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Black cumin seed (BCS): a non conventional adsorbent for the removal of Cu (II) from aqueous solution

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ABSTRACT

The present study reports the use of Black Cumin Seed as a non-conventional adsorbent for the removal of Cu^{2+} from aqueous solution. The various operational parameters such as contact time, pH, concentration, surfactant, and ionic strength have been investigated. The adsorbent was characterized by Fourier transform infrared spectroscopy and SEM analysis. The optimum equilibrium time and pH was found to be 30 min and 6, respectively. The adsorption data was best fitted by pseudo-second order kinetic whereas the adsorption isotherm was best described by Freundlich model. The process was found to be spontaneous and endothermic in nature. The activation energy was also determined and the process was found to be chemisorptions in nature. Ninety-five percent of the adsorbed Cu^{2+} ion could be desorbed by 0.1 N HCl solution and the spent adsorbent can be reused up to five times.

Keywords: Black cumin seed; Adsorption; Cu^{2+}; Freundlich; SEM

1. Introduction

The critical environmental challenge for an industry is the safe disposal of wastewater. In today's world, various industries discharge heavy metals and organic pollutants whose disposal in environment pose a serious threat to human health and organism. Copper is one of the most used heavy metals by various industries and municipal wastewater which causes toxicological problems affecting the brain, heart, kidney, and liver [1]. According to EPA, the permissible limit of copper in the water is about 2.0 mg L^{-1}.

To reduce the toxicity of heavy metals, several physicochemical methods are being used worldwide [2–5] but these are inherently problematic in their application to metal-bearing waste streams [6]. Chemical precipitation, lime coagulation, ion exchange, reverse osmosis, and solvent extraction are the common methods for the removal of heavy metals from water. Nevertheless, disadvantages like incomplete removal, high reagent cost and energy needs, and generation of toxic waste products that need careful disposal have made it imperative to find out a new, cost-effective treatment method that is capable of removing heavy metals from effluents [7]. Adsorption, which is one of the most efficient and economic technique, is used worldwide for removal of heavy metals. Around the world, scientists are trying to evaluate the adsorption capacities of heavy metals towards various low-cost adsorbents, i.e. conventional and non-conventional [8–11].

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Black Cumin seeds (BCS) (*Nigelle Sativa*), a home medicine, has pungent bitter taste and smell. It is used primarily in confectionery and liquors. It is used for medicinal purposes in the Middle East and Africa. It has been traditionally used for the treatments related to respiratory health, stomach and intestinal health, kidney and liver function, and circulatory and immune system support. It is used as analgesic, anti-inflammatory, antiallergic, antioxidants, anticancer, antiviral, and also for general well-being. Compositional analysis revealed that it contains appreciable quantities of carbohydrates, proteins, and fats. Moreover, potassium, calcium, phosphorous, and magnesium were predominant minerals. BCS fixed oil contains appreciable quantities of unsaturated especially polyunsaturated fatty acids; constitute the bulk of oil ranging from 48 to 70%, while monounsaturated (18–29%) and saturated fatty acids (12–25%) are in lesser proportions [12,13]

In this work, BCSs (*Nigelle Sativa*) a non-conventional, economical, and eco-friendly adsorbent was used for the removal of one of the most toxic metal i.e. Cu^{2+}. The adsorption characteristics of cumin seeds was investigated as function of time, concentration, pH, temperature with respect to its kinetics, adsorption, and thermodynamic studies.

2. Materials and methods

2.1. Materials, chemicals and equipment

The BCSs were collected as a waste from the Unani medical college lab, A.M.U. Aligarh. The seeds were then converted into micro particles by grinding them in a mechanical grinder followed by sieving. It was then washed several times with double distilled water to remove dirt, color, and impurities. The characterizations of the adsorbent were done by Fourier transform infrared spectroscopy (FTIR) to study the functional groups in the range of 400–4,000 cm^{-1} using FTIR Spectrophotometer (Inter-spec 2020, spectrolab, UK) in KBr pellets. The morphology of the exterior surface of adsorbent was obtained by Scanning electron microscopy (LEO 450, England). The surface area of the adsorbent was determined by BET (Brunauer-Emmett-Teller) surface area analyzer (Quantachrome Autosorb Instruments, USA).The concentration of metal ions was determined by Atomic Adsorption Spectroscopy (GBC 902, Australia). The pH was measured by pH meter (Elico L1 120, India). All the chemicals purchased were of analytical grade. The proximate composition of the adsorbent (*Nigelle Sativa*) is given in Table 1.

