

## Effect of Modified Eggshell on Adsorption Capacity of Chromium(VI) from Aqueous Solution

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The aim of this work is to investigate the use of eggshell for adsorption of Cr(VI) from aqueous solution and the effect of thermal treatment as well as coating with Fe<sub>2</sub>O<sub>3</sub> of eggshell on the extraction percent of Cr(VI). The XRD, FTIR and SEM techniques proved that the eggshell mainly composed of calcite rhombohedral structure in addition to a trace of quartz silica residual protein fibers. Heating at 550 °C does not decompose eggshell but decomposes the residual protein. The effect of pH, weight of eggshell adsorbent, contact time, and initial concentration of Cr(VI) ions on the adsorption of Cr(VI) on eggshell sorbents were determined under static conditions by the batch equilibrium technique. The sorption kinetic as well as mechanistic isotherm parameters of Cr(VI) on the eggshell sorbent, were analyzed. It was concluded that the adsorption of Cr(VI) on eggshell increases as pH increases in the range 3-7, then, with decreases at higher pH. The extraction percent of Cr(VI) increases with an increase in the dosage of eggshell sorbents. The optimum dosage of eggshell adsorbents was found to be 5 g after which the extraction percent of Cr(VI) did not marked increase. The extraction percent of Cr(VI) by eggshell sorbents rapidly increases within 60 min followed by a slower extraction after that when maximum adsorption was reported. The adsorption capacity of Cr(VI) ions is slightly reduced in case of heated eggshell due to the change that occurs in the pore size distribution and structure of eggshell during heating. Hence, the thermal treatment and coating with Fe<sub>2</sub>O<sub>3</sub> do not affect the chemical structure of eggshell sorbents. The adsorption kinetics data were best fitted with the pseudo-second-order equation and the adsorption isotherms were best fitted with the Langmuir isotherm model.

**Keywords:** Eggshell sorbents, Adsorption, Chromium(VI), Pseudo-second-order sorption, Langmuir isotherm.

### INTRODUCTION

Chromium is one of the heavy metals and its compounds are widely applied in industrial fields such as electroplating, cement, steel, paint, dyes, aluminum, leather tanning, metal finishing and chromate manufacturing industries [1]. Chromium compounds in nature include trivalent Cr(III) and hexavalent chromium Cr(VI). The toxicity of Cr(VI) species is 100 times more than Cr(III) species. Several Cr(VI) compounds act as carcinogens, mutagens and teratogens in biological systems [2]. Various treatment technologies such as chemical precipitation [3], ion-exchange [4], membrane filtration [5], electrocoagulation [6], infiltration percolation [7] and phytoremediation [8] have been reported for the removal of Cr(VI) from water or wastewaters.

Adsorption is considered to be the simplest, most cost-effective, easy and eco-friendly method to handle a large volume of wastewater with a low concentration of Cr(VI) [9]. Numerous

sorbents for Cr(VI) removal from wastewater have been developed, such as activated carbon [10], activated alumina [11], biosorbents [12], modified resins [13], and metal oxides [14]. Most of these sorbents have very low chromium adsorption capacity and slow process dynamics or expensive such as threonine doped polypyrrole [15] and glycine doped polypyrrole nanocomposite [16]. Accordingly, great efforts have been done to develop novel effective low-cost sorbents for the removal of Cr(VI) from water [17]. Carbonate-based sorbents such as dolomite [18], eggshell [19] and nano carbonate-hydroxyl-apatite [20] have high removal capacities towards Cr(VI) via exchange reaction of Cr(VI) ions with the calcium carbonate. Eggshell is a biomass waste rich in calcite (CaCO<sub>3</sub>) and a small amount of organic matter (protein fibers) [21]. Numerous studies have examined the eggshell for removal of Cr(VI) [19,21-28] and Cr(III) [29,30], Cd(II) [31], Cu(II) [32,33], Pb(II) [34], Zn(II) [35,36], Al(III) [37], Fe(III) [38], Ag(I) [39] and phosphorus [40]. This work aims to investigate the use of eggshell

for adsorption of Cr(VI) from aqueous solution and the effect of thermal treatment as well as coating with Fe<sub>2</sub>O<sub>3</sub> of eggshell on the extraction percent of Cr(VI).

### EXPERIMENTAL

All chemical reagents, *viz.* K<sub>2</sub>CrO<sub>4</sub>, diphenylcarbazide, conc. HCl, NaOH, and conc. H<sub>2</sub>SO<sub>4</sub> (98%) used in this work were of analytical grade and purchased from E. Merck, Germany. Distilled water was used throughout the experimental work. Chicken eggshells were obtained from the local food market. Eggshells were washed with water several times to get rid of egg albumin then it has been mixed with water and ground with a kitchen mixer to separate the eggshell membrane, which is decanted after washing with water several times. The produced eggshells had been dried in the dryer at 105 °C overnight. Eggshells then had been ground in the kitchen mill for 10 min and sieved using a 250 μm sieve. The heated eggshell (T) was prepared by heating eggshell in a muffle furnace at 550 °C for 2 h and left to cool down to the room temperature in the furnace. The Fe<sub>2</sub>O<sub>3</sub>-coated eggshell was prepared by dispersing 100 g of eggshell in 500 mL of distilled water in presence of 2.5 mL of methyl methacrylate, heated to 50 °C and stirred at 1000 rpm by a magnetic stirrer with a heater for 1 h. During this period, conc. NH<sub>3</sub> solution (30%) was added to maintain a pH 10, and a 5.1 g Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O dissolved in 50 mL of distilled water was added slowly. The brown product was filtered and washed with distilled water, dried at 105 °C overnight, heated at 500 °C for 2 h in a muffle furnace and left to cool down to room temperature in the furnace [41]. The untreated, heated and coated eggshell adsorbents were denoted as E, T and H, respectively.

