

## Investigating the biosorption potentials of *Arachis hypogaea* shells for chromium ions from the aqueous media

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### Abstract

Biosorption studies of chromium (VI) ions from aqueous solution were investigated for *Arachis hypogaea* (peanut) shell and modified peanut shells. The change of initial chromium ion concentration, contact time, pH and temperature were investigated. Different thermodynamic parameters for the adsorption of Cr (VI) were calculated using Freundlich, Langmuir and D-R models. Various kinetic models like pseudo 1<sup>st</sup> order, pseudo 2<sup>nd</sup> order and intra particle diffusion were also studied. The adsorption was followed by Langmuir isotherm model. The maximum Cr (VI) adsorption capacity  $q_{max}$  calculated from Langmuir adsorption isotherm was 166 mg/g. The thermodynamic factors  $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$  indicated that the adsorption process is spontaneous and exothermic. The kinetic data have indicated that the adsorption followed the pseudo second order kinetic model. This agricultural by-product, peanut shells, were successfully used as biosorbent for effective removal of Cr (VI) from aqueous solution. The adsorption data is better fitted by the Langmuir model and the adsorption capacity increases twice due to chemical treatment of peanut shells.

**Keywords:** *Arachis hypogaea*; Biosorption; Isotherms; Kinetics

### 1. INTRODUCTION

Global environment is contaminating largely by increasing industrialization and rapid urbanization which ultimately contaminate our water systems. Toxic metal ions are randomly introducing in water streams through geological and human activities [1]. In earth crust, chromium is the 21<sup>st</sup> most abundant element and harmless in elemental state [2]. In aqueous medium, it exists as Cr (III) and Cr (VI). Cr (III) is an essential nutritional element at trace level [3] while Cr (VI) has teratogenic and carcinogenic behaviour on the human beings and other animals [4]. The Cr (VI) tolerance limit for inland surface water is 0.1 mg/L and drinking water recommended limit is 0.05 mg/L [5-6]. The toxic chromate comes in water system through chrome leather tanning, chromium plating, mining, textile dyeing, printing inks and wood preservation [7-9].

Recent studies have shown that agricultural wastes are potential biosorbent materials for the elimination of heavy and toxic metals from the waste water [10-11]. Biosorption process is less expensive and economical due to possible regeneration of biosorbents. Garg *et al.*, [12] have used various adsorbent such as sugarcane bagasse, maize corn cob, jatropha oil cake for the exclusion of chromium (VI) from aqueous media. Wang *et al.*, [13] have used newspaper waste for the removal of chromium. Sartape *et al.*, [14] investigated wood apple shell, a low cost biosorbent for the biosorption of chromium. Jing *et al.*, [15] have studied the biosorption of chromium on cationic surfactant modified spent mushroom from waste water. Gopalakrishnan *et al.*, [16] have used *Azadirachta indica* (Neem) leaf powder for the removal of Cr (VI). But less work is available for biosorption of Cr (VI) on peanut shells.

Peanut is an oil plant, cultivated and consumed worldwide. There are good proportion of proteins 8.2%, carbohydrates 2.5%, lignin 28%, cellulose 37% and hemicelluloses 18.7% in peanut shells [17]. In this study, agricultural byproduct, peanut shells powder, was investigated as potential biosorbent material for the removal of Cr (VI).

### 2. EXPERIMENTAL

#### 2.1 Unmodified peanut shells powder (UPS)

Peanuts (*Arachis hypogaea*) were purchased from the local market of Lahore, Pakistan. The biosorbent peanut shells were washed with deionised water, dried in an oven at 45°C. The dried peanut shells were grinded in an electrical grinder with Teflon blades and sieved with stainer of 80 meshes.

#### 2.2 Modified peanut shells powder (MPS)

10 g of peanut shells powder (PS) were stirred with 100 mL of 0.1M NaOH solution for 1 hour at room temperature. After stirring, the solution was filtered, washed and residue was then kept in an oven at 55°C for drying and called as sodified peanut shells (SPS). 0.5g of SPS mixed with 100 mL of 0.5M citric acid solution, stirred for 2 hours, filtered, washed with deionised water and dried in an oven at 55°C.