Table 1
Physical properties of the adsorbent

Proximate composition	%
Moisture	6.46 ± 0.17
Crude protein	22.80 ± 0.60
Crude fat	31.16 ± 0.82
Crude fiber	6.03 ± 0.16
Ash	4.20 ± 0.11
NFE	29.36 ± 0.78

2.2. Batch adsorption studies

The selectivity of the adsorbent was studied for Cu^{2+}, Cd^{2+}, Pb^{2+}, and Ni^{2+}. The adsorbent shows higher adsorption capacity of about 24.5 $mg\,g^{-1}$ for Cu^{2+} ions. Therefore, the further studies were done for Cu^{2+} removal only. The batch experiment was carried out by using 0.1 g of the adsorbent with 50 mL of 50 and 100 $mg\,L^{-1}$ of metal ion solution. The equilibrium was attained in 30 min. The supernatant was analyzed by atomic absorption spectrophotometer (AAS). The adsorption isotherm studies were carried out in the temperature range of 30–50°C and initial concentration range of 20–100 $mg\,L^{-1}$ with 50 mL of Cu^{2+} ion solution. The pH experiment was conducted with 50 mg L^{-1} of Cu^{2+} ion solution in the pH range of 2–6. The pH was adjusted using 0.1 $mol\,L^{-1}$ HCl and 0.1 mol L^{-1} NaOH. The adsorption capacities and % removal was calculated by using the following formula:

$$Q_e = V(C_o - C_e)/W \tag{1}$$

$$\% = 100(C_o - C_e)/C_o \tag{2}$$

where

Q_e = adsorption capacity of metal ion ($mg\,g^{-1}$)
V = volume of the metal ion solution (L)
W = mass of the adsorbent (gm)
C_o = initial metal ion concentration ($mg\,L^{-1}$)
C_e = metal ion concentration at equilibrium ($mg\,L^{-1}$)

Desorption of the adsorbent was carried out by batch process using 0.1 $mol\,L^{-1}$HCl and 0.1 mol L^{-1}acetic acid solution. The amount of Cu^{2+} ion desorbed was analyzed by AAS.

2.3. Adsorption kinetics

In order to investigate the kinetics of Cu^{2+} ion towards cumin seeds, the most commonly used pseudo-first order, pseudo-second order, intraparticle diffusion and Elovich kinetic models were applied, and the equations are given in Table 2.

2.4. Adsorption isotherms

Isotherms of Langmuir, Freundlich and Temkin were used to describe the relationship between adsorbed copper ion per unit mass of cumin seeds (q_e; mg g^{-1}) and unadsorbed metal ion concentration in the solution (C_e; mg L^{-1}) at the equilibrium.

The fitting procedure was performed using R-Software, version 2.10.1 (2009-12-14). To evaluate the fitness of the data, the correlation coefficient (R^2), Residual standard error (RSE), p values, and chi square (χ^2) were calculated as given in Table 2.

2.5. Thermodynamic studies

The thermodynamic parameters such as change in free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) were determined using following equations [23]:

$$K_c = C_{\text{ads}}/C_e \tag{12}$$

$$\Delta G^\circ = -RT \ln K_c \tag{13}$$

$$\log K_c = \Delta S^\circ/2.303R - \Delta H^\circ/2.303RT \tag{14}$$

where K_c is the equilibrium constant, C_{ads} is the amount of metal ions adsorbed on the adsorbent of the solution at equilibrium (mg L^{-1}), C_e is the equilibrium concentration of metal ions in the solution (mg L^{-1}), R is the gas constant, and T is the temperature in Kelvin.

Activation energy of process was determined by using the Arrhenius equation [24] as:

$$\ln K_c = -E_a/RT + \ln K_o \tag{15}$$

where K_c is the equilibrium constant, E_a is the activation energy, and K_o is the constant.

3. Results and discussion

3.1. Characterization of adsorbent

The adsorbent was characterized by FTIR and SEM analysis. Scanning electron microscopy was done to observe the surface morphology of the adsorbent as shown in Fig. 1. According to the SEM images the adsorbent was found to be porous in nature which is observed with higher adsorption capacity of metal ion as in Fig. 1(b). Moreover, the surface of BCSs seemed to be stuffed or tightly packed with biopolymers like lignins or tannins which would have reduced the biosorbent surface porosity [25]. The FTIR before and after adsorption are shown in Fig. 2(A) and (B). From the FTIR spectra, the following conclusions were drawn: the bend in the peak 3,436.50 cm^{-1} corresponds to hydroxyl peak [26]. The peaks at 2,926.68 and 2,926.93 cm^{-1} assigned to methyl and methylene groups. The change in the peak from 1,743.92 to 1,741.61 cm^{-1} was probably due to metal and carboxylic groups bonding [27]. The peak 1,166.56 cm^{-1} corresponds to lignin endemic components. The BET analysis of the adsorbent is presented in Table 3.

