

EQUILIBRIUM AND THERMODYNAMIC STUDIES OF THE REMOVAL OF CHROMIUM (VI) FROM AQUEOUS SOLUTIONS USING GROUNDNUT SHELL

Asfaq Ahmad¹, Anwer Ali², Limit Kumar³, Shobha Ram⁴

¹Civil Engineering Section, Faculty of Engineering & Technology, A.M.U., Aligarh.

²Department of Chemistry, D.S. College, Aligarh, Dr. B. R. A. University, Agra (U.P)

^{3,4}Department of Civil Engineering, Gautam Buddha University, Gautam Buddha Nagar (U.P)

ABSTRACT

In the present study ability of groundnut shell as an adsorbent for the removal of Cr (VI) from aqueous solutions was investigated. The influence of various parameters such as metal ion concentration, contact time, adsorbent dosage, adsorbent particle size, temperature and pH on the removal of Cr (VI) has been studied through batch method. The equilibrium data fitted well to Langmuir and Tempkin isotherm as indicated by high values of correlation coefficient. The maximum adsorption percent was found to be 911.6% at pH 3. The optimum equilibrium time was observed 2 hours. Thermodynamic studies showed that the adsorption of Cr(VI) by groundnut shell was spontaneous and endothermic in nature.

Key words: Adsorption, Groundnut Shell, Chromium, Langmuir, thermodynamic, etc

I. INTRODUCTION

Heavy metals are naturally occurring elements that have a high atomic weight and a density at least 5 times greater than that of water [1]. Among the different heavy metals, hexavalent chromium Cr(VI) is a common and very toxic pollutant [2]. The maximum concentration limit for Cr(VI) for discharge into inland surface waters is 0.1 mg/l and in potable water is 0.05 mg/l [3; 4]. Chromium can be introduced in aquatic systems by a variety of industries such as electroplating, leather tanning, metal finishing, nuclear power plant, textile industries, and chromate preparation discharged into the environment [5]. Acute exposure to Cr(VI) causes nausea, diarrhea, liver and kidney damage, dermatitis, internal hemorrhaging, and respiratory problems. Inhalation may cause acute toxicity, irritation and ulceration of the nasal septum and respiratory sensitization (asthma) and may also increase cancer risk. The skin contact of chromium may cause allergy, dermatitis, skin necrosis and skin corrosion [6; 7]. Therefore it is very necessary to eliminate chromium from water and wastewater. Various methods such as chemical precipitation, ion exchange, electrochemical precipitation, reduction, adsorption, Solvent extractions, membrane separation, concentration, evaporation, reverse osmosis and bio-adsorption has been adopted to remove chromium from wastewaters [8]. The various types of adsorbents used to remove heavy metals including chromium are activated carbon and char [9] the modified clay [10], rice

husk ash, activated alumina, coal fly ash [11] and modified corn stalk [12], etc. The methods mentioned above has few or many drawbacks due to which they have been restricted to few industrial processes. Therefore, there is a need for the development of a methods which could be employed on variety of low cost, easily available materials that which could allow to remove and recover Cr(VI) economically[13]. The objectives of the present work were to evaluate the removal efficiency groundnut shell for the removal of chromium ions from aqueous through bio-sorption process.

II. METHODOLOGY

2.1 Collection and Preparation of adsorbent

Raw groundnuts were purchased from market and their shells were removed. The Groundnut shells then cleaned using tap water to eradicate possible adhering impurities such as dirt and sands. The washed groundnut shells was first dried in sunlight for 2-5 days then crushed into fine particles which in turn sieved through the mesh size of 200 μ . The particles dried again in an oven for 2-5 hours and then stored in an air tight container to use as adsorbent for the removal of Cr(VI) from aqueous solutions.

2.2 Adsorbate solution

The stock solution of 1000 mg/L Cr(VI) ions was prepared by dissolving appropriate amount of potassium chromate, $K_2Cr_2O_7$ salt of MERCK in double distilled water. All working solutions were prepared by diluting the stock solution with distilled water. The pH of solutions was adjusted by using 0.1N HCl and 0.1N NaOH.