## 2.2 Biosorption studies

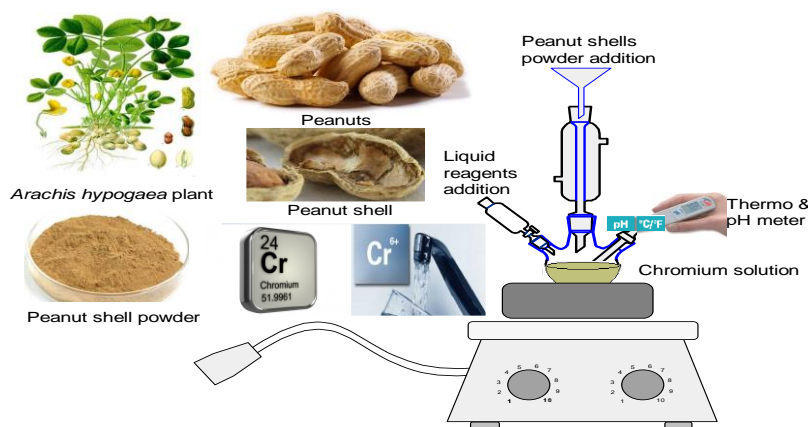
A model batch experiment was designed for the sorption of Cr (VI) on peanut shells. The stock solution of  $K_2Cr_2O_7$  was prepared, from which 50 mg/L Cr (VI) solution was made and used in all experimental runs. Batch experiments were carried out by taking 50 mL of Cr (VI) solution of desired concentration, pH and temperature, together with 0.2 g of the dry sorbent. The effect of adsorbent dose was studied by taking 10 flasks. 50 mL of 50 ppm solution was taken in each flask with adsorbent dose of 0.1 to 1.0 g. Similarly, pH studies were made by taking 10 flasks of pH 1-10 with 0.2 g of adsorbent in each flask. All flasks were shaken for 30 minutes and filtered after 10 minutes of rest. In kinetic experiments, 0.2 g of adsorbent was mixed with 50 mL of 50 ppm Cr (VI) solution at pH 3, the highest adsorption obtained under the employed experimental conditions. The isotherm studies were conducted using 0.2 g adsorbent in Cr (VI) concentration range of 10-100 ppm at pH 3 and at the temperature of 40 °C. The conceptual experimental diagram for biosorption of Cr (VI) on the peanut shells powder is given in Figure 1. Cr (VI) analysis were made by taking the filtrate to atomic absorption spectrophotometer. The percentage metal ions removal efficiency of adsorbent (% R), the biosorption capacity at equilibrium,  $q_e$  (mg/g) and the biosorption capacity at time  $t$ ,  $q_t$  (mg/g) and were calculated as follows:

$$\% R = \frac{C_0 - C_e}{C_0} \times 100 \text{----- (1)}$$

$$q_e \text{ (mg/g)} = (C_0 - C_e) \times \frac{V}{m} \text{----- (2)}$$

$$q_t \text{ (mg/g)} = (C_0 - C_t) \times \frac{V}{m} \text{----- (3)}$$

Where,  $C_0$  (mg/L) and  $C_t$  (mg/L) are the liquid-phase concentration of solutes at the initial and a given time  $t$ , respectively.  $C_e$  (mg/L) is the concentration of Cr (VI) at equilibrium,  $V$  is the volume of the solution in litre and  $m$  is the mass of the peanut shell in grams.



**Fig. 1:** Conceptual experimental diagram for biosorption of Cr (VI) on the peanut shells powder

## 3. RESULTS AND DISCUSSION

### 3.1 Effect of adsorbent dose on Biosorption of Cr (VI) on UPS and MPS

Effect of dose was studied for biosorption of Cr (VI) on unmodified peanut shells and modified peanut shells. The results are given in Figure 2(a). Optimum dose of 0.2 g was obtained for both unmodified and modified peanut shells. On modification removal of Cr (VI) increased i.e. 98.00% and 98.15% respectively. It is due to availability of more and more adsorbent surfaces for Cr (VI). The removal of Cr (VI) increase as the adsorbent dose increases. As equilibrium is established between adsorbate and adsorbent at the optimum dose, thus beyond this optimum dose the increase in Cr (VI) removal is very slow [18].

