zn(II) by clarified sludge may be attributed due to the combined effect of silica, metal oxides and carbon present in it as major constituents. Neem bark contains cellulose based plant fibers

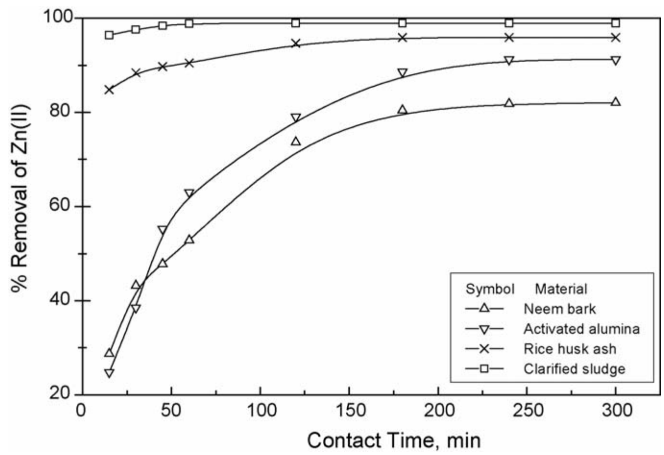

Fig. 5. Effect of contact time on the adsorption of Zn(II) by selected adsorbents: initial Zn(II) concentration 25 ppm, adsorbent dosage 10 g/L, pH 5 and temperature 30 °C.

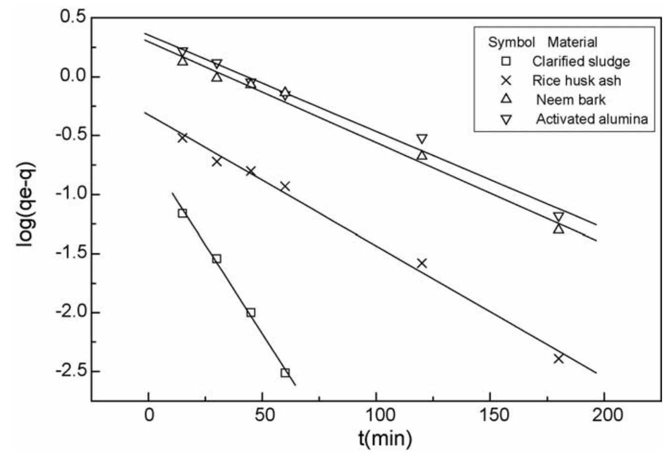

Fig. 6. Lagergren plot for the adsorption of Zn(II) by selected adsorbents: pH 5, initial concentration 25 mg/L, adsorbent dosage 10 g/L and temperature 30 °C.

Table 1
Lagergren rate constants for adsorption of Zn(II) on different adsorbents

Adsorbents	Lagergren rate constants, K_{ad} (min^{-1})	r^2
Clarified sludge	6.90×10^{-2}	0.9958
Rice husk ash	2.55×10^{-2}	0.9922
Activated alumina	1.86×10^{-2}	0.9875
Neem bark	1.95×10^{-2}	0.9880

with many hydroxyl and carboxylic group that are responsible for binding Zn(II) ion from aqueous solution. The availability of a particular functional group or binding site does not necessarily guarantee its accessibility as a sorption site for a metal ion, due to steric, conformational or other types of barriers [56]. The advantage of clarified sludge for the removal of Zn(II) from aqueous solution over the other adsorbents may be arise from the high concentration of active sites and its availability for sorption, making easier penetration of Zn(II) to the sorption sites.

3.4. Effect of contact time and adsorption rate kinetics mechanism

The experimental runs measuring the effect of contact time on the batch adsorption of 25 mg/L Zn(II) at 30 °C and at initial pH value 5 is shown in Fig. 5. It is obvious that increase in contact time from 0.5 to 2.0 h enhanced significantly the percent removal of Zn(II). The initial rapid adsorption gives away a very slow approach to equilibrium. The nature of adsorbent and its available sorption sites affected the time needed to reach the equilibrium. For clarified sludge this time is 1 h. In case of rice husk ash, time needed to reach the equilibrium is 3 h. For other two adsorbents, namely activated alumina and neem bark, a contact time of 4 h is needed for equilibrium to be established. All the other experiments on the physical properties of adsorption are conducted after 4 h of contact time.

