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Optimization of Cr(VI) removal onto biosorbent eggshell membrane: experimental & theoretical approaches

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ABSTRACT

The discharge of heavy metal pollutants, particularly Cr(VI) ions emerging out from the industries into water, has become a serious concern. In the present study, feasibility of eggshell membrane has been tested for the removal of Cr(VI) ions from its aqueous solutions. The membrane was separated from the eggshells, dried at 40˚C for about 3 h and then crushed into powder. The characterization of powdered eggshell membrane was carried out using scanning electron microscopy, FTIR, and XRF analysis. Batch adsorption experiments have been performed for the investigation of the ability of powdered egg membrane to remove Cr(VI) ions from its solution. The effect of pH, Cr(VI) ion concentration, sorbent dosage, contact time, and temperature has been evaluated. The theoretical treatment from the experimentally gathered data has been carried out to measure the effect of these variables using central composite design (CCD). The results of the CCD show that the maximum removal (81.47%) was achieved at temperature 20˚C, pH 3.54, Cr(VI) ion concentration 5.0 mg/L, time 117.52 min, and dosage 3.78 g.

Keywords: Adsorption; Membrane; Chromium; Central composite design

1. Introduction

Chromium is one of the most serious pollutants amongst all industrial effluents. Hexavalent Chromium i.e. Cr(VI) ion is the most toxic form of chromium, which imposes hazardous health effects towards humans as well as animals [1]. A direct contact of Cr(VI) ions to the skin causes allergy and rashes, and on inhalation it irritates, bleeds nose, and poses respiratory problems [2]. Ingestion of Cr(VI) ions upsets stomach, weakens immune system, damages kidney and liver, and forms ulcers, which may lead to complications like anemia, encephalopathy, hepatitis, nephritic syndrome, etc. [3,4]. The high and continuous dosage of Cr(VI) ions is carcinogenic in nature and instigates lung cancer [5,6]. High solubility of Cr(VI) ions in water allows them to enter into drinking water as well as to the soil, which eventually contaminates plants and vegetables.

Keeping the toxicity of Cr(VI) ions in view, several techniques like ionic exchange, precipitation, reverse osmosis, microfiltration, etc. were used by various workers for the removal of Cr(VI) ions. Unfortunately,

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these methods are expensive and also create sludge problem. In the hunt of developing economic, clean, and effective method, adsorption technique was found more effective and promising as this technique has already established itself as a potential excavenger for various types of pollutants [7–18]. In recent years, adsorbents like wheat bran [19], acid-washed crab shells [20], groundnut hull [21], *Rosa Gruss an Teplitz* [22], *Citrus Reticulata* [23], *Daucus Carota* L. [24], *Azadirachta indica* (neem) leaf powder [25], etc. have been claimed as potential and inexpensive adsorbents for the removal of Cr(VI) ions.

Despite these fruitful attempts, there is still a need to search for a noble adsorbent to eradicate the menace of Cr(VI) ions from wastewater and it is therefore envisaged to develop a systematic and exhaustive process for the removal of Cr(VI) ions by introducing an innovative adsorbent. For the present research work, waste material "Eggshell Membrane" is selected to investigate the optimum adsorption parameters for the maximum removal of Cr(VI) ions from wastewater through batch adsorption process.

Eggshell is a well-known waste material, which is disposed off from the kitchen, bakeries, and food industries in huge quantity every day. Its disposal is a great concern to everyone and therefore its usage as a potential adsorbent is a thoughtful endeavor because of its high ion-exchange capacity. Literature survey reveals that in recent past, eggshell has been successfully employed by few workers as an adsorbent for the removal of organic matters and metal ions from industrial effluents [26–29].