3.2. Effect of contact time and pH

The adsorption rate is one of the most important parameter which is designed for batch adsorption experiments. Consequently, it is important to establish the time dependence of such systems under various process conditions. The equilibrium was attained in 30 min for both 50 and 100 mg L^{-1} solution. The maximum adsorption capacity (24.5 mg g^{-1}) was observed at 30 min as shown in Fig. 3. The maximum adsorption was recorded at pH 6 as shown in Fig. 4. After pH 6, solution tends to precipitate due to formation of hydroxide [28–30]. At lower pH values, H_3O^+ ions compete with metal ions for exchange and therefore

Table 2
Equation of models and error functions

S.·No	Models and error functions	Equations	Equation no.	Reference
1	Pseudo-first order	$\text{Log}\ (q_e - q_t) = \log\ (q_e) - (k_1)t/2.303$	3	[14]
2	Pseudo-second order	$t/q_t = 1/(k_2 q_e^2) + t/q_e$	4	[15]
3	Intraparticle diffusion	$q_t = K_{id} t^{0.5} + C$	5	[16]
4	Elovich equation	$Q_t = A + B\ \ln\ t$	6	[17]
5	Langmuir isotherm	$1/q_e = 1/(q_m \times b) + 1/(q_m \times c_e)$	7	[18]
6	Freundlich isotherm	$\text{Log}\ q_e = 1/n\ \log\ C_e + \log\ K_f$	8	[19]
7	Temkin isotherm	$Q_e = B_1(\ln\ c_e) + B_1(\ln\ K_t)$	9	[20]
8	Chi-Square	$(\chi^2) = \sum[(q_e - q_{e\ \text{cal}})^2/q_{e\ \text{cal}}]$	10	[21]
9	Residual sum of square (RSE)	$\text{RSE} = \sum(q_e - q_{e\ \text{cal}})^2$	11	[22]

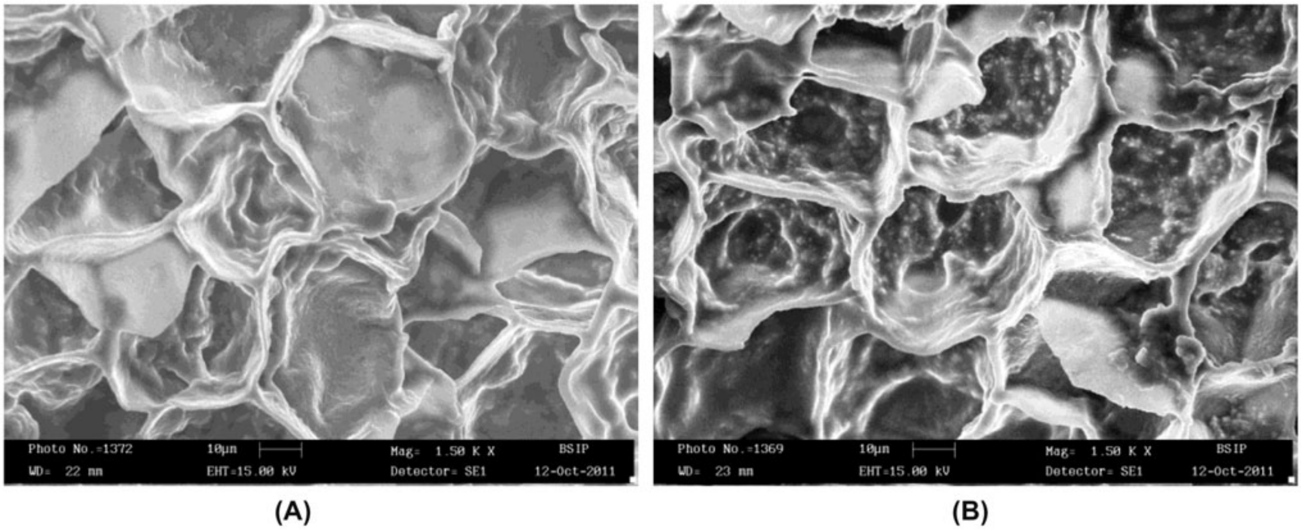

Fig. 1. SEM Micrograph of cumin seed (A) before and (B) after adsorption.