The eggshell sorbents were analyzed by FTIR, XRD, and SEM techniques. A calibrated pH meter (model pH 212 micro-processor pH meter, HANNA Instruments) was used for all pH measurements. The XRD analysis was carried out by a Philips X-ray diffractometer PW 1370, Co. with Ni-filtered CuKα radiation (1.5406 Å). SEM analysis was investigated by a Jeol-Dsm 5400 LG apparatus. FTIR was carried out by an FTIR model 410 JASCO. The percentage of extraction of Cr(VI) using eggshell sorbents were determined in triplicate under static conditions by batch equilibrium technique. The effect of pH on the Cr(VI) extraction was determined by adding 0.5 g of sorbent to a 50 mL of 20 mg/L Cr(VI) solution at pH range 3-11 in a 100 mL measuring flask. For pH adjustment, solutions of 0.1M HCl and 0.1M NaOH were used. The mixture was mechanically shaken for 120 min at room temperature to attain equilibrium. The sorbent was separated by filtration and washed with distilled water; the unretained metal ion in filtrate was determined by the diphenylcarbazide spectrophotometric method. The effect of weight of sorbent (0.5-4.0 g), contact time (15-180 min) and Cr(VI) concentration (10-30 mg/L) on Cr(VI) extraction were also systematically determined at the pH of the highest Cr(VI) extraction.

The sorption kinetic data of Cr(VI) on eggshell sorbents were analyzed in terms of the pseudo-first-order and pseudo-second-order sorption equations. The mechanistic parameters associated with Cr(VI) sorption on eggshell sorbents were deter-

mined by analyzing the results obtained by the adsorption experiments by the adsorption isotherm models given by Freundlich and Langmuir. The kinetic data as well as the mechanistic parameters, will best fit the appropriate sorption kinetic equation and adsorption isotherm model which has a higher correlation coefficient value.

### RESULTS AND DISCUSSION

**Characterization of eggshell sorbents:** Fig. 1 illustrates the X-rays diffraction patterns of eggshell sorbents. The XRD peaks located at 2θ values of 23.2°, 29.4°, 36.0°, 39.4°, 43.2°, 47.4° and 48.5° were attributed to calcite rhombohedral structure (JCPDS 88-1808) [42]. The absence of the characteristic peaks of CaO phase in case of heated eggshell prove that heating at 550 °C does not decompose eggshell because eggshell start decomposing at 650 °C and completed its decomposition at 800 °C [43]. Fig. 2 illustrates the FTIR spectra of eggshell sorbents. The bands at 1464, 882 and 716 cm<sup>-1</sup> are correspond to the stretching vibration of the C-O bonds. The bands at 2988, 2895 and 2530 cm<sup>-1</sup> are correspond to the bending vibration of this bond. The band at 1811 cm<sup>-1</sup> is also related to the carbonate C=O bond. The band at 1109 cm<sup>-1</sup> is related to a trace of quartz silica (SiO<sub>2</sub>) [44-46]. The broad absorption bands that appear around 3475 cm<sup>-1</sup> correspond to the stretching vibration

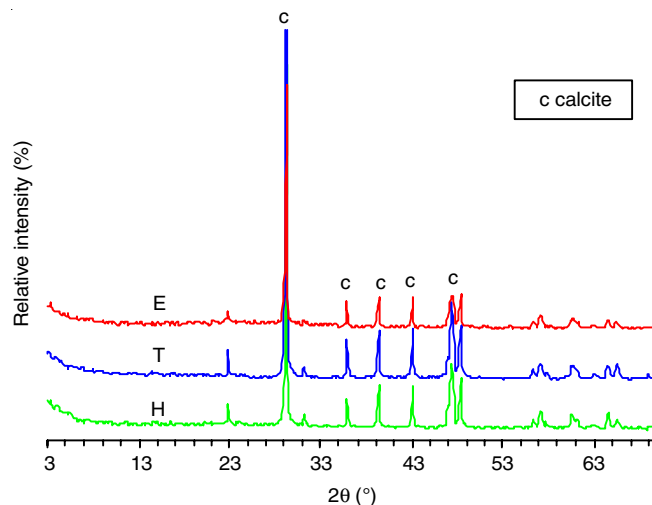


Fig. 1. XRD patterns of eggshell sorbents

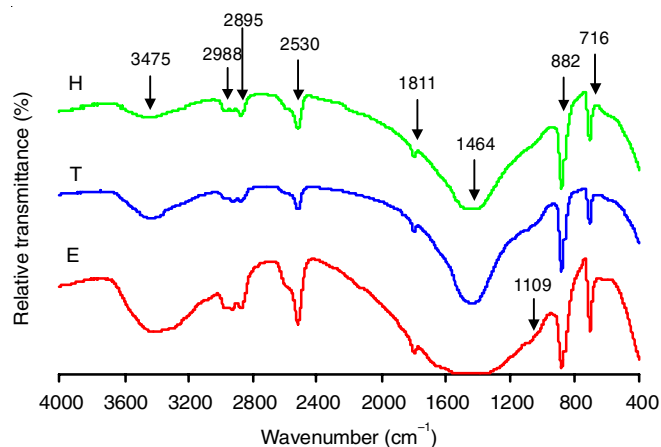


Fig. 2. FTIR spectra of eggshell sorbents

of N-H groups of the residual protein fibers. The band intensity diminishes with heating eggshell due to the denaturation of protein [30]. The XRD and FTIR techniques did not detect the existence of any phases that could arise from coating eggshell sorbent with hematite due to the detection limits. The conventional XRD and FTIR cannot detect phases that make up less than about 5% of sample size [47,48].

**SEM analysis:** Fig. 3 illustrates the SEM photographs of eggshell sorbents. The presence of holes on the surface of thermally treated eggshell may be attributed to the possible surface pyrolysis of calcium carbonate occurred with degassed  $\text{CO}_2$  at  $550^\circ\text{C}$  [49]. The presence of filled holes on the surface of  $\text{Fe}_2\text{O}_3$  coated eggshell may be attributed to the  $\text{Fe}_2\text{O}_3$  coating that fills some of the holes, which progress during the preparation of the coated eggshell adsorbent. The observed surface heterogeneity of the eggshell sorbents may provide a large surface area for adsorption of heavy metal cations.

