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Chromium adsorption and Cr(VI) reduction to trivalent chromium in aqueous solutions by soya cake

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Abstract

Chromium as Cr(VI) is a industrially produced pollutant. Hexavalent chromium can be reduced to the trivalent state using various reductive agents or it can be removed from solution by surface-active adsorbents. In this study, both of these methods were evaluated using soya cake. A high efficiency for reduction of Cr(VI) to trivalent chromium was observed at pH < 1. Increasing the temperature, also increased the yield. Experimentally, the optimum time and soya cake mass were 5 h and 0.7 g, respectively.

In the second treatment method, a high efficiency for adsorption of chromium was also observed at pH < 1. The favorable temperature for adsorption was found to be 20 °C. Experimentally, the best time was 1h and with increasing soya cake mass up to 30 g, the adsorption efficiency was increased. Dissolution of LiCl in the experimental solutions, increased the efficiency of adsorption, however, this effect was not observed in the case of KCl.

Langmuir isotherm constants, Q and b, for ground soybeans, were found to be 2.8×10^{-4} mg/mg and 0.623, respectively. Freundlich isotherm constants, K_f and n, were found to be 1.4×10^{-4} and 4.99, respectively.

Keywords: Soya cake; Adsorption; Reduction; Cr(VI); Cr(III)

1. Introduction

With increasing use of Cr(VI) compounds in various industries such as metal plating, tanneries, etc. large quantities of toxic(chrome) pollutants are produced. Several methods are available to treat wastewaters polluted with Cr(VI) compounds.

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Nomenclature

b	Langmuir isotherm constant
C_0	initial concentration of Cr in solution (mg/l Cr)
C_e	equilibrium concentration of Cr in solution (mg/l Cr)
E(%)	efficiency
K_f	Freundlich isotherm constant
M	mass of soya cake (mg)
n	Freundlich isotherm constant
q_e	milligrams of adsorbed material per milligram of adsorbent
Q	maximum milligrams of adsorbed material per milligram of adsorbent (constant)
t	contact time (h)
T	temperature (°C)
V	volume of solution (l)

Greek letter

θ	percent of sites, which is occupied

Metal plating wastewater can be evaporated to concentrate the chromium solution and reuse it. Using ion exchange resins, the metals in acid chromic solutions can be separated and pure chromic solution can be recovered for reuse. Redox reactions have also been used for treatment of chromium in wastewater. For example, with the use of $FeSO_4$, Cr(VI) is reduced to Cr(III) and then is precipitated by CaO as $Cr(OH)_3$. In general, with these methods large quantities of chemicals and expensive systems are required, and so it is better to use cheaper natural materials as adsorbents for chromium treatment [1]. Different adsorbents such as sugar cane waste [2], decayed leaves [3] and seaweed [4] have been used in wastewater treatment.

Soybean is a very useful plant and for several centuries has been the main food for the Chinese. Soya has abundant proteins and lipids and its bread is useful for diabetic patients because of high nutritional worth [5].

Soybean has industrial uses, also. Soybean cake is used as food for domestic animals [5]. Soybean cake has $–NH_2$ and –COOH and other functional groups. Each of these groups has reductive and adsorptive properties. The adsorptive property of these groups is due to the electrostatic forces between them and Cr(VI) or Cr(III) species [5].

In our study, soya cake was used to remove chromium or its toxicity. For this purpose, the following methods were used:

1. Considering the oxidizing property of Cr(VI) and reducing property of functional groups in soya structure, Cr(VI) was converted to Cr(III), which has little or no toxicity.
2. Considering the adsorptive property of soya particles, the mixture of Cr(VI) and Cr(III) species was isolated from solution by adsorption.

In this study the effect of added salts such as LiCl and KCl to the solution was also studied.

The equation used to calculate efficiency was

$$E(\%) = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

where C_0 and C_e are the initial and equilibrium concentrations of Cr in solution (mg/l Cr), respectively.

