Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2018.22670

122 (2018) 66–77
August

Removal of Zn(II) ions from aqueous solution using chemically modified *Annona reticulata* seeds: kinetics, isotherm and thermodynamics

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Received 8 May 2018; Accepted 22 June 2018

ABSTRACT

In the present study, the removal of Zn(II) ions from synthetic effluent has been studied using sulphuric acid–modified *Annona reticulata* seeds (SMARS) as a biosorbent. The characteristics of the SMARS have been analyzed with scanning electron microscopy and X-ray diffraction analyses. The adsorption influencing parameters such as pH, initial metal ion concentration, time, mass of SMARS and temperature have been experimented and optimized. The optimum conditions for the maximum removal of Zn(II) ion for an initial Zn(II) ion concentration of 50 mg/L was measured as: pH of 6.0, adsorbent dose of 1.0 g/L, contact time of 30 min and temperature of 30°C. The results of the optimization studies have been utilized to analyze the kinetics, equilibrium and thermodynamics on the removal of Zn(II) ions by SMARS. The results of the present research showed that the pseudo-first order and Freundlich models were best obeyed with the experimental data based on the higher correlation coefficient and low error values. The Langmuir maximum monolayer adsorption capacity of SMARS for the removal of Zn(II) ions was calculated as 223.1 mg g^{-1}. The thermodynamic results indicated that the adsorption was found to be spontaneous and exothermic process. The prepared SMARS can be utilized as an effective material for the removal of pollutants from the aquatic systems.

Keywords: Adsorption; Chemical activation; Zinc; *Annona reticulata*; Kinetics; Isotherm; Thermodynamics

1. Introduction

Ground water in different parts of the world is corrupted with a couple of overwhelming metals, which are either result of mechanical anthropogenic exercises or as a result of standard segments such as mineral stores on the planet's body. Ordinary use of water resources radiates an impression of being one of the world's basic natural issues, the response for which, as it were, lies in treating wastewater that starts from human activities in various fields: organizations, (for instance, synthetic, metallurgical, mining, tannery, battery and nuclear), cultivating, conveyance and others. It is especially basic to control substance of generous metals [1–4].

The World Health Organization and Bureau of Indian Standards suggest that most noteworthy allowed unions of Zn(II) particle in drinking water ought not outperform 5.0 mg/L, independently [5,6]. The stresses are particularly honest to goodness in light of the way that mind-boggling

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Presented at the 3rd International Conference on Recent Advancements in Chemical, Environmental and Energy Engineering, 15–16 February, Chennai, India, 2018.

metals can be collected by a living structure: even low levels of introduction can be perilous if drawn out.

For the most part, the overwhelming metal contaminated ground water has acidic to close nonpartisan pH run and in this way the ground water in the pH run must be managed to remove the substantial metals. Heavy metals especially are more dangerous inferable from their non-biodegradability. A response of non-biodegradability is bioaccumulation of deadly overpowering metals in living structures which causes antagonistic effects [7,8].

Among the distinctive metal particles, zinc is of stress on account of its hurtfulness to the marine and terrestrial natural groups. Zinc was picked as a model divalent significant metal molecule as it is used generally in metallurgy, transport, power and improvement wanders. Zinc is in like manner an important micronutrient in the human body.

Regardless, overexposure to zinc can cause stomach fits, skin aggravations, heaving, sickliness, and damage the pancreas, cause arteriosclerosis, incapacitate safe working and trouble protein processing [9–11].

Zinc sulfate heptahydrate is used to supply Zn in fertilizers, and agricultural showers. Zinc was too seen to be in any way neurotoxic, since it induces unfaltering strategy of cell harm, provoking their passing [12–15]. Zinc, but required in little entireties for strong limit of living things, at higher focuses may cause unsafe effects in living things. Zinc is high risk to land and water proficient living creatures, it diminishes maritime life shapes memory, passes on brokenness to pancreas and kidney [16,17].

Expulsion of substantial metals from wastewater is finished using an arrangement of techniques, including compound precipitation [18], particle trade [19,20], filtration [21,22], dissolvable extraction [23], layer filtration [24,25], electrochemical treatment [26,27], reverse osmosis [28] and evaporation [29]. Since most of the beforehand specified techniques high early on wander or have high running costs which supersede the importance of treating waste water. In addition, the abovementioned methodology strategies wind up being either futile or too much expensive, making it difficult to work at low metal core interests. In examination adsorption seems to toll well against the others.

In the present days, adsorption is ended up being one of the least difficult and best treatment strategies for the treatment of substantial metals containing wastewater. The adsorption method is ideal, versatile to work and upkeep, and moreover makes an awesome spouting, despite when metal particles are accessible in low focus in the reinforce wastewater. Thusly, there is a reliable search for adsorbents with higher adsorption constrain, speedier vitality and negligible exertion [30–37]. Materials used as adsorbents should have high adsorption collaboration towards the target contaminants with a specific end goal to satisfactorily clear them from wastewater effluents. The adsorbents may be of mineral, characteristic or natural root – for example, activated carbons, zeolites, mud minerals, present day comes about, agrarian waste, biomass, and polymeric materials [38–41]. Activated carbons are mostly used in absorption of wide variety of water pollutants or in water treatment because of its ability to improve water by removing disagreeable tastes and odours, including objectionable chlorine and many chemicals and dissolved gases, and in some cases it can be effective against microorganisms. A few pros/specialists have made and shown that horticultural waste biomass accept a basic part in substantial metal evacuation. A portion of the blends open in agrarian waste materials, for instance, lignin, lipid, starch, proteins, direct sugars and hemicelluloses, redesign perilous metals departure. *Annona reticulata* seed is a horticultural material that has a farthest point with respect to hazardous generous metals clearing in light of its greater surface locale and other adsorption properties. The heterogeneity of the microporous structure and the vitality heterogeneity are imperative attributes of an adsorbent. The heterogeneity of the micropore structure, identified with the measurements of micropores, and the vivacious heterogeneity of the micropores of adsorbents rely upon their pore estimate dissemination and the idea of the dynamic adsorption focuses. In this manner, the thought of the basic and enthusiastic heterogeneities independently in the feeling of adsorption phenomenon in permeable adsorbents is associated with a few vulnerabilities. The surface of the raw adsorbent material can be chemically altered by concentrated sulphuric acid to enhance the hydrophobicity.