**Effect of adsorption parameters:** Fig. 4a illustrates the effect of pH on the extraction of Cr(VI) by 0.5 g of eggshell sorbents at 120 min and 20 mg/L of Cr(VI). The optimum pH for maximum extraction of Cr(VI) by eggshell sorbents was in the range 6-8. The dependence of Cr(VI) adsorption on the pH is attributed both to the surface charge of eggshell sorbents as well as the solution chemistry of Cr(VI) in an aqueous phase. The chemistry of chromium ions depends on the pH value. The hydrogen chromate ion ( $\text{HCrO}_4^-$ ) is the dominant species in the pH range of 1-6 and chromate ion ( $\text{CrO}_4^{2-}$ ) is dominant above pH 6 [50]. At the same time, the surface charge of the eggshell (calcium carbonate) decreases with increasing the pH [51]. Accordingly, eggshell may have different affinity for adsorption of these different chromium species at different pH values. Hence, adsorption of Cr(VI) on eggshell increases as pH increases in the range 3-7 due to the electrostatic attraction between the growing positive surface charge of eggshell and the ( $\text{HCrO}_4^-$ )

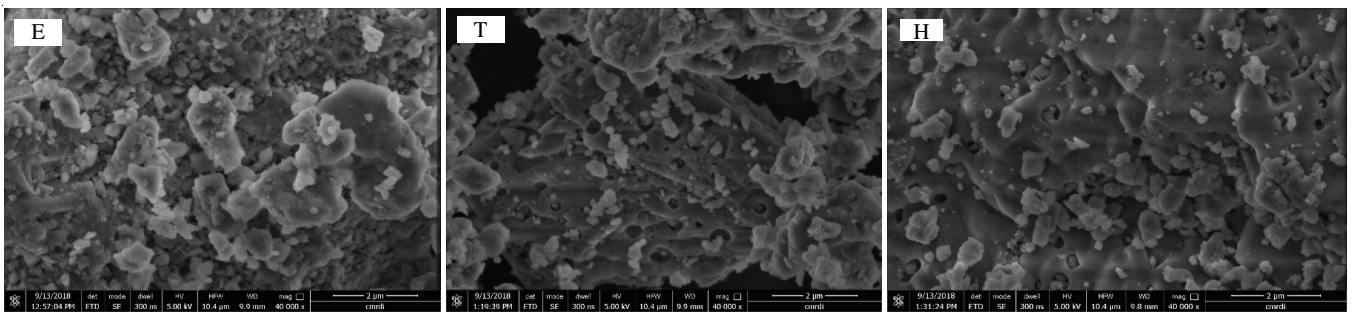


Fig. 3. SEM micrographs of eggshell sorbents

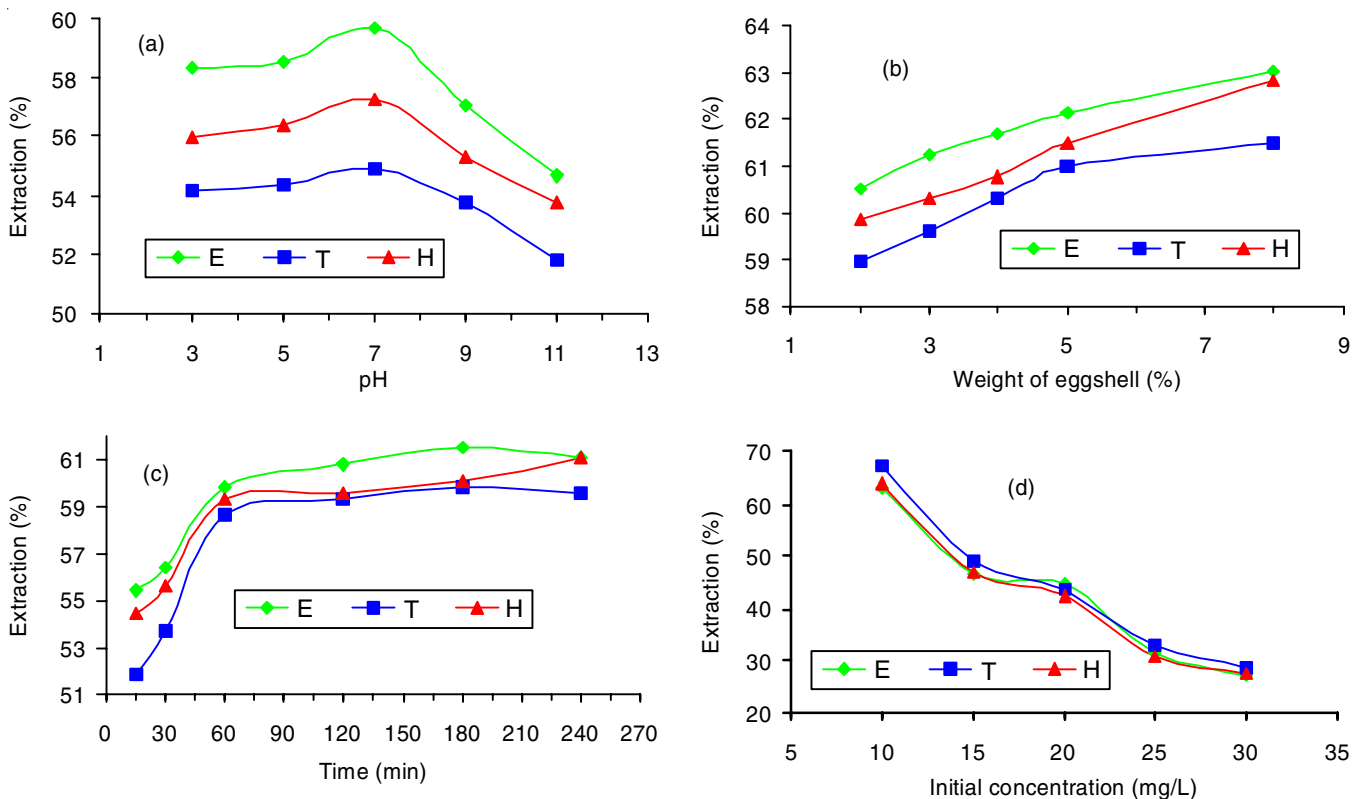


Fig. 4. Effect of various parameters (a) pH, (b) weight of eggshell, (c) contact time and (d) initial concentration of Cr(VI) on the adsorption capacity of the eggshell sorbents

ion. Then, with decreasing of the positive surface charge of the eggshell with the increase of pH and also due to the competition of  $\text{OH}^-$  and  $\text{HCO}_3^-$  ions which are predominant species in  $\text{pH} > 7$  ions, the adsorption affinity of eggshell to chromate ion  $\text{CrO}_4^{2-}$  decrease [52,53]. Fig. 4b illustrates the effect of weight of eggshell on the extraction of Cr(VI) at 120 min, pH 7 and 20 mg/l of Cr(VI). The extraction percent of Cr(VI) increases with an increase in the dosage of the eggshell sorbents. This is due to the reason as the amount in grams of sorbent is increased the total surface area available for the adsorption of Cr(VI) increases [29]. The optimum dosage of eggshell adsorbents was found to be 5 g after which the extraction percent of Cr(VI) does not markedly increase due to the screen effect between the sorbent particles [54].