It must be noted that the term "treatment" is equal to {[adsorption of Cr(VI) + Cr(III)] + [reduction of Cr(VI) to Cr(III)]} and the term "adsorption" is equal to {adsorption of Cr(VI) + Cr(III)}.

2. Experimental methods and materials

A solution of $K_2Cr_2O_7$ of a known concentration and pH was prepared. A specific mass of ground soya cake (150–300 μm) was added. The mixture was agitated for 1 min and allowed to settle for a specific time at a specific temperature. The mixture was then filtered through black ribbon filter paper. In acidic condition, the yellow color of the $K_2Cr_2O_7$ solution changed to green when Cr(III) was produced. A 1 ml aliquot of filtered solution, was diluted to 50 ml using double distilled water and pH adjusted to 1.0 ± 0.3 using NaOH [5, 0.1 M] and H_2SO_4 [5, 0.1 M]. A 1,5-diphenyl carbazide solution (1 ml) was added to the diluted solution and agitated. After 8 min, the absorbency of the purple color in the solution was measured spectrophotometrically at 540 nm in a 1 cm long glass cell. The

Table 1
Experimental conditions for studying the soya effect on treatment and adsorption of chromium solutions

No.	Aim	Experimental Conditions
Table 2	Calculation of Langmuir isotherm constants	$T = 25\,°C$, $t = 15$ h, $V = 0.1$ l, pH = 8
Table 3	Calculation of Freundlich isotherm constants	$T = 25\,°C$, $t = 15$ h, $V = 0.1$ l, pH = 8
Fig. 1	Study of pH effect on treatment of chromium	$C_0 = 489$ mg/l Cr, $M = 1000$ mg, $T = 30\,°C$, $t = 15$ h, $V = 0.075$ l
Fig. 2	Study of pH effect on adsorption of chromium	$C_0 = 49.18$ mg/l Cr, $M = 1000$ mg, $T = 25\,°C$. $t = 18$ h, $V = 0.075$ l
Fig. 3a	Study of Time effect on treatment of chromium	$C_0 = 44.05$ mg/l Cr, $M = 1000$ mg, $T = 25\,°C$, $V = 0.075$ l, pH = 1
Fig. 3b	Study of time effect on treatment of chromium	$C_0 = 44.05$ mg/l Cr, $M = 1000$ mg, $T = 30\,°C$, $V = 0.075$ l, pH = 1
Fig. 4	Study of time effect on adsorption of chromium	$C_0 = 49.24$ mg/l Cr, $M = 5000$ mg, $T = 25\,°C$, $V = 0.075$ l, pH = 8
Fig. 5	Study of temperature effect on treatment of chromium	$C_0 = 48.62$ mg/l Cr, $M = 1000$ mg, $V = 0.075$ l, $t = 5$ h, pH = 1
Fig. 6	Study of temperature effect on adsorption of chromium	$C_0 = 49.16$ mg/l Cr, $M = 5000$ mg, $V = 0.1$ l, $t = 20$ h, pH = 8
Fig. 7	Study of soya mass effect on treatment of chromium	$C_0 = 48.62$ mg/l Cr, $T = 25\,°C$, $t = 5$ h, $V = 0.075$ l, pH = 1
Fig. 8	Study of soya mass effect on adsorption of chromium	$C_0 = 49.10$ mg/l Cr, $T = 25\,°C$, $t = 15$ h, $V = 0.1$ l, pH = 8
Fig. 9	Study of the effect of various concentrations of KCl and LiCl on adsorption of chromium	$C_0 = 49.16$ mg/l Cr, $T = 25\,°C$, $t = 20$ h, $V = 0.075$ l, pH = 8, $M = 5000$ mg

concentration of free Cr(VI) in diluted solution was obtained using calibration curves as described by Clesceri et al. [6].