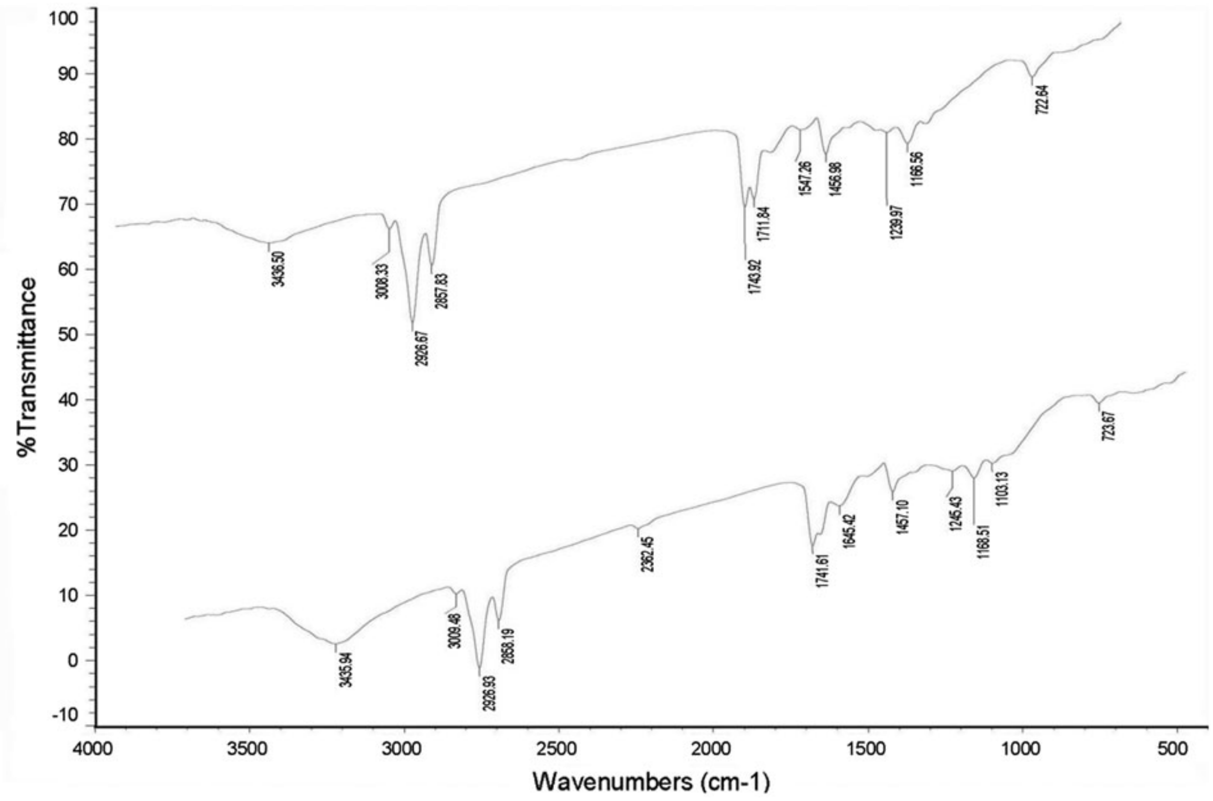

Fig. 2. FTIR Analysis (A) before adsorption (B) after adsorption.

the Cu^{2+} uptake decreased at lower pH. Competitive adsorption occurred between H^+ protons and free Cu^{2+} ions and their hydroxide fixation sites [31]. The rapid sorption was attained initially and it gets slower down as equilibrium was attained. The rapid initial sorption was likely due to extra-cellular binding and the slower sorption resulted from intracellular binding [32]. The plots of metal uptake as a function of time

Table 3
BET surface area analysis for BCSs

Parameters	Measurement
Pore size area	7.036 $m^2 g^{-1}$
R^2	0.618038
Total pore volume	5.6047 cc g^{-1}
Pore diameter	3.205 A○

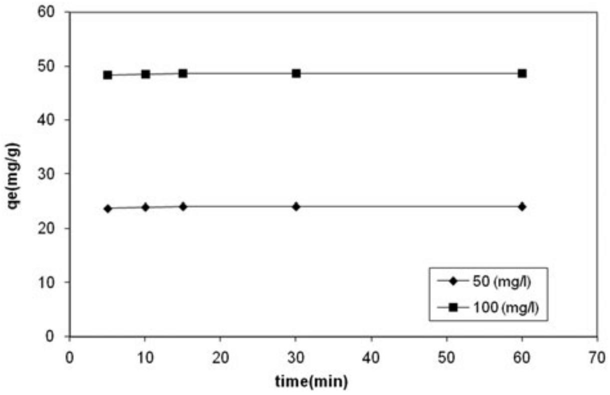

Fig. 3. Effect of contract time for adsorption of Cu^{2+} ion.