Fig. 4c illustrates the effect of contact time on the extraction of Cr(VI) by 2 g of eggshell sorbents at pH 7 and 20 mg/L of Cr(VI). The extraction percent of Cr(VI) by eggshell sorbents rapidly increases within 60 min followed by a slower extraction after that when maximum adsorption was reported. The faster adsorption of Cr(VI) is attributed to a large number of vacant binding sites at the start. As the adsorption process progress, the eggshell surfaces are highly saturated with the adsorbed Cr(VI) ions, forcing Cr(VI) ions to diffuse into the inner part of eggshell surface which reduces the rate of adsorption [54]. As a result, the affinity of eggshell adsorbents towards Cr(VI) ions diminishes as the distribution of Cr(VI) ions on the eggshell surface adsorbing sites reaches equilibrium [55]. Fig. 4d illustrates the effect of initial concentration on the extraction of Cr(VI) at 60 min by 2 g of eggshell sorbents at pH 7. The extraction percent first increases with increasing the initial concentration then decreases. The higher is the initial concentration of Cr(VI) ions, the greater the driving force to overcome the mass transfer resistance through the bulk solution [56]. Thus, extraction percent first increases. Then as most of the adsorption sites on the eggshell sorbents are occupied, with further increase in the concentration of Cr(VI) ions, the extraction becomes slower [57]. The adsorption capacity of Cr(VI) ions is slightly reduced in case of the heated eggshell may be due to the change that occurs in the pore size distribution and structure of eggshell during heating [58]. Also, the adsorption capacity of Cr(VI) ions is slightly reduced in case of the hematite coated eggshell. This indicates that coating of eggshell with magnetite ( $\text{Fe}_3\text{O}_4$ ) rather than hematite ( $\text{Fe}_2\text{O}_3$ ) could improve the removal ability of Cr(VI) ions due to release of  $\text{Fe}^{2+}$  ions, which reduce Cr(VI) ions to Cr(III) ions followed by the co-precipitation of Cr(III) and Fe(III) hydroxides [59,60].

**Adsorption kinetics:** The sorption kinetic data of Cr(VI) measured on eggshell sorbents were analyzed in terms of pseudo-

first-order and pseudo-second-order sorption equations. The pseudo-first-order equation assumes that the rate of change of adsorption with time is proportional to the difference in equilibrium biosorption capacity and the adsorbed amount [61]. The equation is expressed as follows:

$$\log(q_e - q_t) = \log q_e - \left( \frac{k_1}{2.303} \right) t \quad (1)$$

where  $k_1$  ( $\text{min}^{-1}$ ) is the rate constant of the pseudo-first-order sorption,  $q_t$  ( $\text{mmol g}^{-1}$ ) denotes the amount of sorption at time  $t$  (min), and  $q_e$  ( $\text{mmol g}^{-1}$ ) is the amount of sorption at equilibrium.  $k_1$  and  $q_e$  were calculated from the slope and intercepts of the plot of  $\log(q_e - q_t)$  against  $t$ .

The pseudo-second-order equation assumes that the rate-limiting step involves chemisorption [62]. The equation is expressed as:

$$\frac{t}{q_t} = \frac{1}{v_o} + \left( \frac{1}{q_e} \right) t \quad (2)$$

where  $v_o$  is the initial sorption rate ( $\text{mmol g}^{-1} \text{min}^{-1}$ );  $v_o$  and  $q_e$  were calculated from the intercept and slope of plot  $t/q_t$  vs.  $t$ .

Figs. 5 and 6 illustrate the pseudo-first and second order kinetic plots for the sorption of Cr(VI) on eggshell sorbents [plot of  $\log(q_e - q_t)$  against  $t$ ] and [plot of  $t/q_t$  against  $t$ ], respectively. Table-1 represents the parameters of the first order and second order kinetic constants for sorption of Cr(VI) on eggshell sorbents at room temperature. The correlation coefficients  $r^2$  both for the pseudo-first-order sorption equations showed that the adsorption kinetics data were best fitted with the pseudo-second-order equation that gives the higher  $r^2$  values. This proves that the surface of eggshell sorbents were not homogenous and suggested that rate-limiting step in the sorption of Cr(VI) on eggshell sorbents involves chemisorption [63].

**Adsorption isotherms:** To find out the mechanistic parameters associated with Cr(VI) on eggshell sorbents at room temperature, the results obtained by the effect of initial Cr(VI) concentration were analyzed by the adsorption isotherm models given by Freundlich and Langmuir. The sorption isotherms for binding of Cr(VI) to eggshell were determined by the batch technique at pH 7 at the concentration of 1-3 mg/L and shaken for 60 min with a constant weight 2.0 g of eggshell sorbents.

The linear form of Freundlich model, which describe the adsorption characteristics for the heterogeneous surface [64] can be expressed as follows:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (3)$$

TABLE-1  
PARAMETERS OF THE FIRST ORDER AND SECOND ORDER KINETIC CONSTANTS  
FOR BINDING OF Cr(VI) USING EGGSHELL AT ROOM TEMPERATURE

	Pseudo-first-order constants			Pseudo-second-order constants		
	$k_1$	$q_e$	$R^2$	$v_o$	$q_e$	$r^2$
E	-0.00216482	0.014592	0.7923	0.058806	0.236681	0.9997
T	-0.0158907	0.0044055	0.7938	0.042557	0.227894	0.9996
H	-0.0195755	0.021984	0.7934	0.044841	0.235671	0.9996