Consequently, the chemical modifications, for example, chemical pretreatment, oxidation, and additionally the joining of carboxyl gatherings, amines, amides, and so forth, on *Annona reticulata* seeds filaments, that mean to expand the quantity of adsorption locales and augment dangerous metal particle adsorption limit have been tended to. The writing presents comes about that demonstrated exhibitions of biosorbents equivalent to or much higher than regular strategies and adsorbents. Numerous endeavors have been focused on the enhancements of these biosorbents through chemical modifications.

The point of the present examination is to set up the biosorbent material from the seeds and to check its ability to oust the Zn(II) ion from watery courses of action. Sulphuric acid–modified *Annona reticulata* seeds (SMARS) were blended and used as adsorbents for Zn(II) ion evacuation. The adsorbents were depicted by scanning electron microscope (SEM) and X-ray diffraction (XRD) examinations. Adsorption tests were finished to expect adsorption-affecting components: Zn(II) ion concentration, temperature, pH, adsorbent measurements, contact time for the most extraordinary obliteration of Zn(II) ion from wastewater. The distinctive isotherm conditions were associated with test the isotherm data of Zn(II) expulsion by adsorbents. Adsorption thermodynamics and vitality for Zn(II) evacuation was additionally inquired about. Adsorption isotherm data were associated with layout an adsorber.

2. Materials and methods

2.1. Preparation of Zn(II) stock solution

Every one of the chemicals utilized as a piece of the present examination were of investigative survey and utilized everything considered with no extra refinement. Orderly reagent audit of zinc sulfate heptahydrate ($ZnSO_4.7H_2O$) was procured from E. Merck, Mumbai, India. A stock arrangement of various Zn(II) ion arrangement was set up by dissolving fitting measure of salt in 1 L of refined water. The coveted grouping of the working arrangement was set up by diluting the stock arrangement in appropriate extent utilizing refined water. The pH of the Zn(II) ion solution was assessed by utilizing pH meter and balanced by including 0.1 M NaOH or 0.1 M HCl.

2.2. Preparation of *Annona reticulata* seeds

The *Annona reticulata* seeds were gathered from SSN College of Engineering, Chennai, Tamil Nadu, India. The horticultural waste biomass material was proficiently washed with water to clean and discard pollutions present in the seeds. By then, the washed seeds were allowed to dry at room temperature to empty the clamminess content. Using a steel mill, the dried biomass material was ground to a fine powder. The ensuing material was sieved at a particle size of 0.354 mm. The following material was used as an adsorbent for surface adjustment and adsorption considers for the evacuation of Zn(II) ion from watery arrangement. The planning of surface-changed adsorbent was finished by treating one part of *Annona reticulata* seeds powder with 10% solution of concentrated H_2SO_4 for around 24 h. The dried out *Annona reticulata* seeds powder was washed inside and out with twofold refined water to clear the excess of destructive and was continued until the point that the pH of the supernatants remained reliable at 7.0. By then it was dried at 80°C for around 3 h, ground and after that sieved to achieve a size of 0.354 mm. The newly prepared material is called SMARS.

2.3. Characterization of synthesized SMARS

The surface morphology of the surface changed adsorbent material (SMARS) was described by Fourier transform infrared spectroscopy (FTIR) and SEM. The association between the synthetic bonds and the metal particles on the surface of the adsorbent material (SMARS) was analyzed utilizing FTIR inside the scope of 450–4,000 cm^{-1}. The surface structure and morphology of the adsorbent material were described by SEM examinations under a quickening voltage of 10 kV.

2.4. Batch adsorption study

A 100 mL test of known zinc fixation was kept in 100 mL flask for the adsorption investigational study. The required pH was accomplished by including drops of 0.1 N hydrochloric acid or 0.1 N sodium hydroxide. Known measure of adsorbent was taken into the open jars and the whole setup was held in a temperature controlled shaking incubator. The orbital brooding shaker was working at 180 rpm. On accomplishing needed contact time, the flask was taken out and the solution was centrifuged. The supernatants were assembled and the zinc fixation was evaluated using atomic absorption spectrophotometer (AAS). The affecting variables which consolidate adsorbent measurements, pH, contact time, Zn(II) ion fixation and temperature were contrasted and their belongings considered. The removal of zinc from the watery arrangement can be ascertained by utilizing the accompanying mass adjust relationship

$$\text{Percentage removal of Zn}(\text{II}) \text{ ion} = \frac{(C_o - C_e)}{C_o} \text{ x } 100 \tag{1}$$

where C_o and C_e are the initial and equilibrium Zn(II) ion concentration (mg/L). Exactness of the outcomes was accomplished by running every one of the trials in triplicate.

2.5. Zn(II) ion adsorption isotherm experiment

Adsorption isotherm study was directed to break down the dispersal of Zn(II) particle in the adsorbent and in the liquid course of action at balance conditions. The courses of action of different Zn(II) ion fixation (50–250 mg/L) were shaken with a required measure of adsorbent in jars under perfect conditions and at assorted temperatures (30°C–60°C). After adjust was expert, the flasks were ousted from the shaker. The adsorption mixes were detached by filtration. Whatever remains of the Zn(II) ion concentration in the filtrate was analyzed by AAS. The equilibrium adsorption capacity of the adsorbent was calculated by using the following formula:

$$q_e = \frac{(C_o - C_e)V}{m} \tag{2}$$

where q_e is the equilibrium adsorption capacity (mg/L), V is the volume of Zn(II) ion solution (L) and m is the mass of the adsorbent (g).

In the present examination, adsorption isotherm information associated with four particular adsorption isotherm models, for instance, Langmuir, Freundlich, Temkin and Sips isotherm model. The nonlinear relapse examination was finished by using MATLAB R2009a programming to evaluate the isotherm parameters, relationship coefficients (R^2) and mistake values (SSE and RMSE).

Langmuir isotherm model is given as follows [42]:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{3}$$

where q_m is the maximum monolayer adsorption capacity (mg/g), K_L is the Langmuir equilibrium constant (L/mg).

Freundlich isotherm model is given as follows [43]:

$$q_e = K_F C_e^{1/n} \tag{4}$$

where K_F is the Freundlich constant [(mg/g) $(L/mg)^{1/n}$] which can be utilized to guage the adsorption capacity. n is the Freundlich exponent which is utilized to guage the force of adsorption. The importance of n can be recorded as takes after:

If $n = 1$ (linear); $n > 1$ (physical process);
$n < 1$ (chemical process).