The kinetics of Zn(II) adsorption was studies from the time versus %removal curves. The rate kinetics of Zn(II) adsorption on the clarified sludge as well as on the other adsorbents observed to follow the first-order rate law derived by Lagergren (Eq. (2)). Fig. 6 shows the Lagergren plot of $\log(q_e - q)$ versus time (min) for all adsorbents. The linearity of these plots indicates that a first-order mechanism is indeed follow in this process. The rate constants (K_{ad}) for each system were calculated from the linear least square method and are given in Table 1 along with the correlation coefficient (r^2). It is pertinent to mention that pH of the solution does not change significantly during the adsorption process.

3.5. The adsorption isotherms

The relation between the initial concentration of Zn(II) and its percentage removal from solution was studied for all adsorbents included in the study. The initial concentrations of Zn(II) studied were 10, 25, 40, 50, 80 and 100 mg/L at an adsorbent concentration of 10 g/L. The adsorption equilibrium data are conveniently represented by adsorption isotherms, which correspond to the relationship between the mass of the solute adsorbed per unit mass of adsorbent q_e and the solute concentration for the solution at equilibrium C_e.

The equilibrium data for Zn(II) adsorption on different adsorbents were fitted to Langmuir equation (Eq. (3)): an equilibrium model able to identify chemical mechanism involved. Linear plots of C_e/q_e versus C_e (Fig. 7) were employed to determine the value of q_{max} (mg/g) and b (L/mg). The data obtained with the correlation coefficients (r^2) was listed in Table 2. The Langmuir constants q_{max} and b are related to the adsorption capacity (amount of adsorbate adsorbed per unit mass of the adsorbent to complete monolayer coverage) and energy of adsorption, respectively. The value of adsorption capacity q_{max} (maximum uptake) is highest (15.53 mg/g) for clarified sludge. Neem bark shows the

Table 2
Langmuir adsorption isotherm constants for Zn(II) on different adsorbents

Adsorbents	Q (mg g^{-1})	b (l mg^{-1})	r^2
Clarified sludge	15.53	0.299	0.9971
Rice husk ash	14.30	0.222	0.9955
Activated alumina	13.69	0.102	0.9932
Neem bark	13.29	0.047	0.9923

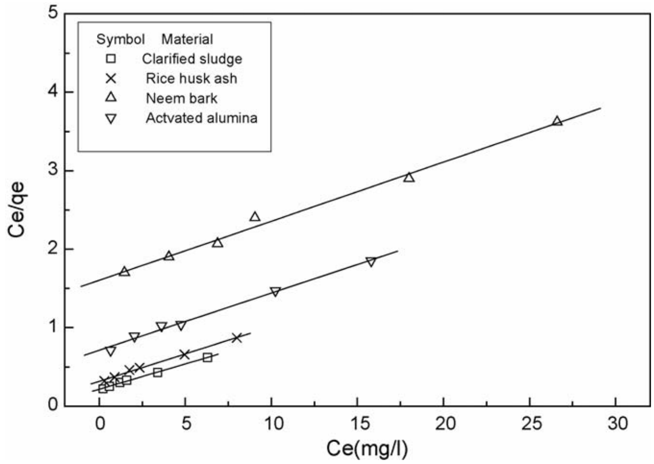

Fig. 7. Langmuir plot for the adsorption of Zn(II) by selected adsorbents: pH 5, adsorbent dosage 10 g/L, contact time 4 h and temperature 30 °C.

lowest value of adsorption capacity q_{max} (13.29 mg/g). However, the isotherm parameters, together with the correlation coefficients, of the Langmuir equation for the adsorption of Zn(II) on different adsorbents show that the Langmuir equation gives a good fit to the adsorption isotherm.

Weber and Chakraborti [57] expressed the essential characteristics and the feasibility of the Langmuir isotherm in terms of a dimensionless constant separation factor or equilibrium parameter R_L, which is defined as,

$$R_L = \frac{1}{1 + bC_0} \tag{7}$$

where b is the Langmuir constant and C_0 is the initial concentration of Zn(II). The R_L value indicates the shape of the isotherm as follows:

R_L value	Type of isotherm
$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$0 < R_L < 1$	Favorable
$R_L = 0$	Irreversible

According to McKay et al. [58] R_L values between 0 and 1 indicate favorable adsorption. The R_L value for the adsorption of Zn(II) on different adsorbents at initial concentration of 3 mg/L (lowest concentration studied) and 100 mg/L (highest concentration studied) are listed in Table 3. The data obtained represent a favorable adsorption for all the adsorbents under study.