2.3 Determination of point of zero charge

The solid addition method was used to determine the point of zero surface charge of the adsorbent. 40 ml of 0.1N KNO_3 solution was transferred to 5 totally different 100 ml conical flasks. The initial pH (pH_i) of the solutions in every flask was roughly adjusted to 2, 4, 6, 8 and 10, respectively, by adding either 0.1N HCl or 0.1N NaOH. the total volume of the solution in every flask was adjusted specifically to 50 ml by adding KNO_3 of a similar strength. Initial pH (pH_i) of the solution was then accurately noted with the assistance of pH meter. 0.5 g material was then added to every flask and then allowed to equilibrate for 24 hours with intermittent manual shaking. the final pH (pH_f) of that liquid was noted. A graph of the difference between initial pH (pH_i) and final pH (pH) values ($\Delta pH = pH_i - pH_f$) was plotted against pH_i . The point of intersection of the resulting curve with abscissa at which $\Delta pH = zero$, gave zero point charge (pH_{zpc}).

2.4 Adsorption studies

Adsorption experiments were performed using standard batch method. In this method, 0.5 g of adsorbent was added to 50 ml of metal ion solution of varying concentrations ranging from 5 to 200 mg/L placed in a set of 100 ml conical flasks and the experiment conditions were optimized at pH range 1 to 10, temperature (30– 50 °C) and contact time (5–120 min). The pH of the sample was adjusted by adding 0.1 M HCl or NaOH solution. The

removal percentage (R %) of metal ions and adsorption capacity or amount of metal ions adsorbed per unit mass of adsorbent (q_e) were calculated by these expression

$$R\% = \frac{(C_i - C_e)}{C_i} \times 100$$

$$q_e = \frac{(C_i - C_e)}{m} \times V$$

where C_i , is the initial concentration of metal ions in the solution (mg/L), C_e is the final concentration of metal ions in the solution (mg/L), V is the volume of the solution and m is the mass of the adsorbent (gram).

2.5 Adsorption isotherms

The analysis of isotherm data by fitting them to different isotherm models is an important step in finding a suitable model that can be used for design purpose. The adsorption capacity of the system was studied with the Langmuir [15], Freundlich [16] and Temkin [17] isotherm models. The equilibrium sorption of Cr(VI) ions was carried out by contacting 0.5g of the groundnut shell with 50 ml solutions of Cr(VI) ions of concentrations ranging from 15 – 200 mg/L in 100 ml conical flasks with intermittent shaking for 2 hours on the rotary shaker.

2.6 Adsorption thermodynamics

To investigate thermodynamic behavior of the Cr(VI) adsorption onto prepared groundnut shell, thermodynamic parameters of Cr(VI) adsorption including Gibbs free energy change (ΔG°), enthalpy change (ΔH°), and entropy change (ΔS°) were determined using the following equations

$$\Delta G^\circ = RT \ln K_c$$

Where, R ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$) is the universal gas constant, T (K) is the temperature, and K_c is the adsorption equilibrium constant which can be calculated as-

$$K_c = \frac{C_{ad}}{C_e}$$

The $\log K_c$ was plotted against T^{-1} and values of standard enthalpy change, ΔH° (KJ/mol) and standard entropy change, ΔS° (KJ/mol K) were calculated from the slope and intercept of plot using following Van't Hoff equation.

$$\ln K_c = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$$

OR

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

The thermodynamic parameters can offer insight into the type and mechanism of an adsorption process. The magnitude of activation energy explains the nature of adsorption. There are two main types of adsorption: Physisorption & Chemisorption. In physisorption, the equilibrium is attained rapidly and is easily reversible as energy requirements are small while chemisorption is specific and involves forces stronger than required in physisorption.

III. RESULTS AND DISCUSSION

3.1 Adsorption studies

3.1.1 Effect of Ph

In this study, the effect of pH on adsorption capacity and removal efficiency of Cr(VI) ions by the prepared groundnut shell was studied in the pH range of 1–10 using 0.5 g of adsorbent in chromium solution with concentration of 50 mg l⁻¹ at 25°C. The effect of pH on adsorption of Cr(VI) on to groundnut shell is shown in “fig. 1”. It has observed that the removal percentage of Cr(VI) increases from 69.62 to 91.96% while pH increases from 1 to 3. Then, the removal percentage decreases to 61.58% with more decrease in pH up to 10.0. The experimental results indicated that the maximum removal percentage of Cr(VI) by the groundnut shell occurred at pH 3.0, and further increase in pH did not illustrate any considerable improvement in Cr(VI) removal efficiency and adsorption capacity. Therefore, the pH value of 3.0 was selected as the optimal pH in other adsorption experiments to achieve suitable removal efficiency and Cr(VI) uptake capacity. At low pH (1–3), removal efficiency was increased due to high protonated adsorbent surface. The high protonated adsorbent surface makes a strong electrostatic attraction between oxy-anion (CrO₄²⁻, Cr₂O₇²⁻, etc.) and positively charged groundnut shell surface. The decrease in removal percentage of Cr(VI) with increase in pH (4–10) may be due to increase in OH⁻ ions on the groundnut shell which improves a repulsive force between negatively charged adsorbent surface and the oxy-anions of chromium.