For determination of the quantity of total free dissolved chromium (uncomplexed Cr(VI) and Cr(III)), the Cr(III) in the solution was converted to Cr(VI) using $KMnO_4$ [6], pH being adjusted and 1,5-diphenyl carbazide added to the solution to react with Cr(VI). A purple color was developed with its absorbency was being measured using spectrophotometer.

When the concentration of the total dissolved chromium (complexed and uncomplexed Cr(VI) and Cr(III)) was measured, the sample was treated by ashing [7] and then with $KMnO_4$ [6] before pH adjustment. Ashing was used for digestion of organic ligands which complex dissolved chromium.

Different calibration curves were required for each of the three cases mentioned above because, for each calibration curve, conditions of standard solutions must be adjusted to mirror those of the experimental methods.

The experimental conditions are shown in Table 1.

3. Results and discussion

3.1. Effect of pH

Experimental results indicate that when the pH decreased the treatment efficiency of chromium (adsorption of chromium+reduction of Cr(VI) to Cr(III)) by soya cake increased.

This treatment is mainly due to the reduction of Cr(VI) to Cr(III) by the soya according to following equation, which is enhanced at low PHS (pH < 1). The results are shown in Fig. 1.

$$Cr_2O_7{}^{2-} + 6e^- + 14H^+ \Leftrightarrow 2Cr^{3+} + 7H_2O$$

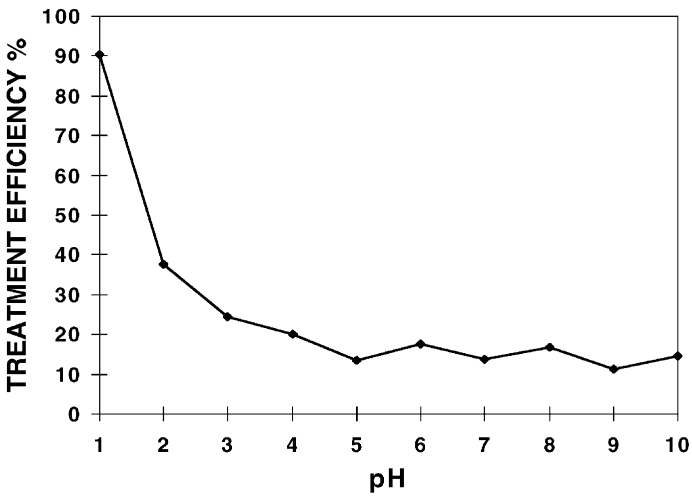

Fig. 1. Treatment efficiency of soya cake on chromium solutions vs. pH.

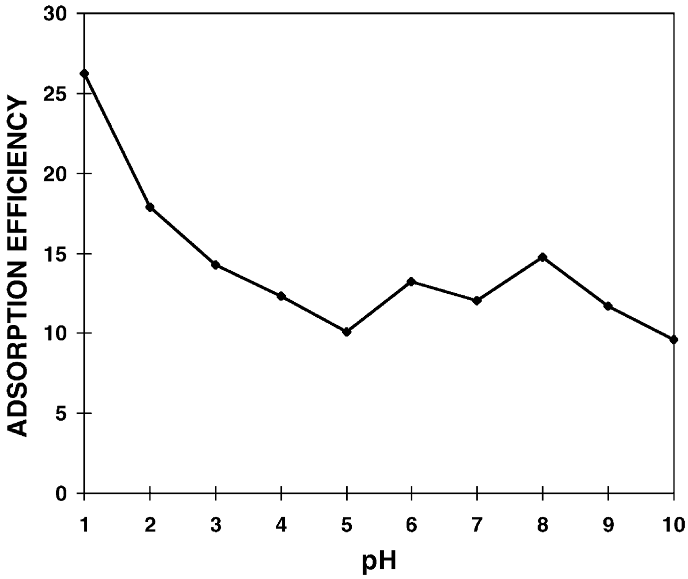

Fig. 2. Adsorption efficiency of soya cake on chromium solutions vs. pH.