### 3.2 Effect of pH on Biosorption of Cr (VI) on UPS and MPS

The pH effect was studied for biosorption of Cr (VI) on UPS and MPS and results are given in Figure 2(b). It was observed that biosorption efficiency is affected by pH change. The removal of Cr (VI) increases as pH of solution decreases [19]. In this study, the optimum pH for biosorption of Cr (VI) on UPS and MPS was 3.0. For UPS, it gives 97.07% efficiency while for MPS it gives 97.08% removal efficiency. At the optimum pH (3),  $HCrO_4^-$ ,  $Cr_2O_7^{2-}$ ,  $Cr_4O_{13}^{2-}$  and  $Cr_3O_{10}^{2-}$  are the dominant species of Cr ions in solution [20]. The cationic species present on the surface of sorbent (PS) react with anionic species in solution. So, these can easily be removed from the solution. At lower pH, metal

cations compete with H<sup>+</sup> for the available adsorption sites whereas adsorption sites do not activate at higher pH. At pH greater than 10, metal cations react with hydroxide ions and precipitate as metal hydroxide [21].

### 3.3 Effect of contact time on biosorption of Cr (VI) on UPS and MPS

Effect of contact time was studied for biosorption of Cr (VI) on UPS and MPS and results are given in Figure 2(c). The optimum time for maximum removal of Cr (VI) was 40 minutes on UPS and MPS. On UPS, the removal efficiency was 94% while on MPS it was increased by 97%. The removal efficiency increases with increase in contact time due to the reason that more time becomes available for the metal ion to bind with the adsorbent surface. At equilibrium, the adsorbate and adsorbent come in contact with each other, so there is a rapid increase in removal efficiency [22] and the reason is that, when easily available active sites become unavailable, metal needs time to find more active sites for binding. Thus the optimum time for maximum binding was 40 minutes.

### 3.4 Thermodynamic Studies

Different thermodynamic parameters for the adsorption of Cr (VI) were calculated by using the relations which are given as;

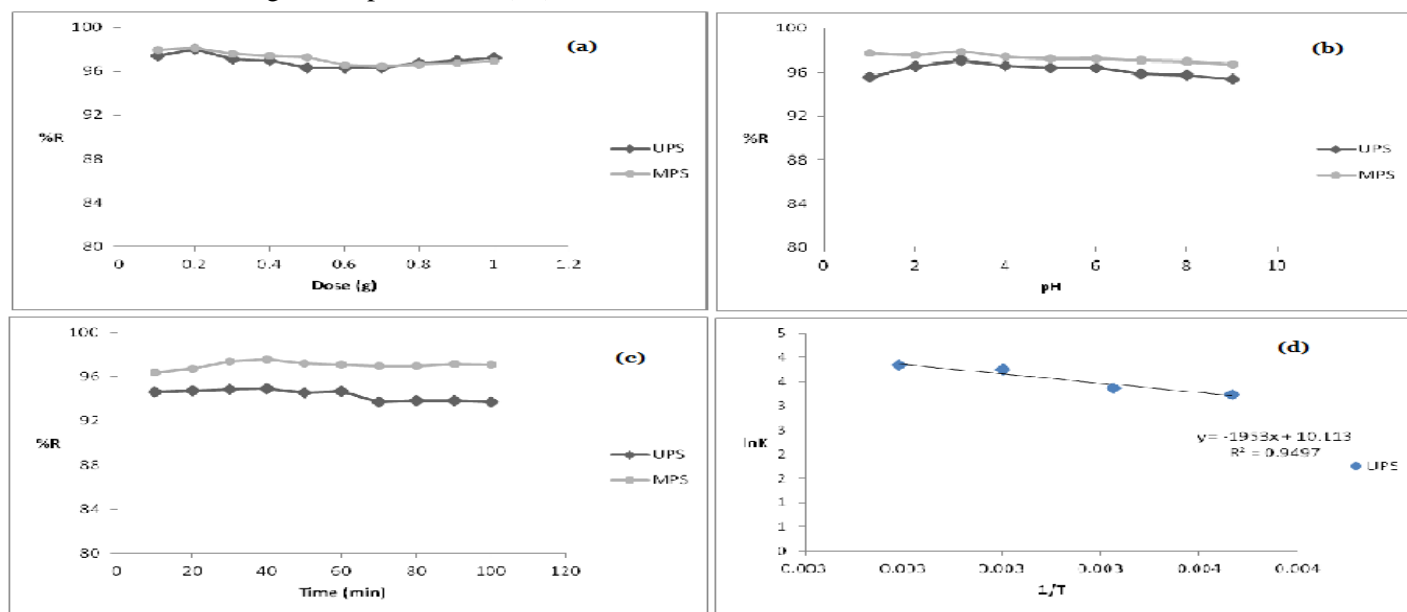
$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \text{----- (4)}$$

$$\Delta G^\circ = -RT \ln K_D \text{----- (5)}$$

$$K_D = \frac{C_{AS}}{C_e} \text{----- (6)}$$

$$\ln K_D = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \text{----- (7)}$$