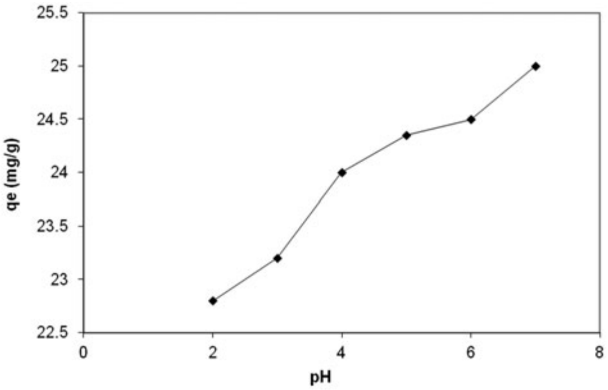

Fig. 4. Effect of pH on adsorption of Cu^{2+} ion.

were single, smooth, and continuous leading to saturation. This suggests possible monolayer coverage of the metal ions on the surface of the adsorbent [33].

3.3. Adsorption kinetics

The kinetic studies were carried out for pseudo-first order, pseudo-second order, intraparticle diffusion, and Elovich equation as shown in Figs. 5–8. According to the regression coefficient (R^2) as shown in Table 4, the kinetic data is best fitted by pseudo-second order. The intraparticle diffusion is the sole rate-determining step. The value of K_{id}, C, and R^2 is given in Table 4. The value of intercept gives an idea of boundary layer thickness, larger the intercept; greater is the boundary layer thickness [34].

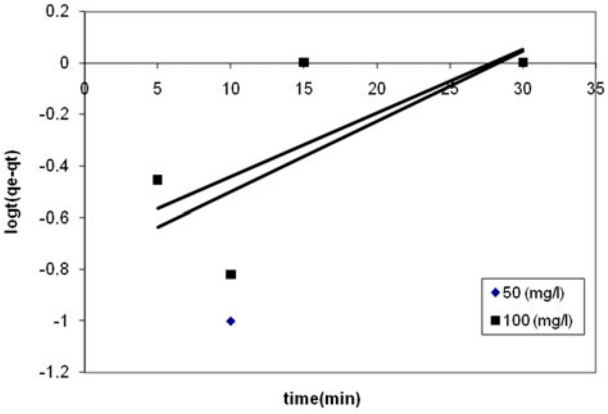

Fig. 5. Plot for pseudo 1st order kinetics.

3.4. Adsorption isotherms

In order to see the adsorption mechanism of Cu^{2+} on the adsorbent, the various isotherm models were applied as given in Table 2. The best fitted isotherm model was observed from the Table 5 which shows values of parameters, regression coefficient (R^2), and error functions.

Langmuir isotherm was observed by a plot of $1/q_e$ vs. $1/C_e$ as shown in Fig. 9 at different temperatures (30–50℃). Freundlich isotherm was observed by a plot of log q_e vs. log C_e as shown in Fig. 10 and Temkin isotherm was observed by a plot of ln C_e vs. q_e as shown in Fig. 11. According to the regression

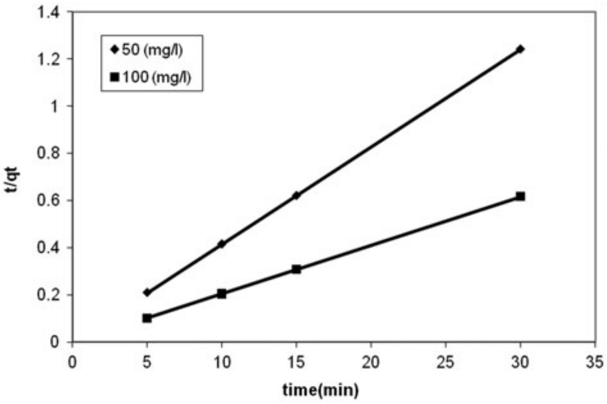

Fig. 6. Plot for psudo 2nd order kinetics.