The purpose of the present study is to investigate the optimum conditions for the removal of Cr(VI) ions from its aqueous solutions using eggshell membrane as a biosorbent. This paper includes results of the effects of pH, temperature, contact time, sorbent dosage, Cr(VI) ion concentration, etc. on its removal along with adsorption isotherms. Attempts have also been made to characterize the biosorbent eggshell membrane. Another prominent feature of the present paper is application of the gathered data on statistical calculations based on "central composite design (CCD)" and theoretical monitoring of effects of various operating variables such as pH, sorbent dosage, Cr (VI) ion concentration, etc. on the performance of the sorption process.

2. Material and methods

Eggshells were collected from the local bakery shop. These were washed in tap water several times and then rinsed in distilled water overnight. The egg-shell material is then dried in an oven at room temperature. From the dried egg-shells, inner layer of membranes was removed and material thus obtained was again washed with de-onized water. Then, the membranes were again dried at 40°C for about 3 h, and crushed to powder of 100 BSS Mesh. This egg-shell membrane powder was finally stored in desiccator until used for the experiments.

All chemicals were procured from M/s Merk. Standard Cr(VI) ions stock solution (1 g/L) was prepared by dissolving dry $K_2Cr_2O_7$ in the double-distilled water and all working solutions were prepared by diluting the stock solution.

To carry out batch adsorption studies, in a 100 mL volumetric flask, 25 mL of the $K_2Cr_2O_7$ solution of known concentration was taken at a fixed temperature and powdered eggshell membrane biosorbent was added into it. The desired pH of the solution was now maintained by 0.1 M HCl and/or 0.1 M NaOH and the mixture was given intermittent shaking on a mechanical shaker. After about 24 h, when equilibrium is thought to be established, the solution was centrifuged and the amount of Cr(VI) ions uptake was monitored spectrophotometrically at the absorbance maximum of Cr(VI) ions viz. $\lambda_{max} = 540$ nm. It is important to note that under batch studies, effects of important parameters such as dye concentration, solution pH, and amount of the biosorbent material, solution temperature, and contact time were observed.

Also, the data analysis was then made to investigate the interactive influence of these independent parameters theoretically. The theoretical treatment was based on factorial design method, which was carried out through a computer program. In order to optimize the biosorption of Cr(VI) ions, response surface methodology was also applied.

A statistical experimental design based on "CCD" was planned [30] and the percentage of removal of Cr(VI) ions was measured for different variables such as temperature, pH, Cr(VI) ion concentration, time, and dosage of biosorbent abbreviated as x_1, x_2, x_3, x_4, and x_5, respectively. These variables were investigated at five levels (−2, −1, 0, 1, and 2) and the dependent variable was chosen as Y. In the present work, Minitab software package was used to design and evaluate these five independent variables at five levels on the responses according to the Eq. (1). The ranges for the selected levels of the five variables are shown in Table 1, while the experimental percentage removal of Cr(VI) ions for different selected levels of these variables is presented in Table 2 for all the 32 runs carried out during the theoretical treatment.

Table 1
Range of values of CCD

Independent variables	Levels				
	$-\alpha^*$	−1	0	1	$+\alpha$
Temperature (°C)	60	50	40	30	20
pH	10	8	6	4	2
Cr(VI) concentration (mg/L)	25	20	15	10	5
Time (min)	130	100	70	40	10
Dosage (g)	4.5	3.5	2.5	1.5	0.5

$^*\alpha$ = star point @ CCD = ± 2.

$$Y = \beta_0 + \sum \beta_j X_i + \sum \beta_{jj} X_j^2 + \sum \beta_{jk} X_j X_k \quad (1)$$

where Y = response, β_0 = intercept, β_j = linear coefficients, β_{jj} = squared coefficients, $\beta_{jk=}$interaction coefficients, and X_i, X_j^2, X_j, X_k = level of independent variables.

3. Results and discussions

3.1. Characterization of sorbent and experimental setup

The morphology of egg-shell membrane was ascertained with the help of scanning electron microscopy (SEM) analysis. Fig. 1 exhibits the SEM images of the membrane and ascertains that this material is porous with vast surface and its structure is fibril. The porous fibril structure of the dried eggshell membrane is indeed responsible for its good adsorbing capacity.