Temkin isotherm model is given as follows [44]:

$$q_e = \frac{RT}{b}(\text{In}AC_e) \tag{5}$$

where A and b are the Temkin isotherm constants.

Redlich–Peterson isotherm model is given as follows [45]:

$$q_e = \frac{K_{\mathrm{RP}} C_e}{(1 + \alpha_{\mathrm{RP}} C_E^{\mathrm{RP}})} \tag{6}$$

where β_{RP} is the example which lies in the vicinity of 0 and 1, K_{RP} is the Redlich–Peterson isotherm consistent (L/g), α_{RP} is the Redlich–Peterson isotherm steady $(\mathrm{L/mg})^{1/\beta_{\mathrm{RP}}}$. The noteworthiness of β is as given as: β = 1 (Langmuir adsorption isotherm demonstrated is an ideal adsorption isotherm show); β = 0 (Freundlich adsorption isotherm display is a best adsorption isotherm display).

2.6. Zn(II) ion adsorption kinetic experiment

Adsorption kinetic examinations were directed to assess the rate of adsorption of Zn(II) ion and the instrument of Zn(II) ion evacuation. They were performed at 10–60 min and at temperatures of 30°C–60°C. The other working parts were kept up as reliable (pH = 6.0, SMARS dose = 1.0 g/L). After the predestined time between time, the adsorption mixes were segregated by filtration. Whatever remains of the Zn(II) ion concentration in the filtrate was analyzed by AAS. The amount of Zn(II) particle adsorbed onto adsorbent at foreordained time interims (q_t) was computed by utilizing the accompanying equation:

$$q_t = \frac{(C_o - C_t)V}{m} \tag{7}$$

where q_t is the measure of Zn(II) ion adsorbed onto the adsorbent at time t (mg/g).

Three adsorption kinetic models were fitted with adsorption active data. The nonlinear relapse examination was finished by using MATLAB R2009a programming to survey the motor parameters, relationship coefficients (R^2) and blunder regards (SSE and RMSE).

The pseudo-first order kinetic model can be described as follows [46]:

$$q_t = q_e[1 - \exp(-k_1 t)] \tag{8}$$

where k_1 is the pseudo-first order kinetic rate constant (min^{-1}).

The pseudo-second order kinetic model can be described as follows [47]:

$$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \tag{9}$$

where k_2 is the pseudo-second order kinetic rate constant (g/mg.min).

The Elovich kinetic model can be described as follows [48]:

$$q_t = (1 + \beta_E)\mathrm{In}(1 + \alpha_E \beta_E t) \tag{10}$$

where α_E is the initial adsorption rate (mg/g min) and β_E is the desorption constant (g/mg) which is identified with the actuation vitality of chemical adsorption.

2.7. Zn(II) ion adsorption thermodynamic study

Thermodynamic examinations were finished by including 1.0 g of SMARS in 100 mL of known centralization of Zn(II) ion solution (50–250 mg/L). The course of action mixes were placed in temperature controlled shaking incubator for different temperatures in the extent of 30°C–60°C at an adjust time of 90 min. Once the framework was refined the amicability time, the examples were pulled once more from the incubator and separated by using Whatman 42 filter paper. The accumulated supernatant liquid was subjected to AAS examination. The thermodynamic lead can be assessed by settling the exploratory data to the thermodynamic conditions. The thermodynamic parameters, for instance, Gibbs free energy ($\Delta G°$), entropy and enthalpy were figured by using the accompanying condition:

$$\Delta G° = -RT\ln(K_c) \tag{11}$$

$$\mathrm{Log}Kc = \frac{\Delta S°}{2.303R} - \frac{\Delta H°}{2.303RT} \tag{12}$$

where K_c is the coefficient of conveyance which is the proportion of Zn(II) ion concentration on the solid stage and the Zn(II) ion concentration in fluid stage at balance. T is the adsorption framework temperature and R is the universal gas constant.

3. Results and discussion

3.1. Characterization of synthesized SMARS

3.1.1. SEM analysis

SEM examination can be used to choose the morphological properties and surface nature of present adsorbent material (SMARS). SEM pictures of SMARS with different intensifications of 10,000×, 5,000×, 2,500× and 1,300× is shown in Fig. 1. The particle size, shape and porosity of SMARS were settled. The surface pores of SMARS have been found which displays that SMARS have uniform flow. The pores are unforgiving and have more pores which demonstrated falls between the structures. The SEM pictures approved that SMARS have more diminutive scale permeable void spaces and noteworthy cavities. SEM investigation suggested that SMARS have a sporadic surface with tremendous openings and full scale pores. These macropores and extensive holes are imperative for metal particle adsorption. The measurement and condition of the pores are sporadic and interrelated. The open pores on the SMARS could shape the lattice layer with a cross-associated framework. These properties exhibited that SMARS have prevalent adsorption characteristics for the evacuation of Zn(II) particle from modern wastewater. Fig. 1 shows that SMARS has gigantic crevices which demands that the SMARS has all around made pores at first look and has unrivaled potential for the evacuation of Zn(II) particle.