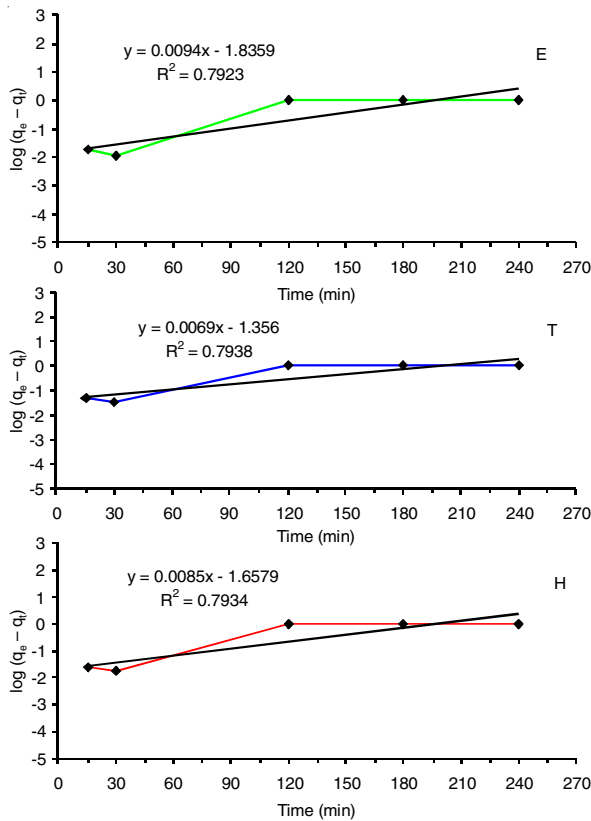


Fig. 5. Plot of  $\log(q_e - q_i)$  against t

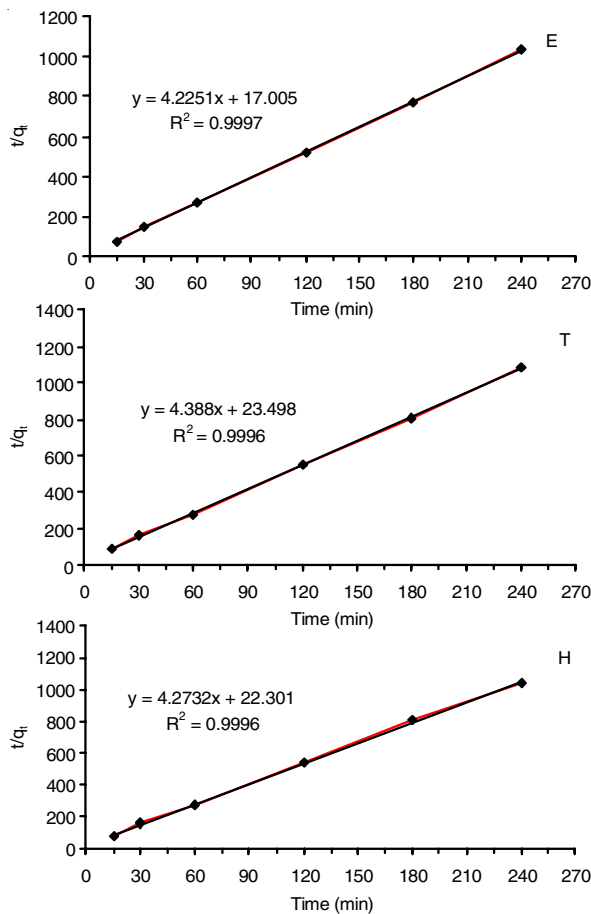


Fig. 6. Plot of  $t/q_i$  against t

where  $K_f$  and  $1/n$  are Freundlich constants (indicators of sorption capacity and intensity, respectively) that can be calculated from the intercept and slope of this linear equation, respectively.

The Langmuir equation, which is valid for monolayer sorption onto a completely homogeneous surface with a finite number of identical sites and with a negligible interaction between adsorbed molecules is given by eqn. 4 [65]:

$$\frac{C_e}{q_e} = \left(\frac{1}{Q_o}\right)C_e + \left(\frac{1}{Q_o b}\right) \quad (4)$$

where  $C_e$  and  $q_e$  are the equilibrium concentrations of adsorbate in liquid and adsorbed phases in  $\text{mmol mL}^{-1}$  and  $\text{mmol g}^{-1}$ , respectively.  $Q_o$  and  $b$  are Langmuir constants and can be calculated from the intercept ( $1/Q_o b$ ) and slope ( $1/Q_o$ ) of the linear plot,  $C_e/q_e$  against  $C_e$ , respectively.

Figs. 7 and 8 illustrate the plots of Freundlich and Langmuir models for the sorption of Cr(VI) on eggshell sorbents (plot of  $\log q_e$  against  $\log C_e$ ) and (plot of  $C_e/q_e$  against  $C_e$ ), respectively. Table-2 represents the parameters of the Freundlich and Langmuir isotherms constants for binding of Cr(VI) on eggshell sorbents at room temperature. The correlation coefficients  $r^2$  both for the Freundlich and Langmuir isotherms models showed that the adsorption isotherms were best fitted with the Langmuir isotherm model that gives higher  $r^2$  values.

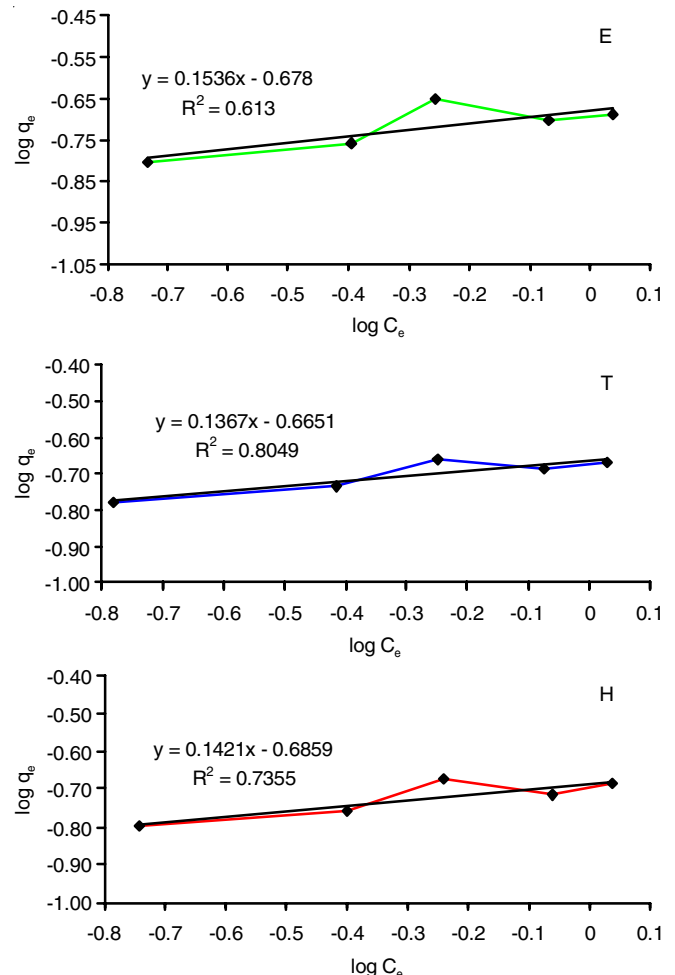


Fig. 7. Plot of  $\log q_e$  against  $\log C_e$

TABLE-2  
PARAMETERS OF FREUNDLICH AND LANGMUIR ISOTHERMS CONSTANTS  
FOR BINDING OF Cr(VI) USING EGGSHELL AT ROOM TEMPERATURE