The chemical characterization of the eggshell membrane was carried out with X-ray fluorescence spectrometer. The results indicate the presence of protein as major constituent in it. Quantitatively, about 66% protein was found to present in the eggshell membrane along with other inorganic components like Calcium, Brimstone, Silica, Zinc, etc. in smaller quantities.

The FTIR spectra of eggshell membrane is shown in Fig. 2, and exhibits the characteristic IR absorption peaks at 3,316, 1,652, 1,427, 875, and 710 cm^{-1}, which correspond to C = O, –CONH–, C–N, N–H, and C–C vibrations, respectively. This indicates the presence of peptide bonds in the egg shell membrane. Moreover, peaks in low wave number range also show less disordering structure of the material [31,32].

3.2. Effects of biosorbent dosage & pH

The effects of pH (2–10) and dosage of biosorbent (0.5–4.5 g) on the adsorption of Cr(VI) ions over membrane were simultaneously monitored at constant Cr(VI) ions concentration and presented in Fig. 3. The graphs indicate that by increasing the amount of biosorbent, the percent sorption of Cr(VI) ions increases at all pH. This is mainly due to increasing active and vacuous surface areas of the biosorbent with the increase in amount of sorbent.

On the other hand, irrespective of amount of biosorbent, the percentage removal of Cr(VI) ions increases till pH 4.0 and then decreases almost linearly. The higher adsorption of the dye at low pH may be due to increased protonation by neutralization of the negative charge at the surface of the

Table 2
Theoretically predicted values of percentage removal of Cr(VI) Ions for the different selected levels of variables

Run	Temperature (°C)	pH	Cr(VI) conc. (mg/L)	Time (min)	Dosage (g)	Observed sorption (%)	Predicted sorption (%)
1	30	4	10	40	3.5	19.56	18.8805
2	50	4	10	100	3.5	7.34	6.5588
3	50	8	10	100	1.5	53.40	52.4980
4	40	6	15	70	2.5	53.81	54.0797
5	40	6	15	70	4.5	28.13	30.1013
6	50	8	10	40	3.5	24.45	27.5930
7	40	6	15	70	2.5	67.46	70.4822
8	40	6	15	70	2.5	16.71	19.6305
9	40	6	15	130	2.5	6.32	3.2297
10	40	6	15	10	2.5	55.24	53.3213
11	50	4	20	40	3.5	70.73	68.6905
12	30	8	20	40	3.5	52.18	50.0388
13	40	10	15	70	2.5	42.60	43.4338
14	60	6	15	70	2.5	10.38	11.1122
15	30	8	10	100	3.5	54.83	55.4413
16	50	8	20	100	3.5	68.48	70.2630
17	30	4	20	100	3.5	43.01	43.6132
18	40	6	5	70	2.5	32.61	31.0732
19	30	8	10	40	1.5	1.43	1.7915
20	50	8	20	40	1.5	64.81	63.5148
21	40	6	15	70	2.5	35.26	41.3682
22	30	8	20	100	1.5	53.60	46.5582
23	30	4	10	100	1.5	46.67	42.6548
24	30	4	20	40	1.5	58.50	61.5815
25	40	6	25	70	2.5	22.63	23.4365
26	20	6	15	70	2.5	69.71	67.9698
27	40	6	15	70	0.5	52.98	52.9423
28	50	4	10	40	1.5	52.58	52.9423
29	40	6	15	70	2.5	53.44	52.9423
30	50	4	20	100	1.5	52.57	52.9423
31	40	6	15	70	2.5	52.98	52.9423
32	40	2	15	70	2.5	52.17	52.9423

biosorbents. This phenomenon helps in the preference of the Cr(VI) ions for the active sites and facilitates the diffusion process in the working solution. While, with increase in alkaline conditions or pH, protonation reduces and electrostatic repulsive force becomes operative, which thereby retards diffusion and adsorption.