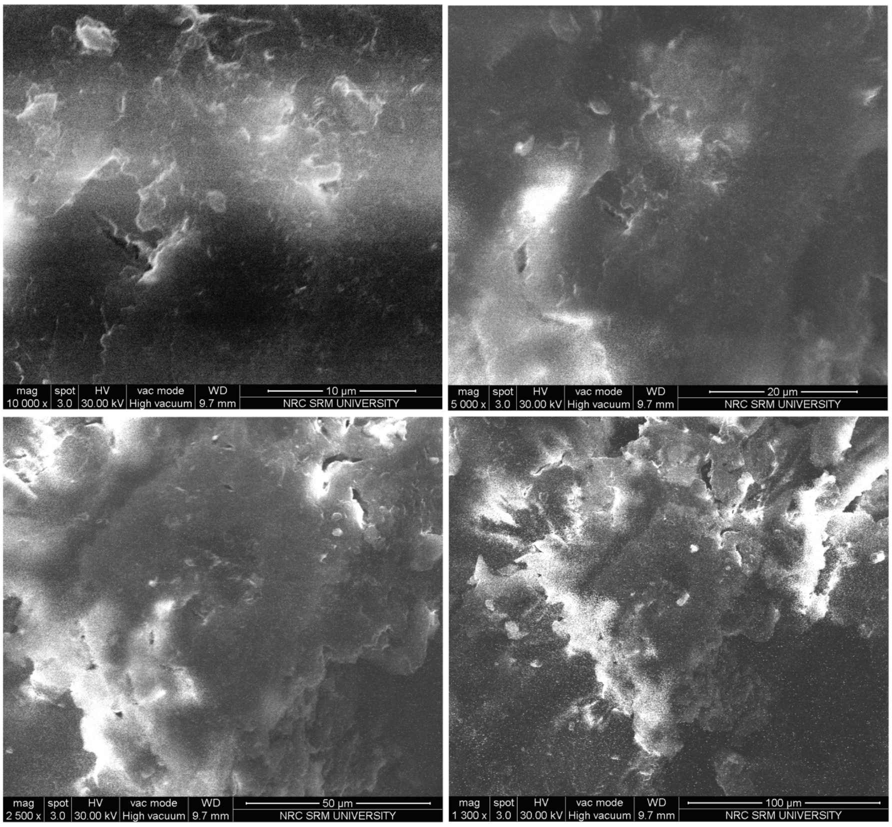
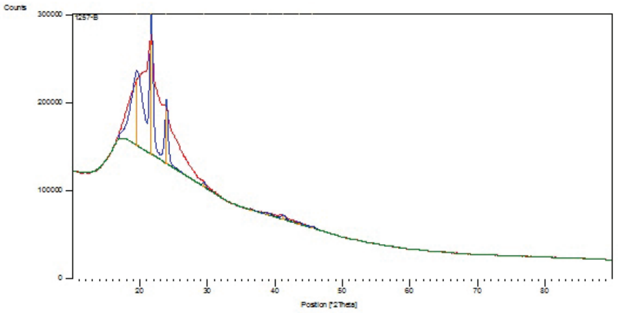


Fig. 1. SEM images of SMARS.

3.1.2. XRD analysis

The crystalline thought of SMARS was set up by XRD examination. XRD is utilized to get a handle on the crystalline idea of adsorbents, for example, XRD image of SMARS is shown in Fig. 2. The outcome demonstrates that SMARS were misty in nature and has all the more effective surface. The diffractograms happened through XRD are extremely similar and in better understanding with the given sample. In any case, couple of undesirable tops in the XRD configuration revealed the proximity of take after measure of degradation in the example. XRD certified the powder case of mixed started carbon SMARS. XRD in like manner had foreseen the atom size of SMARS test in the regard extent of 3–5 mm. The XRD comes to fruition avowing that diffraction record for SMARS was less genuine and it has more adsorption goals for Zn(II) particle adsorption which may be a result of more undefined structures in it. In like way, the XRD ponders demand that the SMARS has sufficient properties to adsorb Zn(II) particle.



Pos. [°2Th.]	Height [cts]	FWHM [°2Th.]	d-spacing [Å]	Rel. Int. [%]
19.5741	74712.84	1.9188	4.53528	54.62
21.6784	136774.30	0.5117	4.09956	100.00
23.8921	65388.21	0.5117	3.72450	47.81
29.4926	5199.80	0.5117	3.02875	3.80
36.3501	850.59	0.7675	2.47158	0.62
38.8958	2192.53	1.0234	2.31548	1.60
41.1957	4438.50	0.7675	2.19137	3.25
43.5053	2164.92	1.0234	2.08024	1.58
45.4610	1249.61	0.9360	1.99354	0.91

Fig. 2. XRD image of SMARS.

3.1.3. FTIR analysis

FTIR examination can be utilized to choose the closeness of fundamental utilitarian gatherings on the surface of the biosorbent [49–51]. Adsorption process relies at first glance association between the biosorbent material and the adsorbate – Zn(II) ion in the fluid arrangement. Fig. 3 shows the FTIR image of SMARS. The FTIR spectroscopy of the biosorbent has been examined for the recurrence in the scope of 650–4,000 cm^{-1}. The intense peak at 3,043 cm^{-1} in the SMARS is corresponding to the alkene group frequency of terminal (vinyl) C–H stretch. The band vibrations at 2,917 and 2,849 cm^{-1} in SMARS relate to aliphatic group frequencies of methyl C–H symmetric stretch. The peak vibrations at 1,705 cm^{-1} indicate that aromatic ring frequency of aromatic combination bands. The FTIR spectrum of SMARS shows that the strong peaks at 1,463 cm^{-1} corresponds to aliphatic

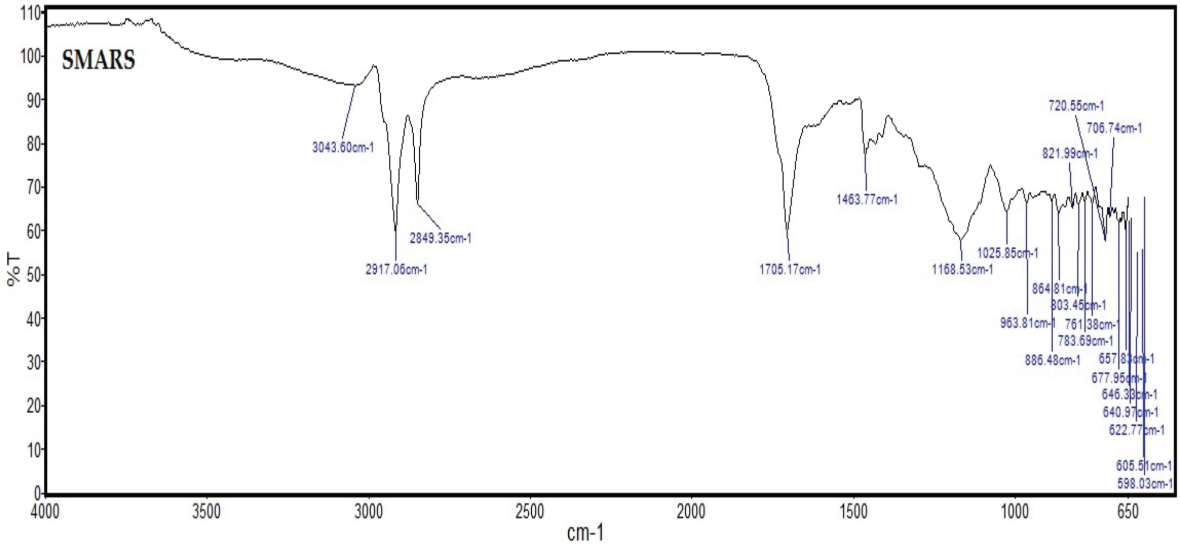


Fig. 3. FTIR images of SMARS.