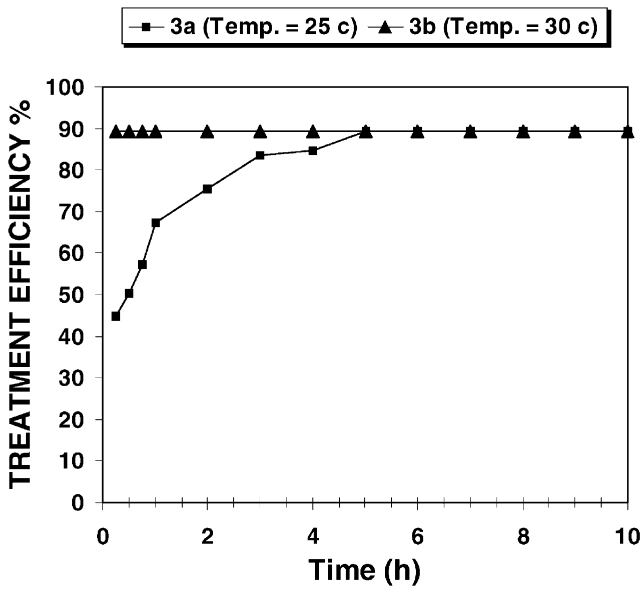

Fig. 3. Treatment efficiency of soya cake on chromium solutions vs. time.

It has also been shown that the adsorption efficiency of chromium by soya cake was inversely proportional to pH (Fig. 2). This affect is due to neutralization of the negatively charged carboxilate anions in the soya structure by H^+ ions and consequently the repulsion between $Cr_2O_7^{2-}$ and surface active sites decreases. The other reason is the reduction of Cr(VI) to Cr(III) and their chelation which causes decreasing of the repulsion between chelated Cr(III) and active sites such as $-NH_3^+$ groups in soya cake structure.

3.2. Study of reaction rate

The best time obtained for treatment process of chromium at pH = 1 and $T = 25\,^{\circ}C$ was 5 h. At the same pH and at $T = 30\,^{\circ}C$, the rate was reduced to 15 min (Fig. 3a and b). The rate of reaction increased with increasing temperature. This affect can accounted for an increase in the reduction–oxidation reaction rate between $Cr_2O_7^{2-}$ and functional groups of the soya cake structure. Therefore, at low temperatures, because of low total rate of interactions, the treatment efficiency was low at short treatment times(comparison of Fig. 3a and b).

The best reaction period for the adsorption of chromium at pH = 8 and $T = 25\,^{\circ}C$ was 1 h (Fig. 4).

3.3. Effect of temperature

According to Fig. 5, the treatment efficiency of chromium using soya cake, increased as the temperature increased. In the previous section, this affect has been explained. The optimum temperature for the adsorption of chromium by soya cake was found to be 20 °C (Fig. 6). At lower temperatures, the kinetic energy of $Cr_2O_7^{2-}$ anions is low. Therefore, contact between $Cr_2O_7^{2-}$ and active sites in the soya structure is insufficient leading to a

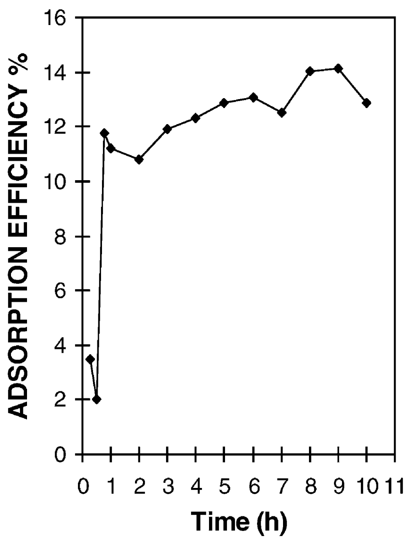

Fig. 4. Adsorption efficiency of soya cake on chromium solutions vs. time.