	Freundlich isotherm constants			Langmuir isotherm constants			
	$K_f$	$1/n$	$r^2$	$Q_o$	B	$r^2$	$R_L$
E	0.20990	0.1536	0.6130	0.216039	17.13104	0.9958	0.9931
T	0.21622	0.1367	0.8049	0.224977	16.95233	0.9945	0.9935
H	0.20610	0.1421	0.7355	0.215401	15.75331	0.9901	0.9996

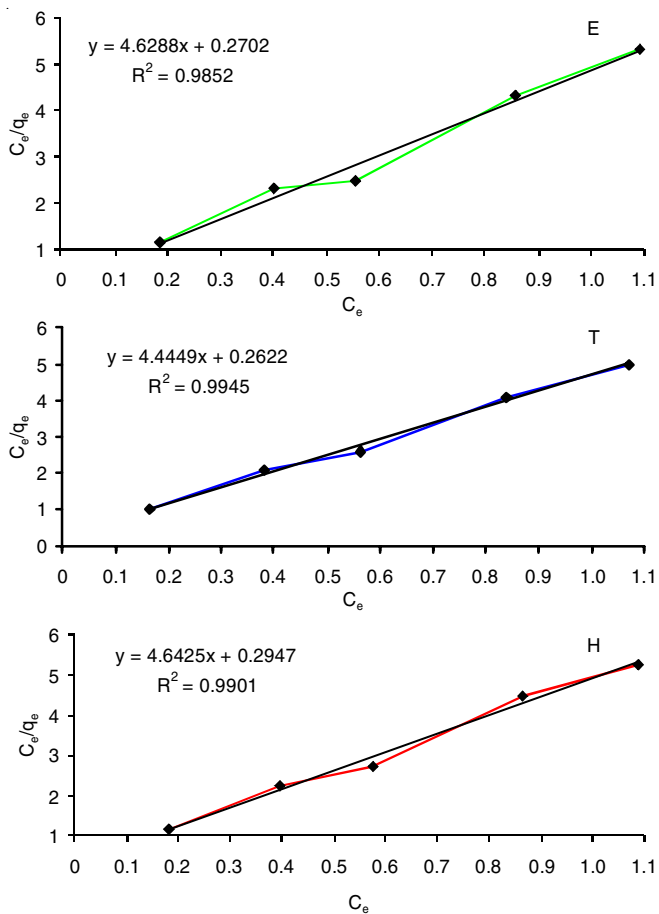


Fig. 8. Plot of  $C_e/q_e$  against  $C_e$

The essential characteristics of the Langmuir isotherm can also be expressed in terms of a dimensionless constant separation factor or equilibrium parameter ( $R_L$ ), which is defined as:

$$R_L = \frac{1}{(1 + bC_o)} \quad (5)$$

where  $b$  is the Langmuir constant (indicates the nature of sorption and the shape of isotherm accordingly) and  $C_o$  is the initial concentration of Cr(VI) ( $4 \times 10^{-4}$  M). The  $R_L$  value indicates the type of the isotherm as follows: unfavorable ( $R_L > 1$ ), linear ( $R_L = 1$ ), favourable ( $0 < R_L < 1$ ) and irreversible ( $R_L = 0$ ). The values of  $R_L$  showed that the adsorption isotherms represent the favourable type.

### Conclusions

This work investigates the effect of thermal treatment as well as coating with  $Fe_2O_3$  of eggshell on the extraction percent

of Cr(VI). The effect of pH, weight of eggshell adsorbent, contact time and initial concentration of Cr(VI) ions on the adsorption of Cr(VI) on the eggshell sorbents were determined under static conditions by the batch equilibrium technique. The sorption kinetic as well as mechanistic isotherm parameters of Cr(VI) on the eggshell sorbent were analyzed. The main conclusions are:

- The eggshell composed mainly of calcite rhombohedral structure in addition to trace of quartz silica residual protein fibers.
- Heating increased the porosity of eggshell surface due to the pyrolysis of calcium carbonate and degassing of  $CO_2$  as well as decomposes the residual protein.
- The conventional XRD and FTIR techniques did not detect the existence of any phases that could arise from coating eggshell sorbent with hematite due to the detection limits.
- The adsorption of Cr(VI) on eggshell depends on the pH, weight of eggshell adsorbent, contact time and the initial concentration of Cr(VI) ions.
- The solution chemistry of Cr(VI), the surface charge of eggshell and accordingly, the adsorption affinity of Cr(VI) on the eggshell depends on the pH. The  $OH^-$  and  $HCO_3^-$  ions in the alkaline conditions compete with chromate ion  $CrO_4^{2-}$  and reduce its adsorption affinity to eggshell.
- The adsorption of Cr(VI) on eggshell is the highest at pH 7. The optimum dosage of eggshell adsorbents was found to be 5 g. The extraction percent of Cr(VI) by eggshell sorbents rapidly reaches the equilibrium increases within 120 min.
- The adsorption kinetics data were best fitted with the pseudo-second-order equation and the adsorption isotherms were best fitted with the Langmuir isotherm model.
- From the economic point of view, the thermal treatment and coating with  $Fe_2O_3$  did not enhance the adsorption capacity of the eggshell.

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### CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

### REFERENCES

1. I.Y. El-Sherif, S. Tolani, K. Ofosu, O.A. Mohamed and A.K. Wanekaya, *J. Environ. Manage.*, **129**, 410 (2013); <https://doi.org/10.1016/j.jenvman.2013.08.004>