The equilibrium data also fitted to Freundlich equation (Eq. (4)), a fairly satisfactory empirical isotherm can be used for non-ideal adsorption. The Freundlich isotherm constants K_f and n are constants incorporating all factors affecting the adsorption process such as of adsorption capacity and intensity of adsorption. The constants K_f and n were calculated from Eq. (4) and Freundlich plots (Fig. 8). The amount of absorbent required to reduce any initial concentration to predetermined final concentration can be calculated. The values for Freundlich constants and correlation coefficients (r^2) for the different adsorbents used during the study are also presented in Table 4. The values of n between 1 and 10 (i.e., $1/n$ less than 1) represent a favorable adsorption [3,30,53]. The adsorption capacity K_f was highest for clarified sludge followed by rice husk ash, activated alumina and neem bark, respectively. The values of n, which reflect the intensity of adsorption, also presented the same trend. The n values obtained for all the four adsorbents considered for study represent a beneficial adsorption.

Table 3
Separation factor or equilibrium parameter R_L for adsorption of Zn(II) on different adsorbents

Adsorbents	Separation factor or equilibrium parameter (R_L)	
	Initial Zn(II) concentration, 10 mg/L	Initial Zn(II) concentration, 100 mg/L
Clarified sludge	0.256	0.033
Rice husk ash	0.312	0.043
Activated alumina	0.495	0.089
Neem bark	0.680	0.178

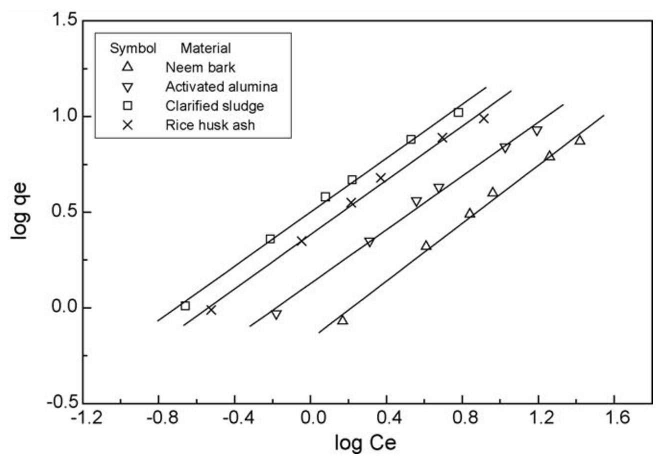

Fig. 8. Freundlich plot for the adsorption of Zn(II) by selected adsorbents: pH 5, adsorbent dosage 10 g/L, contact time 4 h and temperature 30 °C.

3.6. Thermodynamics for adsorption

The process of Zn(II) adsorption can be summarized by the following reversible process, which represents a heterogeneous equilibrium:

$$\text{Zn(II) in solution} \leftrightarrow \text{Zn(II) in adsorbent} \tag{8}$$

The thermodynamic equilibrium constant (K_C°) obtained from calculating the apparent equilibrium constant (K_C') at different

Table 4
Freundlich adsorption isotherm constants for Zn(II) on different adsorbents

Adsorbents	K_f	$1/n$	n	r^2
Clarified sludge	3.16	0.705	1.418	0.9964
Rice husk ash	2.44	0.709	1.410	0.9945
Activated alumina	1.34	0.701	1.426	0.9923
Neem bark	0.687	0.755	1.320	0.9913

Table 5
Thermodynamic equilibrium constant (K_c) and Gibbs free energy (ΔG°) at $30 \pm 2\,^\circ$C for adsorption of Zn(II) on different adsorbents

Adsorbents	Equilibrium constant, K_c	Gibbs free energy, $(-)\Delta G^\circ$ (kJ mol^{-1})
Clarified sludge	0.472×10^2	9.713
Rice husk ash	0.351×10^2	8.964
Activated alumina	0.155×10^2	6.912
Neem bark	0.0616×10^2	4.584

initial concentrations of Zn(II) and extrapolating to zero. The Gibbs free energy for the adsorption process was obtained at 30 °C using Eq. (6) (Table 5). The Gibbs free energy indicates the degree of spontaneity of the adsorption process, where more negative values reflect a more energetically favorable adsorption process. The ΔG° values obtained in this study for the adsorbents confirm the feasibility of these adsorbents and spontaneity of the adsorption. The ΔG° for the clarified sludge shows that it has got the largest capacity and affinity for the selective removal of Zn(II) from aqueous solution over the other adsorbents used in this study. Similar results for ΔG° also reported by the earlier workers for the adsorption of Zn(II) from aqueous solution [39,59].