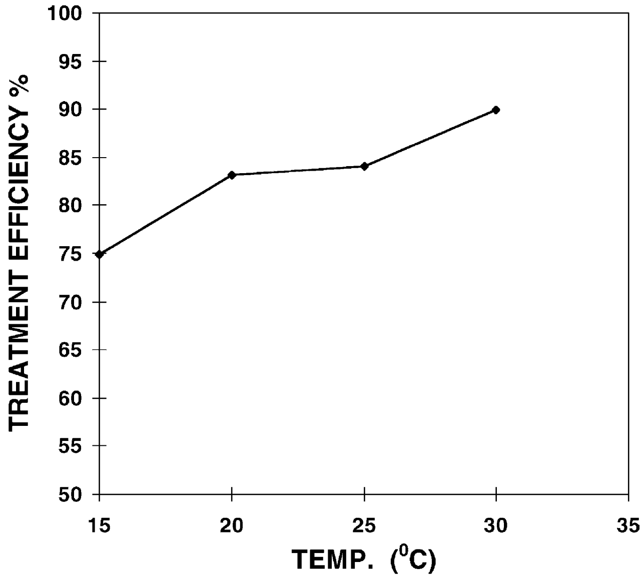

Fig. 5. Treatment efficiency of soya cake on chromium solutions vs. temperature.

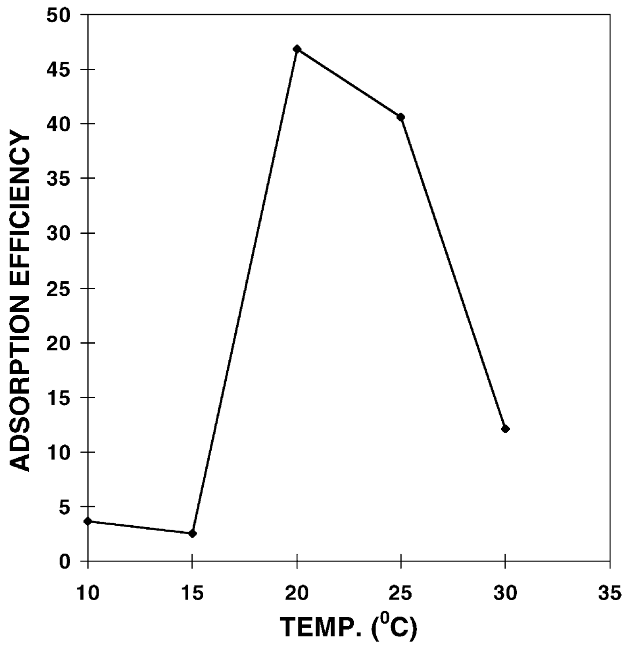

Fig. 6. Adsorption efficiency of soya cake on chromium solutions vs. temperature.

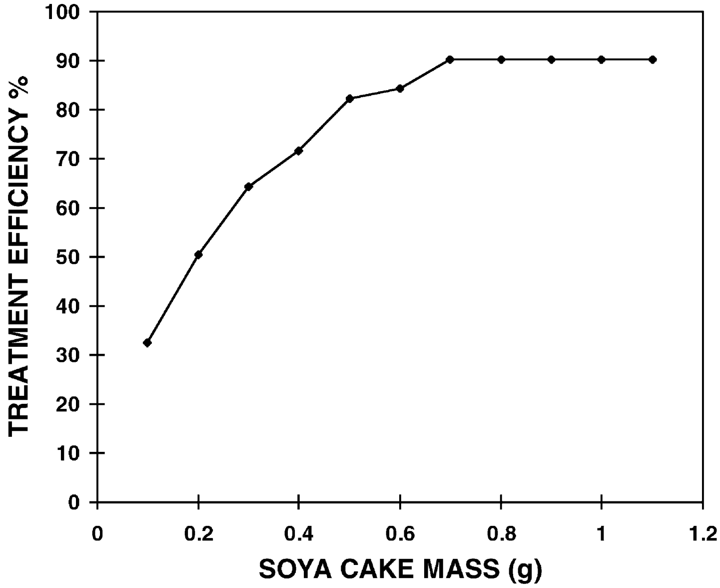

Fig. 7. Treatment efficiency of soya cake on chromium solutions vs. soya mass.