Thus for 5 mg/L potassium dichromate solution, maximum sorption of Cr(VI) ions of about 55% could be achieved at pH 4.0 and biosorbent amount 4.5 g. While minimum sorption of about 10% occurred at pH 10.0 and biosorbent amount 0.5 g at the same concentration of potassium dichromate. Keeping above-mentioned results in view, pH 4.0 and biosorbent amount 4.5 g was chosen for all further studies.

3.3. Effects of contact time & concentration

The sorption experiments were investigated at different contact times and with different Cr concentrations at pH 4 and the results obtained are shown in Fig. 4. The amount of sorption of Cr(VI) ions increases linearly with increasing contact time from 10 to 100 min. From 100 to 120 min, the increase is slow and steady which finally becomes constant beyond 120 min. The rapid and high sorption rate in the initial region may be due to covering of available active functional groups of the biosorbent by the Cr(VI) ions, and as the surface of the sorbent is sufficiently occupied by the Cr(VI) ions their binding becomes slow and finally constant.

Fig. 4 also shows that amount of Cr(VI) ions increases with rise in Cr(VI) ion concentration. This consequentially decreases the removal efficiency of the adsorbent. The maximum sorption in higher concentration range may be credited to the availability of more Cr(VI) ions.

3.4. Effect of temperature

Experiments were carried out at temperatures 20 to 60°C at the concentration of 10 mg L^{-1} (Fig. 5). With the increase in temperature from 20 to 60°C, the uptake of Cr(VI) ions by the biosorbent increases, thereby decreasing its removal efficiency. Equilibrium time for all the temperatures was found to be about 120 min indicating that the equilibrium time is independent of temperature. Also, the results showed that the sorption was exothermic in environment. The decreased sorption with the increase of temperature is also due to breaking of some active and internal bonds in external or inner surface sites of sorbent. Also, with increase in temperature can be a weakening force between the active sites of the membrane and Cr (VI) [31,33].

3.5. Theoretical treatment for deriving optimum conditions

Experimental results presented above reveal that the maximum adsorption of Cr(VI) ions (81.47%) on eggshell membrane powder could be achieved at temperature, pH, Cr(VI) ion concentration, time, and dosage of biosorbent as 20°C, 3.54, 5.0 mg/L, 117.52 min, and 3.78 g, respectively. The optimum conditions of these variables obtained theoretically are used to monitor them, which can be applied to an industrial-scale process.

Further, second-order polynomial equation is proposed for the prediction of percentage removal of Cr (VI) ions as a function of different variables [30].

$$\begin{aligned} Y = {} & -4685.08 - 327.65T - 2989.40D - 18.28t \\ & + 21.96P + 4.21C_{\mathrm{cr}} - 15.60T^2 507.23D^2 - 0.06t^2 \\ & - 11.31P^2 - 70.05T \times D - 1.91T \times t + 18.03T \\ & \times P + 0.39T \times C_{\mathrm{cr}} - 4.14D \times t + 0.34P \times C_{\mathrm{cr}} \end{aligned} \quad (2)$$

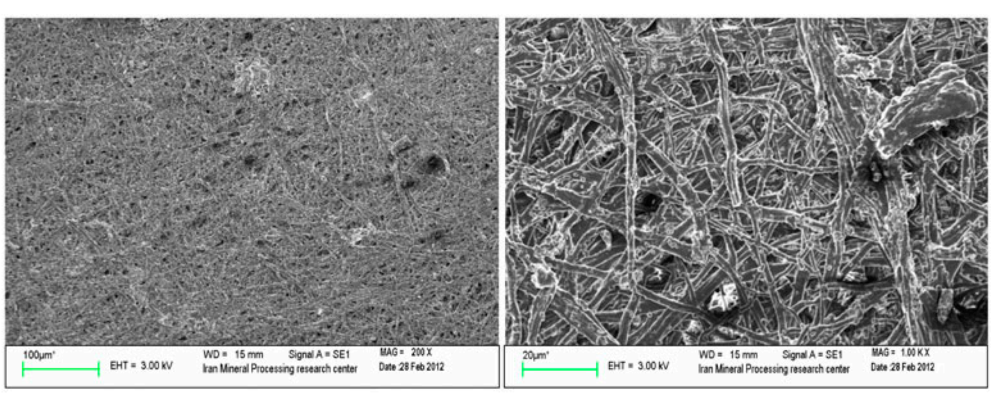

Fig. 1. SEM images of eggshell membrane.