group frequencies of methyl asymmetric C–H stretch. The adsorption peaks at 1,168 and 1,025 cm^{-1} relate to the presence of aliphatic organohalogen compound group frequencies of aliphatic fluoro compounds. FTIR comes about delineated that Zn(II) ion can be interfaced with the alkene, aliphatic, aromatic and organohalogen compound gatherings, which are interconnected and cross-connected system show in the biosorbent. These ionic gatherings frame the covalent bond between the surface of the adsorbent material and the adsorbate. The FTIR peaks demonstrates that the nearness of aliphatic and aromatic groups is major responsible for covalent extension and grid arrangement, which affirms that adsorbent material (SMARS) has prevalent potential for the adsorption of Zn(II) ions from the wastewater. Subsequently, it can be inferred that SMARS had great potential for the expulsion of Zn(II) ions from wastewater by adsorption.

3.2. Impact of pH on Zn(II) ion adsorption

Solution pH is the fundamental essential process parameter for the adsorption methodology; it impacts the substance speciation of Zn(II) ion and the ionization condition of the helpful social affairs introduce on the surface of the adsorbent material. The effect of pH on the adsorption of Zn(II) ion onto SMARS is shown in Fig. 4. Fig. 4 shows that the rate evacuation of Zn(II) ion was expanded with an expansion of course of action pH from 2.0 to 6.0. At acidic condition, the adsorption of Zn(II) ion was relentlessly created record of the electrostatic shock. As the pH raise, the sudden increase of rate clearing of Zn(II) ion may be because of the ionization of carboxyl utilitarian gatherings. Likewise, the carboxyl social events begun as for the electrostatic communication exertion between the adversely charged get-togethers on the adsorbent material and the decidedly charged Zn(II) ion. Also augmentation of plan from 6.0 to 8.0, the adsorption achieves the concordance condition; the rate flight of Zn(II) particle began diminishing steadily in light of the way that the amine bunches are satisfactorily deprotonated at higher pH.

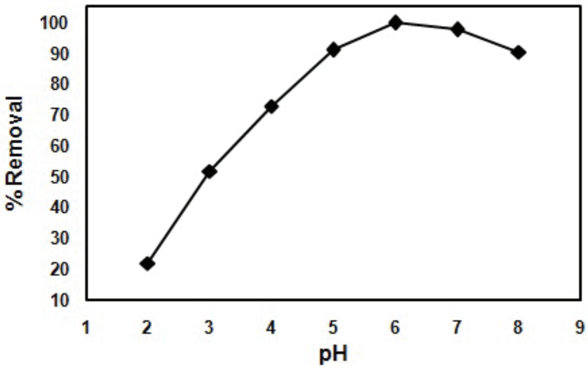


Fig. 4. Effect of solution pH on the removal of Zn(II) ions by SMARS.

3.3. Impact of SMARS dosage on Zn(II) ion adsorption

The effect of SMARS on the adsorption of Zn(II) ion was performed at different estimations from 0.2 to 1.6 g/L and by keeping other working parameters as relentless. Adsorbent estimation is a fundamental parameter to choose the adsorption furthest reaches of the adsorbent. As can be seen from Fig. 5, the rate expulsion of Zn(II) ion was expanded with an expansion of adsorbent estimations from 0.2 to 1.0 g/L. It might be a result of the extension in number of dynamic destinations on the surface of the SMARS with an expansion of adsorbent dose from 0.2 to 1.0 g/L. Past the dosage measure of 1.0 g/L, the rate expulsion of Zn(II) ion was viewed as predictable. The result demonstrates that 1.0 g/L of an adsorbent dose was a perfect aggregate for the evacuation of Zn(II) ion from the liquid game plan.

3.4. Impact of Zn(II) ion concentration on Zn(II) ion adsorption

The effect of sustain concentration on the adsorption of Zn(II) ion onto SMARS was done at different focuses from 50 to 250 mg/L and by keeping the other working parameters unfaltering. Fig. 6(a) exhibits the impact of beginning Zn(II) ion concentration on the adsorption of Zn(II) ion onto

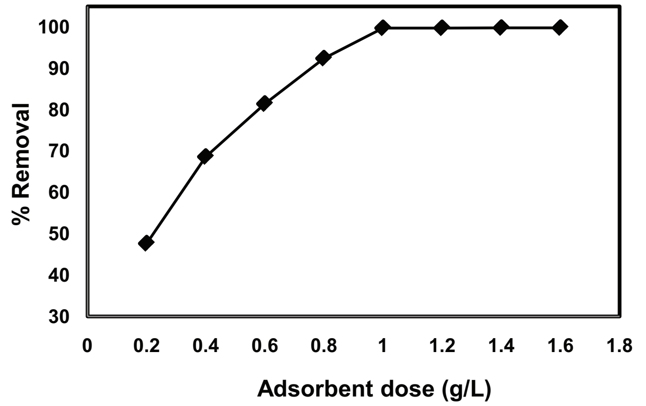


Fig. 5. Effect of adsorbent dosage on the removal of Zn(II) ions by SMARS.