3.1.2 Effect of contact time

In order to optimize the contact time for the maximum uptake of Cr(VI) ions, contact time was varied from 5 to 180 minutes for the removal of Cr(VI) ions from aqueous solutions of 50 mg/L of Cr(VI) ions with adsorbent dose of 0.5 g at optimum pH 3. The effect of contact time on adsorption of Cr(VI) ions is shown in “Fig. 2”. It can be seen that adsorption of Cr(VI) ions increases with increase of contact time until it reaches equilibrium. The rate of Cr(VI) ions removal was very rapid during initial 30 minutes (84.2%) which may be due to the availability of large number of vacant sites on the adsorbent surface during initial stages of adsorption. Thereafter, the rate of adsorption of Cr(VI) ions increased slowly and reached maximum (88%) in 120 minutes and then became almost constant. This showed that equilibrium was established in 120 minutes.

3.1.3 Effect of concentration

The effect of initial Cr(VI) ions concentration (C_i) from 10 – 200 mg/L on the removal of Cr(VI) ions with adsorbent dose of 0.5 g and optimum pH 3.0 was investigated and shown in “Fig. 3”. It was observed that an increase in the initial Cr(VI) ion concentration, decreased cadmium ions uptake from 98.36% to 26.45%. The adsorption capacity (q_e) of adsorbent at initial Cr(VI) ions concentration of 10, 25, 50, 75, 100, 125, 150, 175, 200 and 250 mg/L observed were 1.98, 2.96, 4.62, 7.633, 10.082, 11.35, 13.63, 12.73, 12.475 mg/g, respectively.

3.1.4 Effect of adsorbent dose

Adsorbent dose is a mainly important parameter in adsorption which determines the amount of removal as well as the economics of process. To examine the effect of adsorbent dosage on Cr(VI) adsorption, 0.1 to 2 g/l of groundnut shell were used at room temperature and contact time of 120 min was fixed for initial Cr(VI) concentration of 50 mg/l with pH 3.0 as shown in “Fig. 4”. It was found that the percentage of Cr(VI) removal increased from 19.92 to 97.6% when the adsorbent dosage increased from 0.1 to 2 g/l as at higher dosage of adsorbent, more adsorption sites are available for Cr(VI) ions. The adsorption capacity was observed to decreased from 4.98 to 1.25 mg/g when the adsorbent dosage increased from 0.1 to 2 g/l. The decrease in the Cr(VI) adsorption capacity with increase in adsorbent dosage is due to more active sites of adsorbent remained unsaturated during the Cr(VI) adsorption process.