2. H. Javadian, *J. Ind. Eng. Chem.*, **20**, 4344 (2014); <https://doi.org/10.1016/j.jiec.2014.01.042>
3. N. Meunier, P. Drogui, C. Montane, R. Hausler, G. Mercier and J.F. Blais, *J. Hazard. Mater.*, **137**, 581 (2006); <https://doi.org/10.1016/j.jhazmat.2006.02.050>
4. S.K. Sahu, P. Meshram, B.D. Pandey, V. Kumar and T.R. Mankhand, *Hydrometallurgy*, **99**, 170 (2009); <https://doi.org/10.1016/j.hydromet.2009.08.002>
5. P. Religa, A. Kowalik and P. Gierycz, *Sep. Purif. Technol.*, **82**, 114 (2011); <https://doi.org/10.1016/j.seppur.2011.08.032>
6. A.K. Golder, A.N. Samanta and S. Ray, *Sep. Purif. Technol.*, **53**, 33 (2007); <https://doi.org/10.1016/j.seppur.2006.06.010>
7. S. Tiglyene, A. Jaouad and L. Mandi, *Environ. Technol.*, **29**, 613 (2008); <https://doi.org/10.1080/09593330801983888>
8. L. Mandi, S. Tiglyene and A. Jaouad, eds.: M. El Moujabber, L. Mandi, G. Trisorio-Liuzzi, I. Martín, A. Rabi and R. Rodríguez, Depuration of Tannery Effluent by Phytoremediation and Infiltration Percolation Under Arid Climate, In: Technological Perspectives for Rational Use of Water Resources in the Mediterranean Region, Bari CIHEAM, pp. 199-205 (2009).
9. M. Bhaumik, K. Setshedi, A. Maity and M.S. Onyango, *Sep. Purif. Technol.*, **110**, 11 (2013); <https://doi.org/10.1016/j.seppur.2013.02.037>
10. Y. Sun, Q. Yue, Y. Mao, B. Gao, Y. Gao and L. Huang, *J. Hazard. Mater.*, **265**, 191 (2014); <https://doi.org/10.1016/j.jhazmat.2013.11.057>
11. N. Sankararamakrishnan, M. Jaiswal and N. Verma, *Chem. Eng. J.*, **235**, 1 (2014); <https://doi.org/10.1016/j.cej.2013.08.070>
12. N.A. Fathy, S.T. El-Wakeel and R.R. Abd El-Latif, *J. Environ. Chem. Eng.*, **3**, 1137 (2015); <https://doi.org/10.1016/j.jece.2015.04.011>
13. M. Naushad, Z.A. AlOthman, G. Sharma and Inamuddin, *Ionics*, **21**, 1453 (2015); <https://doi.org/10.1007/s11581-014-1292-z>
14. A.A. Alqadami, M. Naushad, M.A. Abdalla, T. Ahamad, Z. Abdullah Alothman and S.M. Alshehri, *RSC Adv.*, **6**, 22679 (2016); <https://doi.org/10.1039/C5RA27525C>
15. A. Amalraj, M.K. Selvi, A. Rajeswari, E.J.S. Christy and A. Pius, *J. Water Process Eng.*, **13**, 88 (2016); <https://doi.org/10.1016/j.jwpe.2016.08.013>
16. N. Ballav, A. Maity and S.B. Mishra, *Chem. Eng. J.*, **198-199**, 536 (2012); <https://doi.org/10.1016/j.cej.2012.05.110>
17. A. Bhatnagar and M. Sillanpaa, *Chem. Eng. J.*, **157**, 277 (2010); <https://doi.org/10.1016/j.cej.2010.01.007>
18. A.B. Albadarin, C. Mangwandi, A.H. Al-Muhtaseb, G.M. Walker, S.J. Allen and M.N.M. Ahmad, *Chem. Eng. J.*, **179**, 193 (2012); <https://doi.org/10.1016/j.cej.2011.10.080>
19. A. Rajendran and C. Mansiya, *Br. J. Environ. Climate Changes*, **1**, 44 (2011).
20. W.Q. Tang, R.Y. Zeng, Y.L. Feng, X.M. Li and W. Zhen, *Chem. Eng. J.*, **223**, 340 (2013); <https://doi.org/10.1016/j.cej.2013.02.094>
21. M.J. Quina, M.A.R. Soares and R. Quinta-Ferreira, *Resour. Conserv. Recycling*, **123**, 176 (2017); <https://doi.org/10.1016/j.resconrec.2016.09.027>
22. K. Kumaraswamy, B.V. Dhananjayyulu, P. Vijetha and Y.P. Kumar, *J. Pharm. Biol. Chem. Sci.*, **6**, 529 (2015).
23. H. Daraei, A. Mittal, M. Noorisepehr and J. Mittal, *Desalination Water Treat.*, **53**, 214 (2015); <https://doi.org/10.1080/19443994.2013.837011>
24. H. Daraei, A. Mittal, J. Mittal and H. Kamali, *Desalination Water Treat.*, **52**, 1307 (2014); <https://doi.org/10.1080/19443994.2013.787374>
25. T. Ravi and S. Sundararaman, *J. Environ. Chem. Eng.*, **8**, 103877 (2020); <https://doi.org/10.1016/j.jece.2020.103877>
26. H.J. Park, S.W. Jeong, J.K. Yang, B.G. Kim and S.M. Lee, *J. Environ. Sci. (China)*, **19**, 1436 (2007); [https://doi.org/10.1016/S1001-0742\(07\)60234-4](https://doi.org/10.1016/S1001-0742(07)60234-4)
27. D. Chen, X. Xiao and K. Yang, *RSC Adv.*, **6**, 35332 (2016); <https://doi.org/10.1039/C6RA05034D>
28. C.J. Xin and N. Ngadi, *PERINTIS eJournal*, **8**, 86 (2018).
29. S. Elabbas, L. Mandi, F. Berrekhis, M.N. Pons, J.P. Leclerc and N. Ouazzani, *J. Environ. Manage.*, **166**, 589 (2016); <https://doi.org/10.1016/j.jenvman.2015.11.012>
30. K. Chojnacka, *J. Hazard. Mater.*, **121**, 167 (2005); <https://doi.org/10.1016/j.jhazmat.2005.02.004>
31. J.V. Flores-Cano, R. Leyva-Ramos, J. Mendoza-Barron, R.M. Guerrero-Coronado, A. Aragón-Piña and G.J. Labrada-Delgado, *J. Appl. Surf. Sci.*, **276**, 682 (2013); <https://doi.org/10.1016/j.apsusc.2013.03.153>
32. M. Ahmad, A.R.A. Usman, S.S. Lee, S.C. Kim, J.H. Joo, J.E. Yang and Y.S. Ok, *J. Ind. Eng. Chem.*, **18**, 198 (2012); <https://doi.org/10.1016/j.jiec.2011.11.013>
33. W. Zheng, X.M. Li, Q. Yang, G.M. Zeng, X.X. Shen, Y. Zhang and J.J. Liu, *J. Hazard. Mater.*, **147**, 534 (2007); <https://doi.org/10.1016/j.jhazmat.2007.01.048>
34. D. Liao, W. Zheng, X. Li, Q. Yang, X. Yue, L. Guo and G. Zeng, *J. Hazard. Mater.*, **177**, 126 (2010); <https://doi.org/10.1016/j.jhazmat.2009.12.005>
35. S.M. Shaheen, F.I. Eissa, K.M. Ghanem, H.M.G. El-Din and F.S. Al Anany, *J. Environ. Manage.*, **128**, 514 (2013); <https://doi.org/10.1016/j.jenvman.2013.05.061>
36. S.E. Ghazy and A.H.M. Gad, *Indian J. Chem. Technol.*, **15**, 433 (2008).
37. S.E. Ghazy and A.H.M. Gad, *Arab. J. Chem.*, **7**, 277 (2014); <https://doi.org/10.1016/j.arabjc.2010.10.031>
38. N. Yeddou and A. Bensmaili, *Desalination*, **206**, 127 (2007); <https://doi.org/10.1016/j.desal.2006.04.052>
39. M. Baláz, J. Ficeriová and J. Brianèin, *Chemosphere*, **146**, 458 (2016); <https://doi.org/10.1016/j.chemosphere.2015.12.002>
40. O. Eljamal, J. Okawauchi, K. Hiramatsu and M. Harada, *Environ. Earth Sci.*, **68**, 859 (2013); <https://doi.org/10.1007/s12665-012-1789-6>
41. A.K. Patra, A. Dutta and A. Bhaumik, *Chem. Eur. J.*, **19**, 12388 (2013); <https://doi.org/10.1002/chem.201301498>
42. T. Zaman, M. Mostari, M.A.A. Mahmood and M.S. Rahman, *Ceramica*, **64**, 236 (2018); <https://doi.org/10.1590/0366-69132018643702349>
43. F. Shen, M. Qiu, Y. Hua and X. Qi, *ChemistrySelect*, **3**, 586 (2018); <https://doi.org/10.1002/slct.201702496>
44. Z. Zhang, Y. Xie, X. Xu, H. Pan and R. Tang, *J. Cryst. Growth*, **343**, 62 (2012); <https://doi.org/10.1016/j.jcrysgro.2012.01.025>
45. Y. Wang, Y.X. Moo, C. Chen, P. Gunawan and R. Xu, *J. Colloid Interface Sci.*, **352**, 393 (2010); <https://doi.org/10.1016/j.jcis.2010.08.060>
46. P.S. Guru and S. Dash, *J. Dispers. Sci. Technol.*, **34**, 1099 (2013); <https://doi.org/10.1080/01932691.2012.737752>
47. J.A. Newman, P.D. Schmitt, S.J. Toth, F. Deng, S. Zhang and G.J. Simpson, *Anal. Chem.*, **87**, 10950 (2015); <https://doi.org/10.1021/acs.analchem.5b02758>
48. S. Kaufhold, M. Hein, R. Dohrmann and K. Ufer, *Vib. Spectrosc.*, **59**, 29 (2012); <https://doi.org/10.1016/j.vibspec.2011.12.012>
49. M. Fuji, J. Zhane, T. Takel, T. Watanabe, M. Chikazawa, T. Watanabe and K. Tanabe, *Inorg. Mater.*, **4**, 330 (1997).
50. N. Ballav, H.J. Choi, S.B. Mishra and A. Maity, *J. Ind. Eng. Chem.*, **20**, 4085 (2014); <https://doi.org/10.1016/j.jiec.2014.01.007>
51. P. Cubillas, S. Köhler, M. Prieto, C. Chairat and E. Oelkers, *Chem. Geol.*, **216**, 59 (2005); <https://doi.org/10.1016/j.chemgeo.2004.11.009>
52. B. Liu and Y. Huang, *J. Mater. Chem.*, **21**, 17413 (2011); <https://doi.org/10.1039/c1jm12329g>
53. J.M. Zachara, D.C. Girvin, R.L. Schmidt and C.T. Resch, *Environ. Sci. Technol.*, **21**, 589 (1987); <https://doi.org/10.1021/es00160a010>
54. Z.T.A. Ali, M.A. Ibrahim and H.M. Madhloom, *Al-Nahrain Univ. Coll. Eng. J.*, **19**, 186 (2016).
55. N. Ahalya, T.V. Ramachandra and R. Kanamadi, *Res. J. Chem. Environ.*, **7**, 71 (2003).