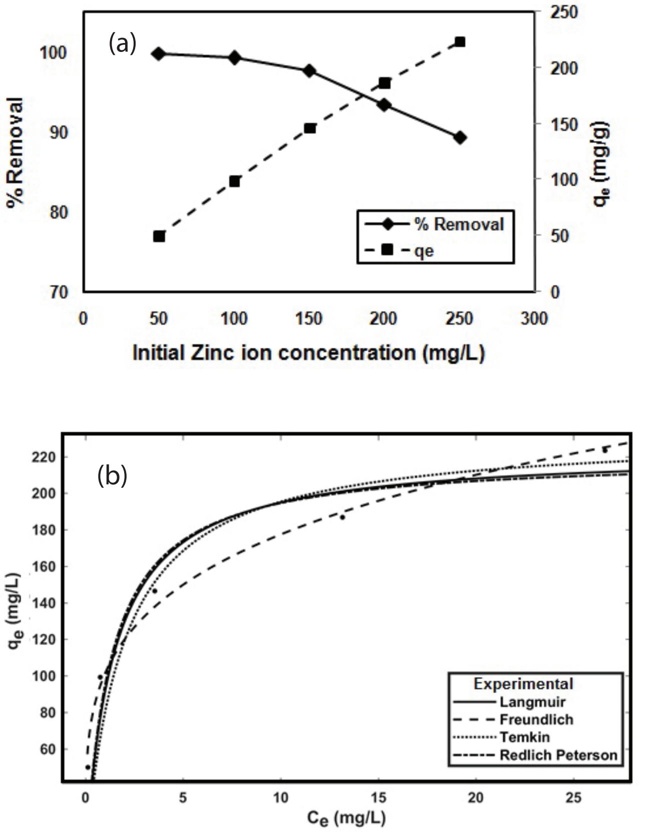


Fig. 6. (a) Effect of initial Zn(II) ion concentration on the removal of Zn(II) ions by SMARS. (b) Adsorption isotherm fit for the removal of Zn(II) ions by SMARS.

SMARS. As can be seen from Fig. 6(a), the expulsion of Zn(II) ion was reduced with an expansion in the fixation from 50 to 250 mg/L. It has been found that Zn(II) ion arrangement of lower concentration demonstrated higher rate evacuation when it was differentiated and the higher Zn(II) ion concentration. The reason for this behaviour was settled measure of adsorbent was used for the diverse Zn(II) ion concentration. The settled measure of adsorbent can prepared to oust a particular measure of Zn(II) ion from the aqueous solution. At bring down Zn(II) ion concentration, all the Zn(II) ion may get adsorbed onto the adsorbent surface in light of the availability of the dynamic locales. Be that as it may, at higher Zn(II) ion fixation, the extent of Zn(II) particle to the dynamic destinations was seen to be low which comes to fruition in the decline in the removal of Zn(II) ion from the watery arrangements.

3.5. Adsorption isotherm of Zn(II) ion removal by SMARS

Adsorption isotherm has an imperative impact in the outline of an adsorption framework. The communication between the adsorbate in the liquid arrangement and in the solid adsorbent at a balance conditions was controlled by using the few isotherm models. Langmuir, Freundlich, Temkin and Redlich–Peterson models were used to look at the exploratory adsorption isotherm information by using MATLAB R2009a programming. Adsorption isotherm study was used to assess the adsorption isotherm parameters, R^2 and mistake regards. The isotherm reliable characteristics were used to survey the surface properties and the favouritism between the metal particles and the adsorbent. Fig. 6(b) shows the adsorption isotherm investigation of Zn(II) adsorption by SMARS. The adsorption isotherm parameters, relationship coefficient esteems (R^2) and blunder regards (SSE and RMSE) were proficient by fitting the adsorption isotherm data to the adsorption isotherm models and the discovered characteristics were shown in Table 1. The best isotherm fitted show is recognized in regards to high R^2 regards with low mistake regards. As can be seen from Table 1, Freundlich model showed a higher association coefficient regards and the lower blunder regards. The Freundlich isotherm demonstrates that the adsorption force is predominant for bring down concentration however not for higher concentration which furthermore prescribes that the adsorption of Zn(II) ion onto SMARS was heterogeneous in nature. The nature of adsorption in the adsorption system was determined by using the $1/n$ esteem which exhibited that the adsorption methodology is common and significant only for bring down concentration contemplates.

Table 1
Adsorption isotherm results for the removal of Zn(II) ions by SMARS

S. no	Isotherm model	Parameters	R^2	SSE	RMSE
1	Langmuir	q_m = 223.1 mg/g, K_L = 0.693 L/mg	0.8918	25.31	22.64
2	Freundlich	K_F = 101.3 (mg/g)(L/mg)$^{(1/n)}$, n = 4.108 g/L	0.9881	19.51	8.662
3	Temkin	A = 0.526, b = 1.369	0.8569	27.13	26.03
4	Redlich–Peterson	α_{RP} = 0.265 L/mg$^{1/\beta_{RP}}$, β_{RP} = 2.85, K_{RP} = 16.64 L/g	0.8997	22.02	21.8