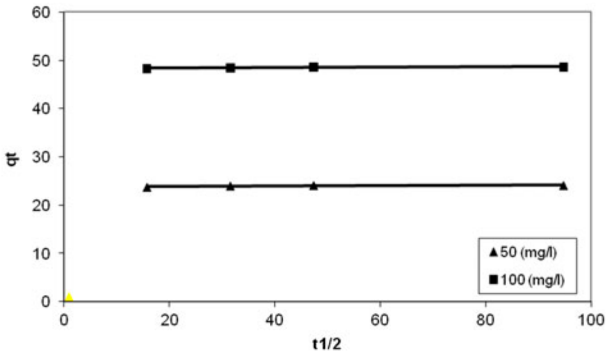

Fig. 7. Plot for intraparticle diffusion.

coefficient (R^2) and error factors shown in Table 4, it is best fitted by Freundlich model due to higher regression coefficient and lower error values i.e. (χ^2) and RSC. The value of n greater than unity corresponded to the distribution of bonded ions on the sorbent surface, which was indicative of a constant partitioning of the sorption mechanisms, where sorbate penetrated the sorbent and therefore showed good adsorption [35].

3.5. Effect of surfactant

Presence of surfactant in aqueous solution is likely to affect the adsorption capacity of the adsorbent. This is very important for potential applications of adsorbents because surfactants are widely employed in the industry and are commonly present in real wastewaters. In the presence of surfactants, the adsorption of metal ions onto the active sites of adsorbent is affected by the charge density of the interface. In this study, the effect of anionic SDS, cationic CTAB, and non-ionic TritonX-100 surfactant was studied in the

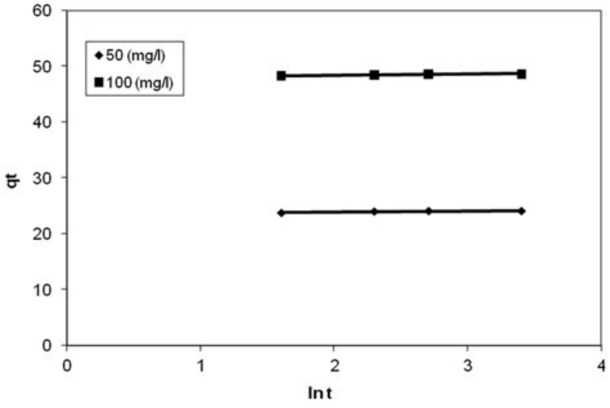

Fig. 8. Plot for Elovich equation.

Table 4
Kinetic parameters of Cu (II) ion

Kinetic parameters	50 (mg L^{-1})	100 (mg L^{-1})
Pseudo 1st order		
Q_e (exp) (mg g^{-1})	24.1	48.65
Q_e (cal)	−5.929	−4.89
K_1 (min^{-1})	−0.0628	−0.0568
R^2	0.3845	0.4519
Pseudo 2nd order		
Q_e (exp) (mg g^{-1})	24.1	48.65
Q_e (cal)	24.1	48.78
K_2(g mg^{-1}min^{-1})	0.717	0.8405
R^2	1	1
Intraparticle diffusion		
Kid	0.0036	0.00038
C	23.816	48.34
R^2	0.5583	0.6255
Elovich equation		
A (mg g^{-1}min^{-1})	23.492	48.014
B (g mg^{-1})	0.1978	0.2038
R^2	0.8067	0.85

Table 5
Constants for adsorption isotherms of Cu (II) ion and Error models

Isotherms model	30℃	40℃	50℃
Langmuir isotherm			
Q_m (mg g^{-1})	85.49	86.78	214.4
B	0.233	0.157	0.1127
R^2	0.9316	0.9345	0.9121
RSC	0.007528	0.006896	0.008464
p-value	2.499	1.276	6.073
f-stat	95.38	116.9	72.63
(χ^2)	31.3	9.19	4.017
Freundlich isotherm			
K_f (mg g^{-1})(1/mg)$^{1/n}$	16.36	17.11	21.56
N	0.961	0.891	1.298
R^2	0.9959	0.9602	0.9361
RSC	0.01601	0.04999	0.06259
p-value	1.312	3.701	1.967
f-stat	169.1	169	102.6
(χ^2)	2.17	2.17	2.5
Temkin isotherm			
B_1	25.018	28.443	19.403
K_t (mg^{-1})	2.05	1.918	3.479
R^2	0.9379	0.9923	0.967
RSC	3.548	1.253	2.57
p-value	1.78	1.145	1.919
f-stat	105.7	907.5	205.3
(χ^2)	5.85	0.496	1.3349

concentration range of 20–50 mg L^{-1}. There is no effect of any surfactant on the adsorption capacity of metal ion on the adsorbent [36].