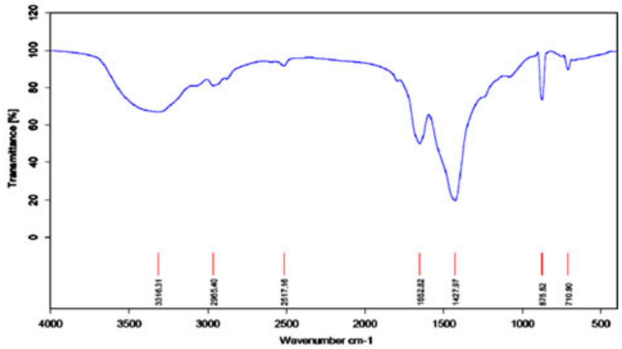

Fig. 2. FTIR spectrum of eggshell membrane.

where T is temperature, P is pH, C_{cr} is Cr(VI) ion concentration, t is time, and D is dosage of adsorbent.

The response surface model which was obtained from an experimental design was evaluated using ANOVA and analysis of residuals was made. The results of the statistical analyses including the estimated regression coefficients, t-test, and p-values of the sorption are tabulated in Table 3. The regression coefficient (R^2) adjusted by the sorption was found close to unity, which indicates that the developed models are able to fully predict the percentage removal of Cr(VI). The linear regression coefficients of the sorption were also found as 0.9855, which shows good performance of the model on the experimentally observed as well theoretically predicted percentage removal of Cr(VI) ions [30].

Table 3 exhibits that larger the t-value and the smaller the p-value, the more significant is the corresponding coefficient. Based on the statistical results (ANOVA) with confidence level of 95%, the effect of each term in the models could be significant, provided that its p-value is smaller than 0.05. It is imperative to realize that even though p-value is more than 0.05 for

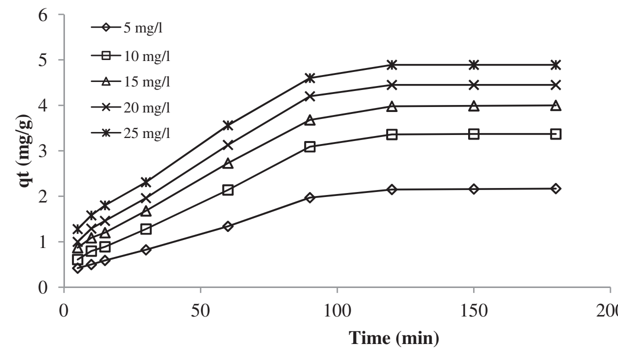

Fig. 4. Effect of contact time on the Cr(VI) ions uptake over eggshell membrane at 20°C [Cr(VI) ion concentration = 5 to 25 mg/L, sorbent dosage = 3.5 g and pH = 4].

the linear terms of C_{cr}, due to hierarchy rule in which the p-value is smaller than 0.05 for the higher order ($T \times C_{cr}$) of this variable, the effect of linear terms is considered in the model [34,35].

3.6. Variables affecting ongoing sorption

3.6.1. Temperature

As shown in Fig. 6, the percentage sorption decreases with increase in the temperature and at temperature of 20°C, maximum sorption (81.47%) was obtained. This decrease in sorption efficiency may be due to the increase in the Cr(VI) ions concentration and unclenching force between the accessible sites of the sorbent and Cr (VI) ions [36].