$\Delta G^\circ$  is change in Gibbs free energy,  $\Delta H^\circ$  is change in enthalpy, T is the temperature (K),  $\Delta S^\circ$  is change in entropy, R is universal gas constant (8.314 J/mol K),  $K_D$  is distribution coefficient,  $C_{AS}$  is adsorbed amount of adsorbate and  $C_e$  (mg/L) is concentration of MV at equilibrium. The results of performed thermodynamic studies are shown in Figure 2(d). The negative value of  $\Delta G^\circ$  indicates that sorption of Cr (VI) on adsorbent is thermodynamically feasible and spontaneous. The negative value of  $\Delta H$  showed that reaction is exothermic. The positive value of  $\Delta S$  showed the randomness at the solid-solution interface during the sorption of Cr (VI).



**Fig. 2(a):** Effect of adsorbent dose on Biosorption of Cr (VI) on UPS and MPS **(b)** Effect of pH on Biosorption Cr (VI) on UPS and MPS **(c)** Effect of contact time for Biosorption Cr (VI) on UPS and MPS **(d)** Thermodynamic Studies for Biosorption Cr (VI) on UPS

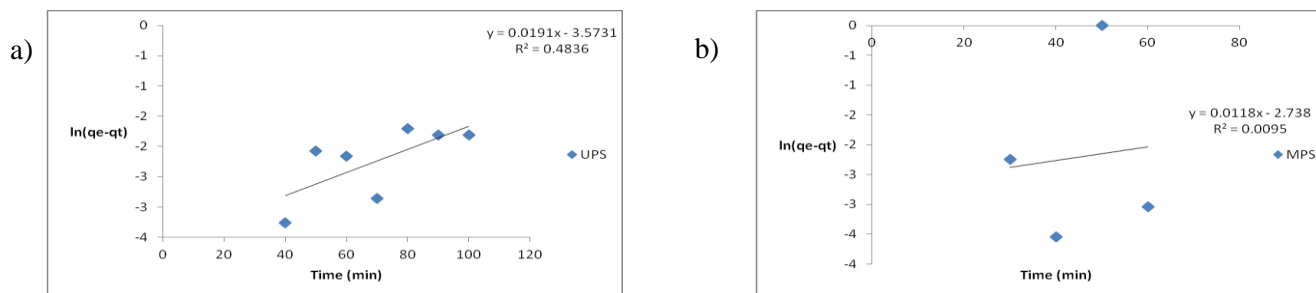
### 3.5 Kinetic studies

Adsorption kinetics is one of the most important characteristics to be responsible for the efficiency of adsorption. Different kinetic models like pseudo 1<sup>st</sup> order, pseudo 2<sup>nd</sup> order and intra particle diffusion were studied.

Pseudo 1<sup>st</sup> order kinetics was studied and the results are given in Figure 3 for unmodified and modified peanut shells. Pseudo 1<sup>st</sup> order equation can be written as;

$$\ln(q_e - qt) = \ln q_e - k_1 t \text{-----(8)}$$

$k_1$  is the pseudo 1<sup>st</sup> order rate constant ( $\text{min}^{-1}$ ). The plot was formed between  $\ln(q_e - qt)$  and  $t$  for both PS and MPS Figure 3(a) and Figure 3(b) respectively. The values of  $R^2$  0.483 for UPS and 0.009 for MPS are less than that of 2<sup>nd</sup> order. So, this model is not applicable.