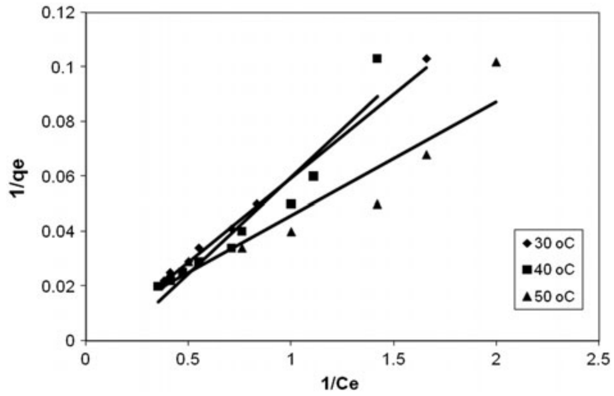

Fig. 9. Plot for Langmuir Isotherm.

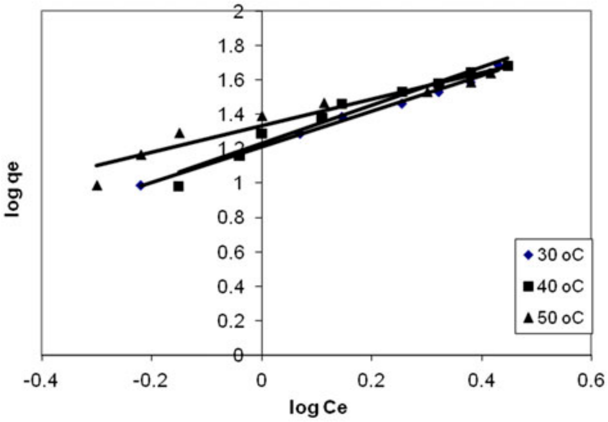

Fig. 10. Plot for Freundlich Isotherm.

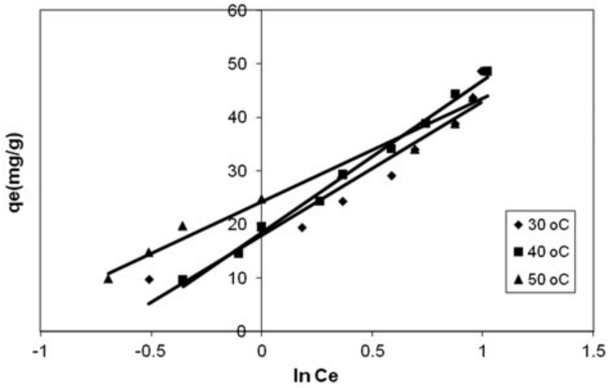

Fig. 11. Plot for Temkin Isotherm.

3.6. Effect of ionic strength

The effect of ionic strength was studied by using 0.01 mol L^{-1} $NaNO_3$, 0.1 mol L^{-1} $NaNO_3$, and 0.5 mol L^{-1} $NaNO_3$ solution. The effect of ionic strength on the adsorption was observed more in case of 0.1 mol L^{-1} $NaNO_3$ and further decreases with increase in electrolyte concentration. It is also suggested that increasing electrolyte concentration can cause screening of surface negative charges by the electrolyte ions leading to a drop in the adsorption of the metal ions [37]. Therefore, a decrease in adsorption of metal ion with increasing ionic strength of electrolyte implies that increasing ionic strength is making the potential of the adsorbent surface less negative and thus would decrease metal ion adsorption [38].

3.7. Thermodynamic studies and activation energy

The effect of temperature for the adsorption of Cu^{2+} on cumin seeds was studied in temperature range of 30–50°C. The values of ΔG°, ΔH°, and ΔS° were calculated by a plot of log K_c vs. $1/T$ in the temperature range of 30–50°C as shown in Fig. 12 and Table 6. The values of ΔG° increases with increase in temperature correspond to spontaneity in nature. The positive value of ΔH° shows that the process is endothermic in nature. While the positive value of ΔS° indicates randomness at solid/liquid solutions interface during adsorption of Cu^{2+} ion.