56. H. Pahlavanzadeh, A.R. Keshtkar, J. Safdari and Z. Abadi, *J. Hazard. Mater.*, **175**, 304 (2010);  
<https://doi.org/10.1016/j.jhazmat.2009.10.004>
57. W. Xiaofu, Z. Fang, C. Mingli, Z. Yangli, Z. Chong and Z. Hailan, *J. Adsorp. Sci. Technol.*, **26**, 145 (2008);  
<https://doi.org/10.1260/026361708786036115>
58. E. Stefaniak, B. Bilinski, R. Dobrowolski, P. Staszczuk and J. Wojcik, *Colloids Surf. A Physicochem. Eng. Asp.*, **208**, 337 (2002);  
[https://doi.org/10.1016/S0927-7757\(02\)00160-7](https://doi.org/10.1016/S0927-7757(02)00160-7)
59. H.S. Altundogan, *Process Biochem.*, **40**, 1443 (2005);  
<https://doi.org/10.1016/j.procbio.2004.06.027>
60. X. Lv, Y. Hu, J. Tang, T. Sheng, G. Jiang and X. Xu, *Chem. Eng. J.*, **218**, 55 (2013);  
<https://doi.org/10.1016/j.cej.2012.12.026>
61. M. El Haddad, R. Slimani, R. Mamouni, M.R. Laamari, S. Rafqah and S. Lazar, *J. Taiwan Inst. Chem. Eng.*, **44**, 13 (2013);  
<https://doi.org/10.1016/j.jtice.2012.10.003>
62. Q. Qin, J. Ma and K. Liu, *J. Hazard. Mater.*, **162**, 133 (2009);  
<https://doi.org/10.1016/j.jhazmat.2008.05.016>
63. N. Fiol, I. Villaescusa, M. Martínez, N. Miralles, J. Poch and J. Serarols, *Separ. Purif. Tech.*, **50**, 132 (2006);  
<https://doi.org/10.1016/j.seppur.2005.11.016>
64. N.D. Hutson and R.T. Yang, *Adsorption*, **3**, 189 (1997);  
<https://doi.org/10.1007/BF01650130>
65. M. Erhayem, F. Al-Tohami, R. Mohamed and K. Ahmida, *Am. J. Anal. Chem.*, **6**, 1 (2015);  
<https://doi.org/10.4236/ajac.2015.61001>