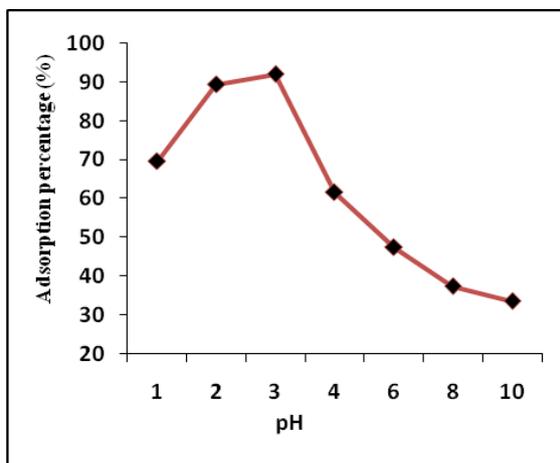


Fig. 1 Effect of pH

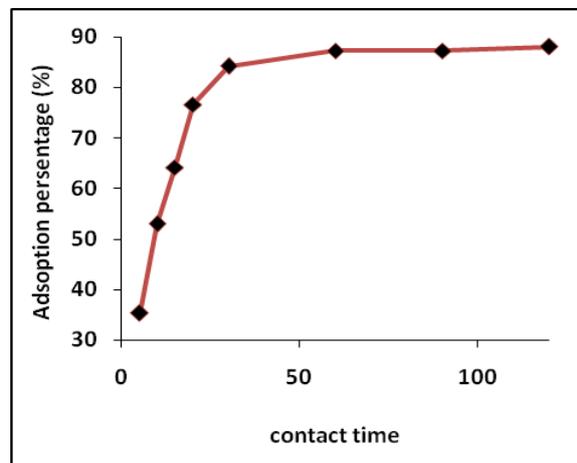


Fig. 2 Effect of contact time

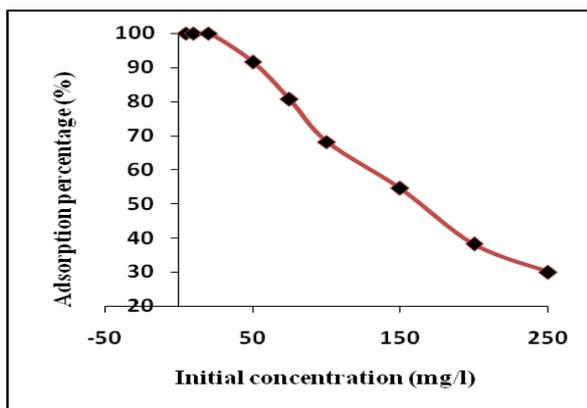


Fig. 3 Effect of Cr(VI) ions concentration

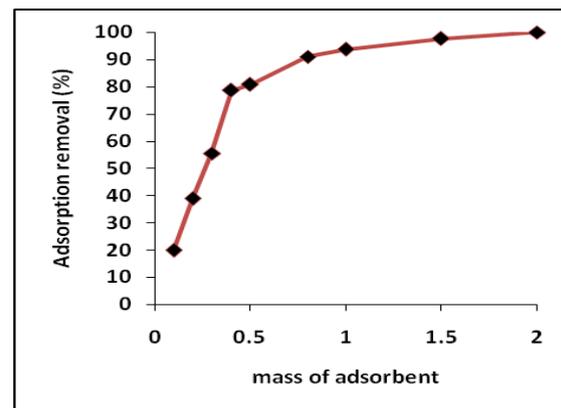


Fig. 4 Effect of adsorbent dose

3.2 Adsorption isotherms studies

The distribution of adsorbed molecules between the liquid and solid phase at equilibrium is indicated by adsorption isotherm. The obtained experimental data was analysed with Langmuir and Tempkin adsorption isotherm and shown in “Fig. 5 and 6”. The values of correlation coefficients, R^2 and constants of these isotherms

shown in table 1 which indicated that Langmuir model dominates with $R^2 \approx 0.997$ in the applicability of experimental data on isotherm models. The monolayer adsorption capacity, q_m of groundnut shell for Cr(VI) ions calculated from Langmuir plot of $1/q_e$ vs $1/C_e$ shown in “Fig. 6” was found to be 6.816 mg/g. The values of A, B and R^2 obtained from the graph of $\ln C_e$ vs q_e for Tempkin isotherm shown in “Fig. 7” are listed in “Table 1”.

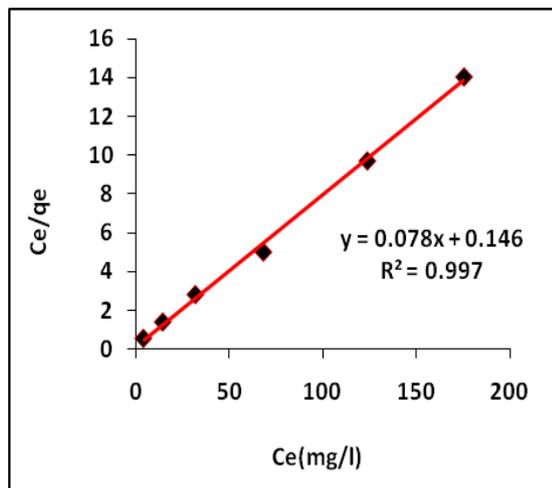


Fig. 5 Langmuir adsorption isotherm

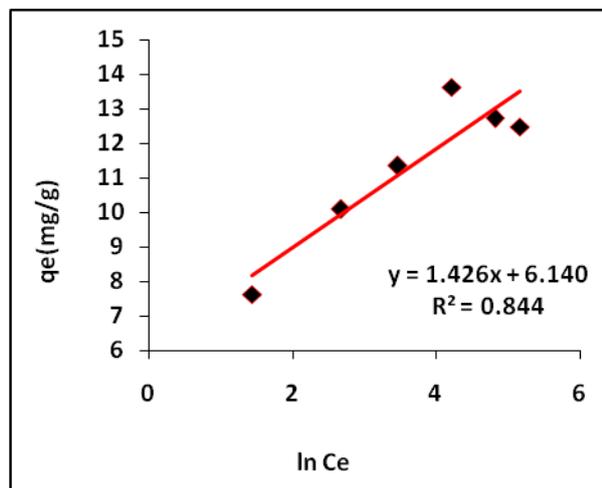


Fig. 6 Tempkin adsorption isotherm

Table: 1 Langmuir and Tempkin isotherm constants for the adsorption of Cr(VI)