The magnitude of activation energy explains the type of sorption. Two main types of adsorption can occur, physical or chemical. In physical adsorption, the equilibrium is usually attained rapidly and easily reversible, because the energy requirements are small. The activation energy for physical adsorption is not more than 4.2 kJ mol^{-1}, because the forces involved in physical adsorption are weak. Chemical adsorption is specific and involves forces much stronger than physi-

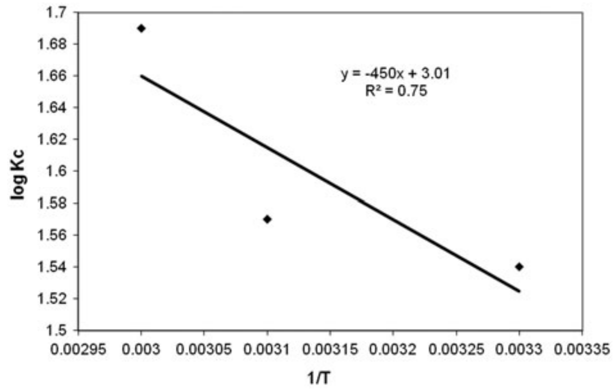

Fig. 12. Plot for log K_c vs. $1/T$.

Table 6
Thermodynamic parameters and activation energy of Cu (II) ion

Temp (°C)	ΔG (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS (kJ mol^{-1}K^{-1})	R^2	E_a (kJ mol^{-1})	K_o	R^2
30	−8.97						
40	−9.42	8.61	0.057	0.75	8.78	2.57	0.77
50	−10.44						

Table 7
Comparison of the uptake capacities for copper (II) ions of various adsorbents

Adsorbent	$q_{\max}$ (mg g−1)	Reference
Activated carbon from almond shell	8.85	[41]
Bagasse fly ash	2.26	[42]
Low-rank Turkish coals	1.62	[43]
Coirpith carbon	39.7	[44]
Peanut hull carbon	65.57	[45]
Pine bark	9.47	[46]
Sawdust	1.79	[21]
Washed sugar beet pulp	21.1	[47]
Activated sugar beet pulp	17.1	[48]
Activated carbon from sugar beet pulp	63.69	[49]
Sphagnum moss peat	12.4	[50]
Tree fern	10.6	[51]
Padina sp.	50.8	[52]
M. spicatum	10.37	[53]
Kaolinite	10.79	[54]
Dehydrated wheat bran	51.51	[55]
Black Cumin Seed	85.49	[This Study]

cal adsorption. Therefore, activation energy for chemical adsorption is of larger magnitude as compared to physical adsorption [39].

A plot of ln K_c vs. $1/T$ gives the value of activation energy (E_a), K_o, and R^2. The value of activation energy for Cu^{2+} ion on cumin seeds was found to be 8.5 KJ mol^{-1} as shown in Table 6 which supports the adsorption process to be chemisorptions in nature.

3.8. Desorption and regeneration studies

The Desorption of the Cu^{2+} was done by batch process. The metal ions were desorbed for more than 95% in case of 0.1 mol L^{-1} HCl. In order to make the process more economical and feasible, the material was regenerated. If the material can be regenerated and reused as an adsorbent after the first cycle of the adsorption process, then significant improvement in the economy of the process can also be achieved [39]. The Cu^{2+} ion could be regenerated by Cumin seeds up to five cycles by 0.1 N HCl. The adsorption capacity slightly decreases with increase in regeneration cycle. This may be attributed to slight damage of the original surface layer of cumin seeds proceeds by means of an acid treatment [40].

3.9. Comparative study of the adsorbent

In order to evaluate the feasibility of the adsorbent and to compare the adsorption capacity with other non-conventional adsorbent a comparative study is presented in Table 7. It is evident from the table that BCS has got the highest monolayer adsorption capacity (85.49 mg g^{-1}) among all the adsorbents.

4. Conclusion

In this work, the BCS were used for the biosorption of Cu^{2+} from aqueous solution. The material was characterized by SEM and FTIR. The adsorption follows pseudo-second order kinetic model and intraparticle diffusion is the rate determining step. By the use of R-Software version 2.10.1 (2009-12-14), it is concluded that Freundlich isotherm is best fitted isotherm with higher R^2 value and low error factors. The process was found to be spontaneous, endothermic with randomness at solid–liquid solutions interface. The activation energy of the process leads to conformation of chemisorption. Nienty five percentage of the Cu^{2+} ion could be desorbed by using 0.1 mol L^{-1} HCl solution and adsorbent can be successfully regenerated up to five times.

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