decrease in adsorption efficiency. At higher temperatures, the kinetic energy of $Cr_2O_7^{2-}$ anions is higher than attraction potential between $Cr_2O_7^{2-}$ and active sites in the soya cake structure. This condition causes decrease in adsorption efficiency, showing that adsorption is more of a physical than a chemical property.

3.4. Effect of soya cake mass

The optimum soya cake mass for the treatment of chromium was found to be 0.7g/75 ml of experimental solution (Fig. 7). In this case, soya mainly acts as a reductive agent that reduces Cr(VI) to Cr(III) and this of amount (0.7 g) is enough to this reaction.

However, the optimum soya cake mass for the adsorption of chromium increased to 30 g (Fig. 8). The mechanism for adsorption is different from the treatment because, amount of soya used by each of these two methods is very different.

In adsorption experiments, because of water sorption by soya cake and formation a paste, the use of soya cake with quantities >30 g was impossible. This result is due to difficulties in the separation of solution from the paste.

The maximum adsorptive capacity of soya was obtained to be $Q = 2.8 \times 10^{-4}$ mg/mg.

3.5. The effect of various concentrations of KCI and LiCl on adsorption of chromium by soya cake

Fig. 9 shows that by increasing the LiCl concentration, the efficiency of adsorption of chromium was increased. However, in the case of KCl, this effect was not observed. This

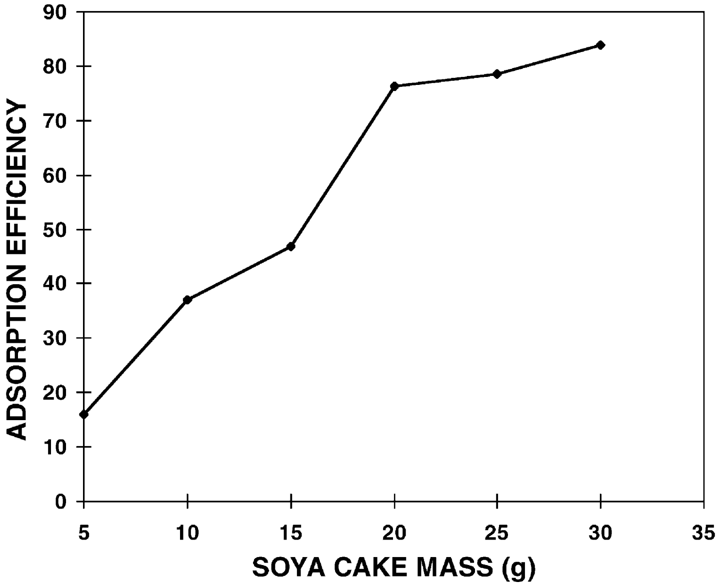

Fig. 8. Adsorption efficiency of soya cake on chromium solutions vs. soya mass.