Metal	Langmuir isotherm				Tempkin isotherm		
	q_m	b	R^2	R_L	A	B	R^2
Cr(VI)	6.816	1.878	0.997	0.0105	1.2613	6.1404	0.8447

3.3. Adsorption thermodynamics

Temperature had an obvious effect on the extent of hexavalent chromium adsorbed onto groundnut shell. To investigate the effect of temperature on the removal percentage of Cr(VI), experiments were carried out at different temperatures, i.e. 30, 40, and 50°C using optimum adsorbent dose (0.5 g/l) with initial concentration of 50 mg/l and pH equal to 3.0. The effect of temperature on Cr(VI) removal is shown in “fig. 5”. The removal percentage of Cr(VI) from aqueous solution was 83.2% at 30°C which increased to 93.6% at 50°C. The increase in removal efficiency with the increase in temperature shows that the Cr(VI) adsorption process is endothermic in nature and thermodynamically favourable. The plot of $\ln K_c$ vs $1/T$ gives a straight line and the values of ΔH° and ΔS° were calculated from the slope $(\frac{\Delta H^\circ}{RT})$ and intercepts $(\frac{\Delta S^\circ}{R})$ of plot shown in fig. 8 and listed in table 2. The negative values of Gibbs free energy change confirm that the process is feasible and spontaneous. Decrease in values of ΔG° with an increase in temperature suggests more Cr(VI) adsorption at higher temperature. According to data presented in Table 2, the positive value of ΔH° confirms the endothermic nature of the

process. The magnitude of ΔH° may give an idea about the type of adsorption process involved. When enthalpy change is less than 20 kJ mol⁻¹, it indicates the adsorption is physical in nature. The positive value of entropy change (ΔS°) indicates the increase in irregularity and randomness at the solid–aqueous solution interface during the adsorption of Cr(VI) ions onto prepared adsorbent.

Table: 2. Thermodynamic parameters for Cr(VI) ion adsorption onto the groundnut shell

Temperature	K_c	ΔG°	ΔH°	ΔS°	R^2
303	4.952	-4.426	7.658	6.318	99.56
313	7.196	-5.627			
323	14.625	-7.873			