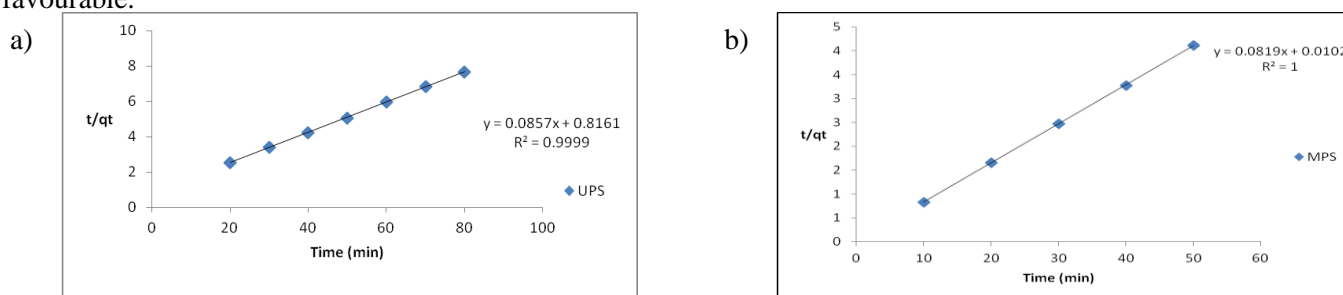


**Fig. 3:** Pseudo 1<sup>st</sup> order model for biosorption of Cr(VI) on a) UPS and b) MPS

From all the models, pseudo 2<sup>nd</sup> order model is applicable. The results are given in Figure 4 for unmodified and modified peanut shells. Pseudo 2<sup>nd</sup> order equation can be written as;

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \text{----- (9)}$$

Value of the equilibrium adsorption capacity ( $q_e$ ) and rate constant ( $k_2$ ) for pseudo-second-order can be determined experimentally by plotting the graph between  $t/q_t$  and where  $q_e$  and  $q_t$  are sorption capacities at equilibrium and at time  $t$ , respectively ( $\text{mgg}^{-1}$ ).  $k_2$  is the overall rate constant of pseudo 2<sup>nd</sup> order kinetics ( $\text{gmg}^{-1}\text{min}$ ). The plot of  $t/q$  against  $t$  show a linear relationship for unmodified and modified peanut shells in figure 4(a) and Figure 4(b) respectively. The value of  $R^2$  is 0.999 for unmodified peanut shells and 1 for modified peanut shells. The value of  $q$  is 11.76 for unmodified peanut shells and 12.34 for modified peanut shells. The increase in the value of  $R^2$  and  $q$  shows that the modification is favourable.



**Fig. 4:** Pseudo 2<sup>nd</sup> order model for biosorption of Cr (VI) on a) UPS and b) MPS

Intra particle diffusion (IPD) equation can be written as;

$$qt = k_{id} \sqrt{t} + c \text{----- (10)}$$

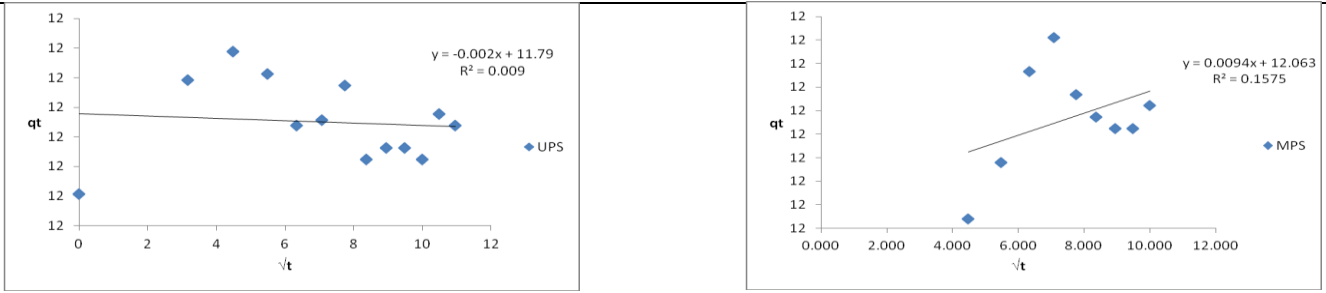
- By plotting a graph between  $q_t$  ( $\text{mg/g}$ ) and square root of time ( $t^{1/2}$ ), a straight line is obtained and the pass of straight line through the origin shows that it is the rate controlling step. A graph was plotted between  $q_t$  and  $t^{1/2}$ . The results of IPD model are given in the plot of  $qt$  against  $\sqrt{t}$  in Figure 5(a) and Figure 5(b) respectively. The value of  $C_i$  is greater than unity for both UPS and MPS, So, this model is not applicable.

### 3.6 Adsorption Studies

Equilibrium data is generally known as adsorption isotherms is the main requirements to understand the adsorption mechanism. Here, Langmuir, Freundlich and D-R model were studied.