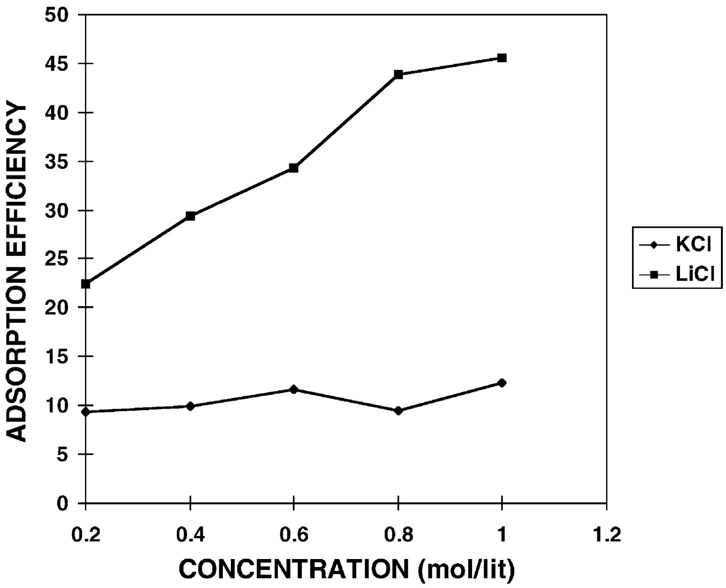

Fig. 9. Adsorption efficiency of soya cake on chromium solutions vs. Li^+ and K^+ concentration.

result is because of the high positive charge density on Li^+ cations, which causes neutralization of carboxilate anions in soya cake structure and consequently decreases repulsion between $Cr_2O_7{}^{2-}$ and soya cake structure. With the use of KCl, because of low positive charge density on K^+ cations, such an effect was not observed.

3.6. Calculation of langmuir isotherm constants

Langmuir isotherm is expressed as

$$\theta = \frac{q_e}{Q} = \frac{bC_e}{1 + bC_e} \tag{2}$$

where

$$q_e = (C_0 - C_e)\frac{V}{M} \tag{3}$$

where θ is percent of sites which are occupied, q_e the milligrams of adsorbed material per milligram of adsorbent, Q the maximum milligrams of adsorbed material per milligram of adsorbent (constant), b the constant of Langmuir isotherm, V the volume of solution (l), M the mass of soya cake (mg).

Inverting Eq. (2) we obtain

$$\frac{Q}{q_e} = \frac{1 + bC_e}{bC_e} \tag{4}$$

then

$$\frac{1}{q_e} = \frac{1}{Qb}\frac{1}{C_e} + \frac{1}{Q} \tag{5}$$

By plotting $1/q_e$ against $1/C_e$ using experimental data, a straight line is obtained (Table 2).

Using the slope and the intercept of this line, b and Q were found to be

$$Q = 2.8 \times 10^{-4}, \qquad b = 0.623$$

Assuming $C_0 = 50$ mg/l Cr, $R_L = 0.03$ was calculated from the relation

$$R_L = \frac{1}{1 + bC_0} \tag{6}$$

Since the obtained value R_L is in the range of zero and one, the adsorption is favorable [8].

Table 2
Data for calculation of Langmuir isotherm constants from experiments on effect of soya cake mass on chromium adsorption in aqueous solutions (initial data for calculations can be extracted from this table and Fig. 8)

C_e (mg/l Cr)	q_e (mg/mg)	$1/C_e$	$1/q_e$
34.25	0.0003	0.029	3367
21.97	0.00027	0.046	3685.96
14.89	0.00023	0.067	4384.68
5.25	0.00022	0.191	4561
3.27	0.00018	0.31	5454.94
1.97	0.00016	0.51	6365.37

Table 3
Data for calculation of Freundlich isotherm constants from experiments on effect of soya cake mass on chromium adsorption in aqueous solutions (initial data for calculations can be extracted from this table and Fig. 8)

C_e (mg/l Cr)	q_e (mg/mg)	Log C_e	Log q_e
34.25	0.0003	1.53	−3.53
21.97	0.00027	1.34	−3.57
14.89	0.00023	1.17	−3.64
5.25	0.00022	0.72	−3.66
3.27	0.00018	0.52	−3.74
1.97	0.00016	0.29	−3.80

3.7. *Calculation of freundlich isotherm constants*

The Freundlich isotherm is expressed as

$$q_e = K_f C_e^{1/n} \quad (7)$$

where K_f and n are constants of Freundlich isotherm.

Taking logarithm from Eq. (7) one drives the following

$$\log q_e = \log K_f + \left(\frac{1}{n}\right) \log C_e \quad (8)$$

By plotting $\log q_e$ against $\log C_e$ using our experimental data, a straight line is obtained (Table 3).