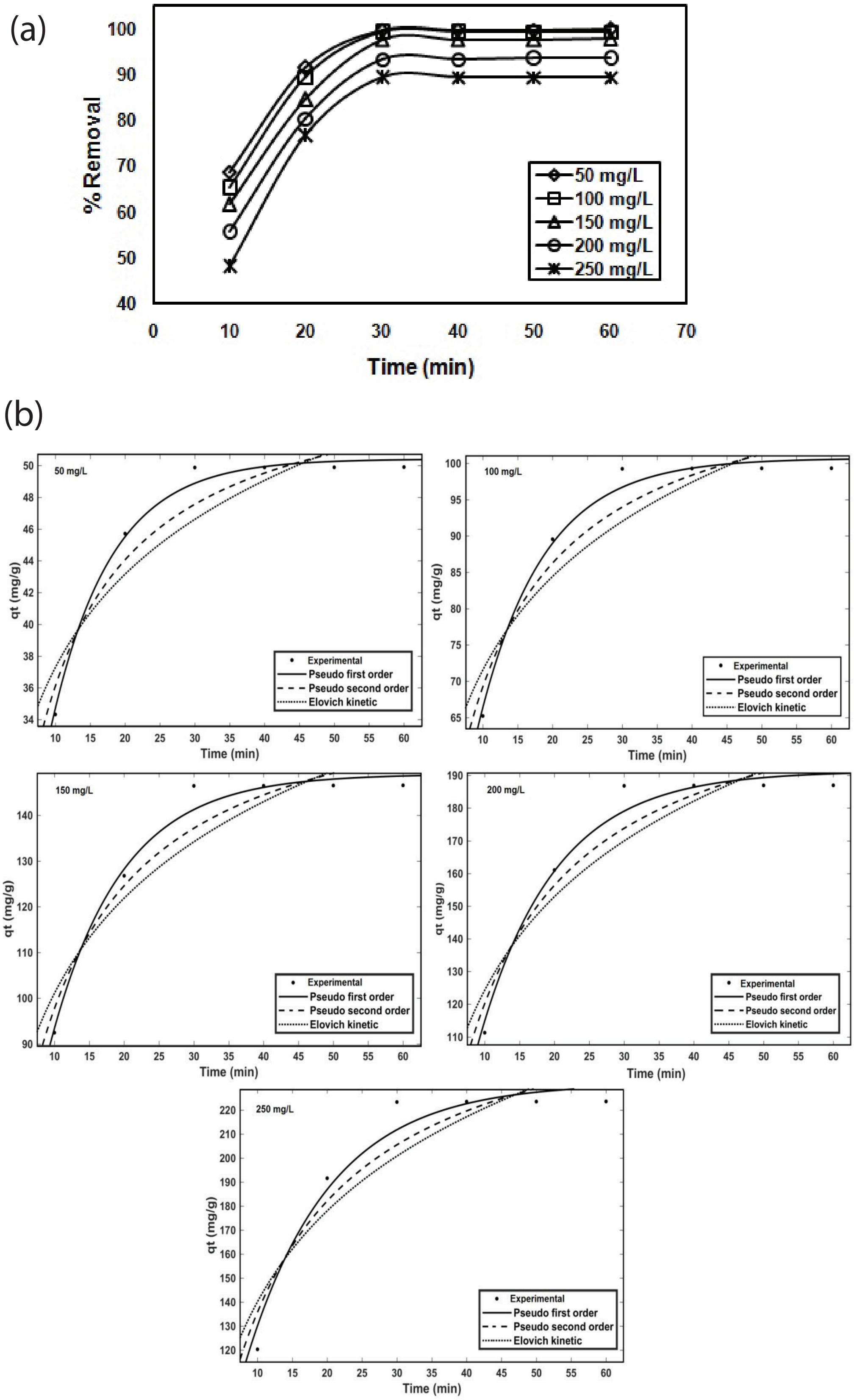


Fig. 7. (a) Effect of contact time on the removal of Zn(II) ions by SMARS. (b) Adsorption kinetic fit for the removal of Zn(II) ions by SMARS.

3.6. Impact of contact time on Zn(II) ion adsorption

In the adsorption technique, effect of contact time expects an essential part. The effect of contact time on the adsorption of Zn(II) ion onto SMARS was performed by moving the contact time from 10 to 60 min and keeping distinctive parameters as predictable (Fig. 7(a)). Fig 7(a) expresses that the rate expulsion of Zn(II) ion was expanded with an expansion of contact time from 10 to 60 min and additional raise in time has no distinguishable outcome on Zn(II) ion adsorption. The reason might be that at beginning an extensive surface range gives copious surface dynamic regions to Zn(II) ion adsorption however completed the entire arrangement SMARS surface may have been totally depleted understanding no further adsorption process. No critical enlargement in rate evacuation was searched for all tested Zn(II) ion focus after 30 min of contact time. The study exhibits that contact time was fixed as 30 min for moreover tries.

3.7. Adsorption kinetics of Zn(II) ion removal by SMARS

Adsorption kinetic models were used to look at the probable adsorption system and to assess the adsorption rate by testing the contact time data with the different adsorption dynamic models. In the dynamic examination, pseudo-first order, pseudo-second order and Elovich kinetic models were used to fit the contact time data by using the MATLAB R2009a programming. Fig. 7(b) shows the adsorption dynamic examination for the adsorption of Zn(II) ion onto SMARS. Table 2 clearly displays the estimations of the rate consistent close by relationship coefficient esteems (R^2) and mistake regards (SSE and RMSE) for the adsorption kinetic models. The kinetic model with the best fit was recognized by looking at balance adsorption limit esteems ($q_{e,\text{exp}}$) with the computed equilibrium adsorption limit esteems ($q_{e,\text{cal}}$) values. It is obvious from Table 2 that the computed adsorption limit estimations of pseudo-first order show were closer to the trial adsorption limit. In addition, the pseudo-first order kinetic model has higher relationship coefficient esteems with low mistake regards stood out from other dynamic models. The results were suggested that pseudo-first order kinetic model was the best fitted motor model for the adsorption of Zn(II) onto SMARS. The fitted pseudo-first order kinetic model exhibits that the adsorption framework might be possible in perspective of the solution concentration concerning Zn(II) particle.

3.8. Impact of temperature on Zn(II) ion adsorption

The impact of temperature is the indispensable parameter in the adsorption methodology. The exploratory examinations were performed at different temperatures in the extent of 30°C–60°C, beginning Zn(II) ion concentration of 50 mg/L, course of action pH of 6.0, SMARS estimation 1.0 g and contact time of 30 min and the trial comes about are shown in Fig. 8(a). It is seen from Fig. 8(a) that the rate evacuation of Zn(II) ion was decreased with an expansion of temperature from 30°C to 60°C. At higher temperature, surface zone of adsorptive regions was diminished, less number of adsorptive goals were available. The result concluded that adsorption process was exothermic in nature.

3.9. Adsorption thermodynamics of Zn(II) removal by SMARS

The possibility of the adsorption system, for instance, unconstrained, inconsistency, exothermic or endothermic was controlled by the thermodynamic parameters, for instance, Gibbs free energy ($\Delta G°$), entropy ($\Delta S°$) and enthalpy ($\Delta H°$). The estimation of changes in Gibbs free energy was controlled by using Eq. (12). The estimations of changes in enthalpy and changes in entropy were figured from slant and catch by the plot between ln K_c vs. $1/T$. The thermodynamic