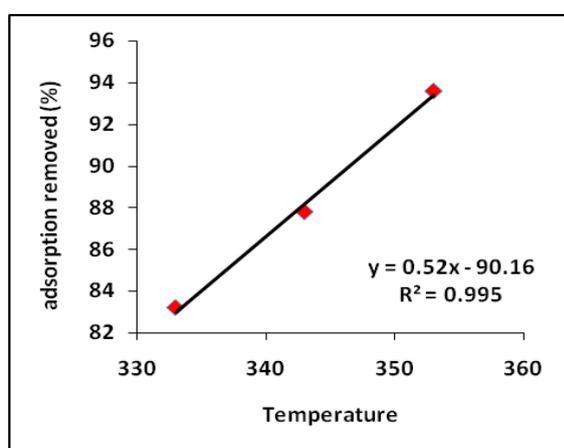


Fig. 7 Effect of temperature

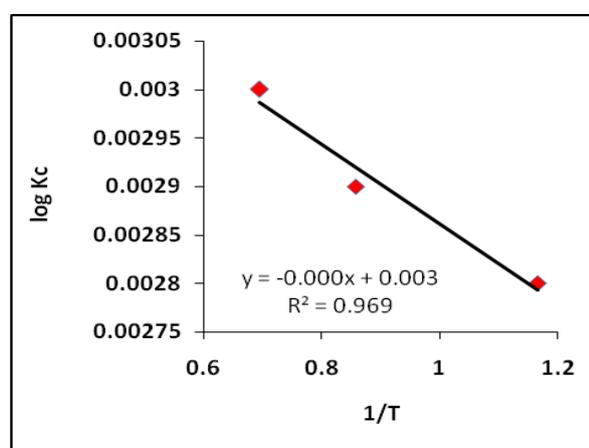


Fig. 8 Vant Hoff's plot

VI. CONCLUSION

A technically simple, cost effective and environment friendly treatment procedure was proposed for the removal of Cr(VI) ions by adsorption on Groundnut Shell. The present investigation reveals that Groundnut Shell is an excellent free of cost available adsorbent used for the removal of Cr(VI) ions from aqueous solutions. The adsorption parameters such as solution pH, adsorbent dose, initial Cr(VI) ions concentration and contact time were studied in the experiment and found to be very effective in analyzing the efficiency of Groundnut Shell for the removal Cr(VI) ions. The maximum adsorption of Cr(VI) ions was found 91.96 % at pH 3 using 50 mg/L of Cr(VI) ions solution with 0.3 g of adsorbent dose. Adsorption equilibrium data obeyed both Langmuir and Tempkin isotherm models but best fitted to Langmuir model. The maximum adsorption capacity, q_m obtained from Langmuir model was 6.816 mg/g. It indicated that the adsorption process was found to be physical in nature and occurred by forming monolayer of Cr(VI) ions. The adsorption process reached equilibrium in 120 minutes. The regeneration of Groundnut Shell is not essential because it is free of cost and easily available material. These observations concluded that groundnut shell has good adsorption capacity, inexpensive, available in bulk and non-hazardous agriculture waste which could be used as an effective indigenous material for treatment of water and wastewater stream containing chromium ions.

REFERENCES

1. Srivastava, N.K. and C.B. Majumder, Novel biofiltration methods for the treatment of heavy metals from industrial wastewater, *J. Hazard. Mat.*, 151(1),2008, 1-8..
2. Agarwal, G.S., H.K. Bhuptawat and S. Chaudhar, Biosorption of aqueouschromium(VI) byTamarindusindica seeds, *Biores. Tech.*, 97, 2006, 949–956.
3. Dubey, S.P. and K. Gopal, Adsorption of chromium(VI) on low cost adsorbents derived fromagricultural waste material: a comparative study, *J. Hazard. Mat.*, 145, 2010, 465–470.
4. Gupta, S., and B.V. Babu, Modeling, simulation, and experimental validation for continuous Cr (VI)removal from aqueous solutions using sawdust as an adsorbent, *Biores. Tech.*, 100, 2011, 5633–5640.
5. Sarin, V., and K.K. Pant, Removal of chromium from industrial waste by using eucalyptusbark,*Biores. Tech.*, 97, 2010, 15–20.
6. Srivastava, S. and I.S. Thakur, Isolation and process parameter optimization ofAspergillus sp. Forremoval of chromium from tannery effluent, *Biores.Tech.*,97, 2010, 167–1173.
7. Bayat, B., Comparative study of adsorption properties of Turkish fly ashes: II. The case ofchromium (VI) and cadmium (II), *J. Hazard. Mat.*, 95, 2002, 275–290.
8. Bansal, M., D. Singh, V.K. Garg, A comparative study for the removal of hexavalent chromium from aqueous solution by agriculture wastes carbons, *J. Hazard. Mat.*, 171, 2011, 83-92.
9. Natale, F. D., A.Lancia, A. Molino, D. Musmarra, Removal of chromium ions form aqueoussolutions by adsorption on activated carbon and char, *J. Hazar. Mat.*, 145, 2011, 381–390.
10. Gładysz-Plaska, A., M. Majdan, S. Pikus, D. Sternik, Simultaneous adsorption ofCr(VI) and phenol on natural red clay modified by HDTMA, *Chem. Engg. J.*, 179, 2012, 140–150.
11. Bhattacharya, A.K., T.K. Naiya, S.N. Mandal andS.K. Das, Adsorption, kinetics and equilibriumstudies on removal of Cr(VI) from aqueous solutions using different low-cost adsorbents,*Chem. Engg. J.*, 137,2010, 529–541.
- 12.. Chen, S., Q. Yue,B. Gao andQ. Li, Adsorption of hexavalent chromium from aqueous solution bymodified corn stalk: a fixed-bed column study, *Biores. Tech.*, 113, 2012, 114–120.
13. Klimaviciute, R., J. Bendoraitiene, R. Rutkait andA. Zemaitaitis, Adsorption of hexavalent chromium on cationic cross-linked starches of different botanic origins, *J. Hazard. Mat.*, 181, 2010, 624–632.