Using the slope and the intercept of this line, n and K_f were found to be $1/n = 0.20$ and $K_f = 1.4 \times 10^{-4}$.

Since $n > 1$, the adsorption is favorable [8].

Comparison of Langmuir and Freundlich isotherms constants with literature data (Table 4) [9–12] shows that soybean is not a strong adsorbent for chromium, therefore, it must be used for treatment of wastewaters with low chromium quantities.

Table 4
Comparison of Langmuir and Freundlich constants derived from literature for chitosan with this study of soya effect on chromium adsorption in aqueous solutions

Source	b	Q (mg/mg)	K_f	$1/n$
Findon et al. [10] (Cu)	0.02	0.059	0.00244	1.64
McKay et al. [11] (Cu)	0.03	0.288	–	–
Udaybhaskar et al. [12] (Cu)	0.62	0.0563	–	–
R. Schmuhl et al. [9] (Cu)	–	–	0.00098 ± 0.00016[a]	0.64 ± 0.08[a]
R. Schmuhl et al. [9] (Cu)	–	–	0.00012 ± 0.00010	0.98 ± 0.08
R. Schmuhl et al. [9] (Cr)	0.0037 ± 0.0003[a]	0.078 ± 0.030[a]	–	–
R. Schmuhl et al. [9] (Cr)	0.004[b]	0.050[b]	–	–
This study	0.623	0.00028	0.00014	0.20

[a] Data of non-cross-linked Chitosan.
[b] To less data point to carry out statistics.

4. Conclusions

This study shows that soya cake can assist in chromium pollution control, two ways. In the first process, the reductive functional groups in soya cake structure cause the conversion of Cr(VI) to Cr(III) according to the following reaction:

$$Cr_2O_7{}^{2-} + 6e^- + 14H^+ \Leftrightarrow 2Cr^{3+} + 7H_2O$$

In contrast to Cr(VI), the Cr(III) has little or no toxicity. This reaction had high efficiency at pH < 1. For a volume of 75 ml Cr(VI) solution with approximate concentration of 50 mg/l Cr, at pH $= 1$ and 25 °C, the best time for treatment of chromium (adsorption of chromium + reduction of Cr(VI) to Cr(III)) in contact with 1 g Soya cake was 5 h. For the same solution at pH $= 1$ and in contact with 1 g soya, if the temperature was increased from 15 to 30 °C, the treatment efficiency of chromium was increased. This result is because of increasing oxidation–reduction reaction rate by increasing in the temperature. The best soya cake mass for the same solution at pH $= 1$ and $T = 25$ °C, was 0.7 g/75 ml of experimental solution.

In the second process, using the adsorptive property of soya cake, chromium is removed from solution. This process was more efficient in acidic solutions, specially at pH $= 1$ or lower. For 100 ml of solution with approximate concentration of 50 mg/l Cr at pH $= 8$ and 25 °C, the adsorption efficiency was increased with increasing in soya cake mass up to 30 g. For the same solution, in contact with 5 g soya cake, the optimum temperature was 20 °C. For 75 ml of this solution in contact with 5 g soya cake, the optimum time, was 1 h. Dissolution of LiCl in the solutions, increased the efficiency of adsorption, however, this effect was not observed in the case of KCl.

The adsorbed chromium species can be recovered by burning the used soya cake.

Finally, Langmuir and Freundlich isotherm constants were determined from experimental data. Langmuir isotherm constants, Q and b were found to be 2.8×10^{-4} mg/mg and 0.623, respectively. The Freundlich isotherm constants, K_f and $1/n$ were found to be 1.4×10^{-4} and 0.20, respectively. From the values $R_L = 0.03$ and $n = 4.99$, we conclude that the adsorption is favorable but soybean is not a very strong adsorbent for chromium and must be used in low quantities of wastewater or in low pollutions.

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