Table 6
Comparison of adsorption capacities of the adsorbents for the removal of Zn(II) with those of other adsorbents

S.no.	Adsorbent	Adsorption capacities (mg/g)	Reference
1	Phosphatic clay	25.10	[60]
2	Sunflower stalks	30.73	[36]
3	*Penicillium chrysogenum*	11.11	[61]
4	*Streptoverticillium cinnamoneum*	9.15	[61]
5	Peanut husks	13.08	[67]
6	Activated carbon	31.11	[62]
7	Sugar beat pulp	17.78	[26]
8	Red mud	14.51	[39]
9	Baggage fly ash	13.21	[48]
10	Coffee residues binding with clay as adsorbent (hereafter called C–C adsorbent)	13.40	[59]
11	Calcined phosphate	20.60	[37]
12	Low-grade phosphate	10.32	[16]
13	Sugar beat pulp	0.176	[66]
14	Fly ash	11.11	[66]
15	Low rank Turkish coal	1.66	[63]
16	Tannic acid immobilized activated carbon	1.23	[64]
17	Groundnut shells (undyed and dyed with C.I. Reactive Orange 13)	7.62 (undyed), 9.57 (dyed)	[65]
18	Saw dust (undyed and dyed with C.I. Reactive Orange 13)	10.96 (undyed), 17.09 (dyed)	[65]
19	Carbon aerogel	1.183	[68]
20	Carrot residues	29.61	[69]
21	Clarified sludge	15.53	Present work
22	Rice husk ash	14.30	Present work
23	Activated alumina	13.69	Present work
24	Neem bark	13.29	Present work

3.7. Comparison of Zn(II) removal with different adsorbents reported in literature

The adsorption capacities of the adsorbents for the removal of Zn(II) have been compared with those of other adsorbents reported in literature and the values of adsorption capacities have been presented in Table 6. The values reported in the form of monolayer adsorption capacity. The experimental data of the present investigations are comparable with the reported values.

4. Conclusions

In this study, batch adsorption experiments for the removal of Zn(II) from aqueous solutions have been carried out using four different adsorbents. The adsorption characteristics have been examined at different pH values, initial metal ion concentrations, contact time and adsorbent dosages. The obtained results can be summarized as follows:

1. The pH experiments showed that the governing factors affecting the adsorption characteristics of all adsorbents are competition of the H^+ ions with Zn(II) ions at low pH values, maximum adsorption at pH 5 and at higher pH precipitation of zinc hydroxyl species onto the adsorbents (pH 6–11).
2. Increase in mass of adsorbent leads to increase in Zn(II) adsorption due to increase in number of adsorption sites. Maximum uptake of Zn(II) obtained at adsorbent dose of 10 g/L for all the adsorbents.
3. Adsorption of Zn(II) for all the adsorbents were found to follow the first-order Lagergren rate kinetics.
4. The Langmuir and Freundlich adsorption isotherm models were used to represent the experimental data. Both the models were fitted well. The highest monolayer adsorption capacity was obtained 15.53 mg/g for clarified sludge and lowest for neem bark 13.29 mg/g at optimum pH 5.0.
5. Thermodynamic calculations showed that the Zn(II) adsorption was spontaneous in nature. The range of Gibbs free energy (ΔG°) values varies from −9.713 kJ/mol for clarified sludge to −4.584 kJ/mol for neem bark.
6. The best adsorbent for the Zn(II) removal is the clarified sludge. The optimum conditions were pH 5, adsorbent dosage level 10 g/L, equilibrium contact time 1 h.
7. The adsorption capacities of the adsorbents for the removal of Zn(II) have been compared with other adsorbents reported in the literature.

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