3.6.2. Cr(VI) ion concentration & contact time

Figs. 6 and 7 exhibit that by increasing the Cr(VI) ion concentration, a decrease in the percentage removal of Cr(VI) ions sorption is observed and maximum

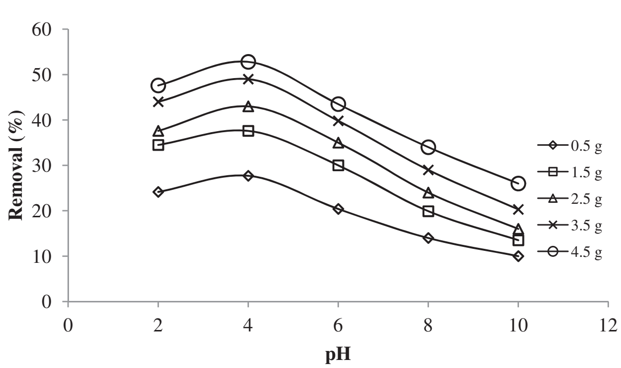

Fig. 3. Effect of pH on the removal of Cr(VI) ions by eggshell membrane at 20°C [Cr(VI) concentration = 5 mg/L, contact time = 60 min, sorbent dosage = 0.5 to 4.5 g].

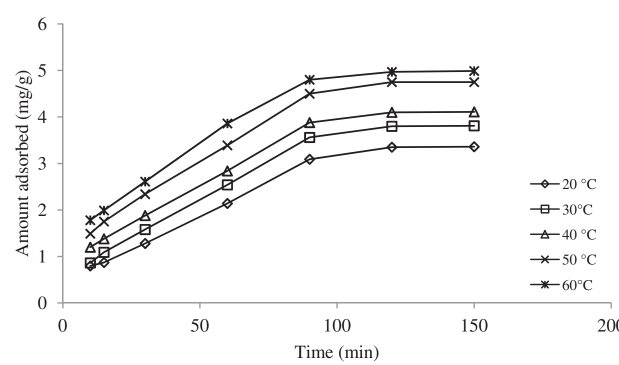

Fig. 5. Effect of temperature on the Cr (VI) ions uptake by eggshell membrane at pH 4 [Cr (VI) ion concentration = 5 mg/l, dosage of sorbent = 3.5 g, contact time = 15, 30, 60, 90, 120, and 150 min].

Table 3
Observed regression coefficients, *t*-test, and *p*-values

Term	Sorption		
	Regression coefficients	*t*-value	*p*-value
Constant	−4685.08	−7.026	0.000
T (°C)	−327.65	−5.077	0.000
D (g)	−2989.40	−6.962	0.000
t (min)	−18.28	−3.607	0.004
pH	21.96	0.286	0.780
C_{cr} (mg/L)	4.21	3.448	0.005
T^2 (°C)^2	−15.60	−5.193	0.000
D^2 (g)^2	−507.23	−6.754	0.000
t^2 (min)^2	−0.06	−2.989	0.012
pH^2	−11.31	−2.410	0.035
$C_{cr}{}^2$ (mg/L)^2	−0.00	−0.274	0.789
T (°C) × D (g)	−70.05	−3.444	0.005
T (°C) × t (min)	−1.91	−5.628	0.000
T (°C) × pH	18.03	3.546	0.005
T (°C) × Cp (mg/L)	0.39	4.797	0.001
D (g) × t (min)	−4.14	−2.443	0.033
pH × D (g)	−9.87	−0.388	0.705
C_{cr} (mg/L) × D (g)	0.49	1.216	0.250
pH × t (min)	0.33	0.789	0.447
C_{cr} (mg/L) × t (min)	−0.00	−0.665	0.520
pH × C_{cr} (mg/L)	0.34	3.297	0.007

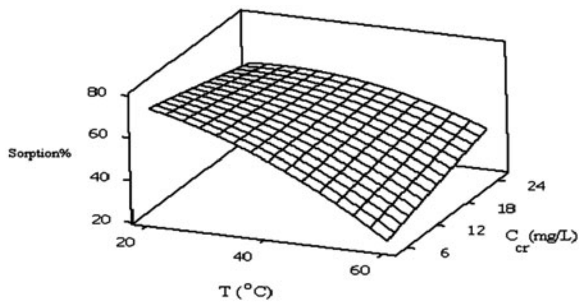

Fig. 6. Response surface of the percentage sorption of Cr (VI) ions versus temperature and Cr(VI) ion concentration [dosage of sorbent = 3.78 g, contact time = 117.52 min, pH = 3.54].