Table 2
Adsorption kinetic results for the removal of Zn(II) ions by SMARS

Kinetic model	Parameters	Zn(II) ion concentration (mg/L)				
		50	100	150	200	250
Pseudo-first order	k_1 (min^{-1})	0.1166	0.1077	0.098	0.091	0.082
	$q_{e,\text{cal}}$ (mg/g)	50.41	100.7	149	191.3	231.2
	$q_{e,\text{exp}}$ (mg/g)	50.231	99.425	149.85	187.25	223.95
	R^2	0.9922	0.9889	0.9849	0.9805	0.9651
	SSE	1.519	10.39	36.17	91.21	102.3
	RMSE	0.6163	1.612	3.007	4.775	8.682
Pseudo-second order	k_2 (g/mg/min)	0.0031	0.0013	0.0007	0.0005	0.0003
	$q_{e,\text{cal}}$ (mg/g)	56.54	114.4	171.9	223.8	276.7
	R^2	0.9217	0.9208	0.931	0.9211	0.9025
	SSE	15.26	74.08	164.8	368.7	841.9
	RMSE	1.953	4.304	6.439	9.601	14.51
Elovich	α_E (mg/(g.min))	2.827	0.6006	0.2044	0.0954	0.040
	β_E (g/mg)	2.717	7.199	12.41	17.71	24.47
	R^2	0.8222	0.829	0.8547	0.8463	0.8317
	SSE	34.65	160	349.2	718.4	1453
	RMSE	2.943	6.324	9.343	13.4	19.06

examination of Zn(II) ion onto SMARS is shown in Fig. 8(b). The thermodynamic parameters for the adsorption of Zn(II) ion onto SMARS is shown in Table 3. It was seen from the association report, it was watched that the negative estimation of Gibbs free energy guarantees that the adsorption system was achievable and unconstrained in nature. Generally, Gibbs free energy can be doled out as tails: (I) –20 to 0 kJ/mol addressed as physical adsorption (ii) –80 to –400 kJ/mol spoke to as substance adsorption. In the present research, the estimations of Gibbs free energy were accomplished amidst –20 to 0 kJ/mol at all the temperatures which addresses that present adsorption system is physical adsorption. Moreover, the negative estimations of Δ*H*° tending to that adsorption of Zn(II) ion onto SMARS was exothermic in nature. The elucidation behind this direct may be a consequence of sensitive adsorptive characteristics between Zn(II) ion and the surface of the SMARS. The negative estimations of Δ*S*° tending to that lessening in Zn(II) ion concentration in strong fluid interface demonstrates that an improvement in the Zn(II) ion concentration with the surface of the adsorbent. It also supports that decreased abnormality at the strong fluid interface amidst the adsorption system.

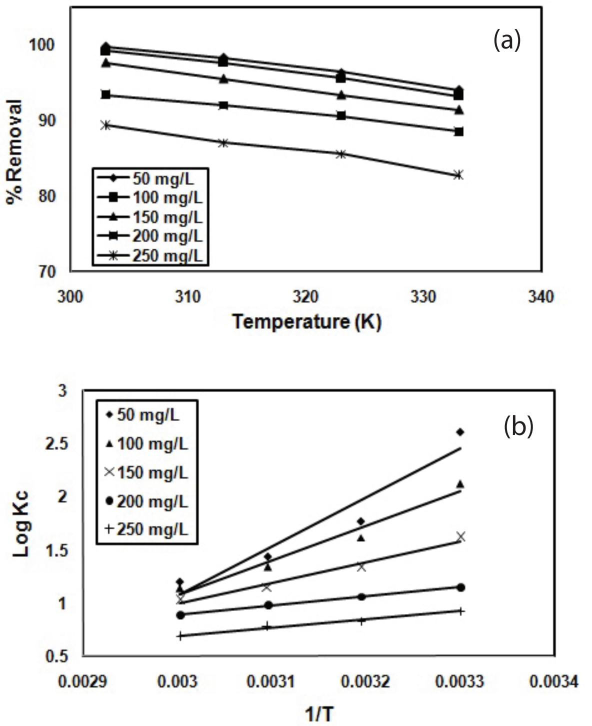


Fig. 8. (a) Effect of temperature on the removal of Zn(II) ions by SMARS. (b) Thermodynamic analysis on the removal of Zn(II) ions by SMARS.

Table 3
Thermodynamic results for the removal of Zn(II) ions by SMARS

Concentration of Zn(II) ions (mg/L)	Δ*H*° (kJ/mol)	Δ*S*° (J/mol/K)	Δ*G*° (kJ/mol)			
			30°C	40°C	50°C	60°C
50	–89.066	–246.81	–15.138	–10.596	–8.873	–7.623
100	–62.515	–166.93	–12.290	–9.686	–8.287	–7.253
150	–37.769	–93.87	–9.371	–7.975	–7.099	–6.552
200	–16.774	–33.22	–6.681	–6.359	–6.095	–5.656
250	–15.214	–32.53	–5.358	–4.973	–4.794	–4.330

3.10. Comparison study

Table 4 showed the examination of Langmuir monolayer adsorption capacity (q_m) of the present adsorbents (SMARS) with different adsorbents for the removal of Zn(II) ion. From the association report, it was watched that as of late arranged SMARS has higher limit with regards to the removal of Zn(II) ion.

4. Conclusion

The SMARS were prepared and properly utilized as an effective adsorbent for the removal of Zn(II) ions. It was observed that the surface of the *Annona reticulata* seed was effectively modified with the help of concentrated sulphuric acid. The optimum removal of Zn(II) ions was observed by

Table 4
Comparison of maximum monolayer adsorption capacity of SMARS for the adsorption of Zn(II) ion with various adsorbents

S. no	Adsorbents	q_m (mg/g)	References
1	SMARS	223.1	This study
2	Poly (azomethinethioamide) resin	105.4	[52]
3	Surface modified *Strychnos potatorum* seeds	98.75	[53]
4	Eucalyptus seeds activated carbon	80.37	[7]
5	*Azadirachta indica* bark	33.49	[54]
6	Activated carbon from bagasse	31.11	[55]
7	Cashew nut shell	24.98	[56]
8	Lignocellulosic substrate	16.02	[57]
9	Rice bran	14.17	[58]
10	Chitosan/PVA blend	5.917	[59]
11	Bael tree leaf powder	2.083	[60]

fixing the experimental conditions with an initial Zn(II) ions concentration of 50 mg/L, adsorbent dose of 1.0 g/L, contact time of 30 min, pH of 6.0 and temperature of 30°C. The adsorption experimental data have been analyzed with the Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherm models. The isotherm results indicated that the equilibrium data were best fitted and explained by the Freundlich model. The Langmuir monolayer adsorption capacity of SMARS for Zn(II) ions has been estimated as 223.1 mg/g. The removal of Zn(II) ions by the SMARS followed the pseudo-first order kinetic model. The thermodynamic analysis on the removal of Zn(II) ions by the SMARS has explained that the adsorption was a feasible, spontaneous and exothermic process. Finally it was concluded that the SMARS has also been applied to the industrial wastewater treatment.

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