sorption (81.47%) could be achieved at 5.0 mg/L Cr (VI) ion concentration. The decrease in percentage of adsorption at higher concentration is mainly due to unavailability of sorption sites at the sorbent for larger number of adsorbing Cr(VI) ions. On the other hand, by increasing the time up to 117.52 min, the percentage sorption increases and a plateau is reached at around 130 min (Fig. 7) [34].

3.6.3. pH & biosorbent dosage

By increasing the pH, the sorption of Cr(VI) ions increases significantly up to pH 4 and then a decrease is observed till pH 10 (Fig. 8). At low pH range i.e. in pH < 4, the surface of the sorbent is surrounded by positively charged Cr(VI) ions and substantial attraction is taking place between the sorbent and Cr(VI) ions (23). However, at pH > 4, turbidity in reaction mixture is observed, mainly due to dissolution of fat from the sorbent to the water, which results into decrease in the percentage sorption of Cr(VI) ions.

Increasing the dosage of sorbent up to 3.78 g increase in sorption of Cr(VI) ions is observed, which eventually becomes constant at 4.5 g (Fig. 8). This

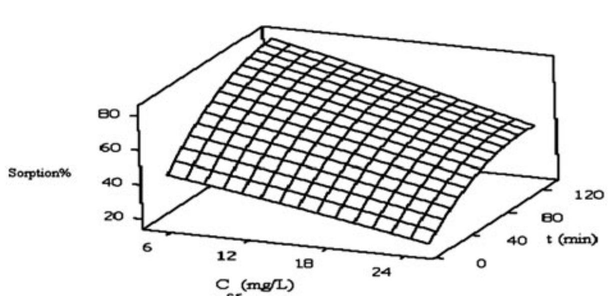

Fig. 7. Response surface of the percentage sorption of Cr (VI) ions versus Cr(VI) ions concentration and contact time at 20˚C [dosage of sorbent = 3.78 g, pH = 3.54].

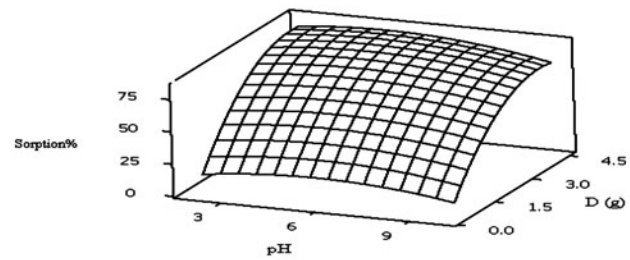

Fig. 8. Response surface of the percentage sorption of Cr (VI) ions versus pH and dosage of sorbent at 20˚C [contact time = 117.52, Cr(VI) ion concentration = 5.0 mg/L].

increase in adsorption is due to increase of contact surface of the sorbent and also increase in the active and accessible linking sites in the sorbent [37].

4. Conclusion

Eggshell membrane is a solid waste material obtained in large quantity from the food industries. The results presented above clearly exhibit its role as an effective sorbent for the removal of hazardous chromium (VI) ions from its aqueous solutions. The results indicate that removal of Cr(VI) by egg membrane powder is dependent on the pH, and temperature and maximum Cr(VI) ions removal efficiency can be achieved at pH 4 and 20˚C temperature. The sorption process is exothermic in nature at high temperature. The theoretical treatment by CCD gave interactive influence of various parameters on the efficiency of Cr(VI) ions removal. Thus, on the basis of experimental and theoretical data, it can be safely concluded that eggshell membrane can be efficiently used as a low cost biosorbent for the removal of Cr(VI).

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