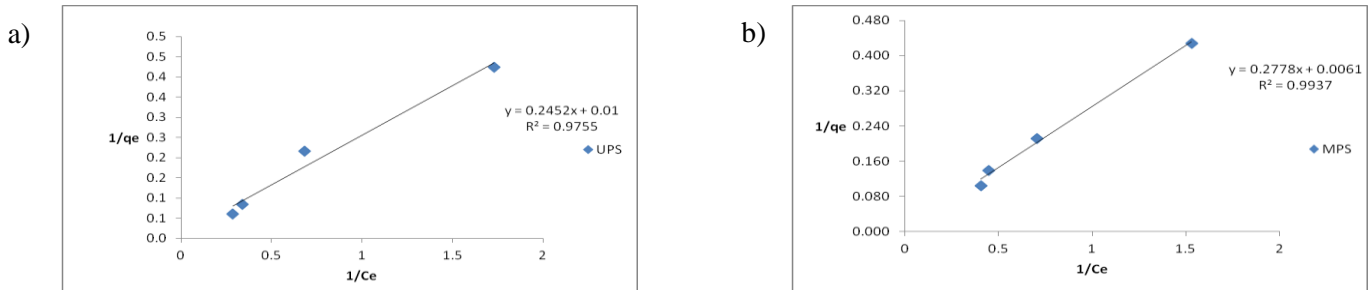
**3.6.1 Langmuir Adsorption Isotherm:** Langmuir adsorption isotherm finds the relationship between the surface concentration  $q_e$  and the equilibrium concentration  $C_e$ . It assumes that equilibrium is attained when a monolayer of the adsorbate molecules saturates the adsorbent surface [23] and indicate the surface homogeneity of the sorbent. This isotherm model [24] can be represented by simplest linear form which is given as:

$$\frac{C_e}{q_e} = \frac{1}{K_L \cdot q_m} + \frac{C_e}{q_m} \text{----- (11)}$$



**Fig. 5:** Inter particle diffusion model for biosorption of Cr (VI) on a) UPS and b) MPS

The results are shown in the plots of  $1/C_e$  against  $1/q_e$  in Figure 6 (a) and (b) for UPS and MPS respectively. The value of  $R^2$  is 0.975 for UPS and 0.993 for MPS. Similarly, the value of  $q_{max}$  for UPS is 100 and for MPS it is 166. These values show that this model is applicable. The increase in the value of  $R^2$  and  $q_{max}$  indicate that modification is favourable.

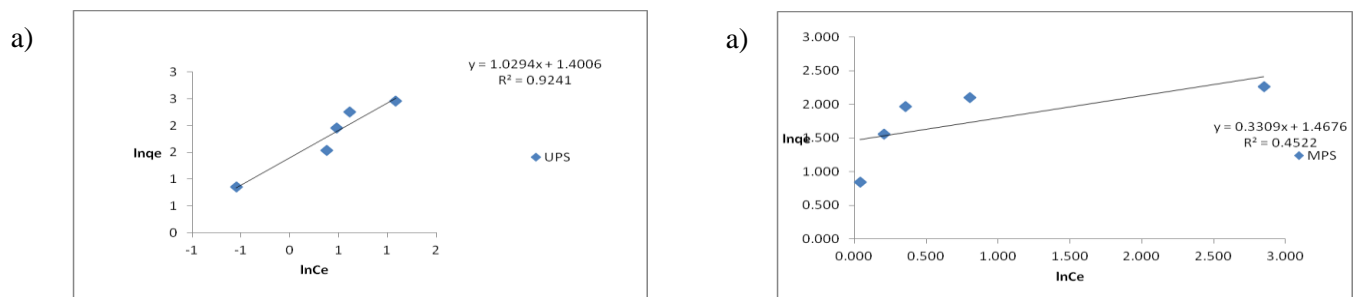


**Fig. 6:** Langmuir Adsorption Isotherm for Biosorption of Cr(VI) on a) UPS and b) MPS

**3.6.2 Freundlich Adsorption Isotherm:** The Freundlich adsorption isotherm represents the relationship between the metal amount adsorbed per unit mass of the adsorbent  $q_e$  and the concentration of the metal in solution at equilibrium [25]. This isotherm model [26] is represented by the linear form equation which is given as:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \text{ ----- (12)}$$

$n$  is the dimensionless Freundlich constant that represent extent of the degree of nonlinearity and  $K_F$  ( $\text{dm}^3 \text{g}^{-1}$ ), Freundlich constants that represent the extent of adsorption. It indicates the surface heterogeneity of the sorbent. Freundlich studies were done and results given in Figure 7 (a and b) for UPS and MPS respectively. These results show that this model is not applicable.



**Fig. 7:** Freundlich Adsorption Isotherm for Biosorption of Cr (VI) on a) UPS and b) MPS

**3.6.3 Dubinin-Radushkevich Adsorption Isotherm:**

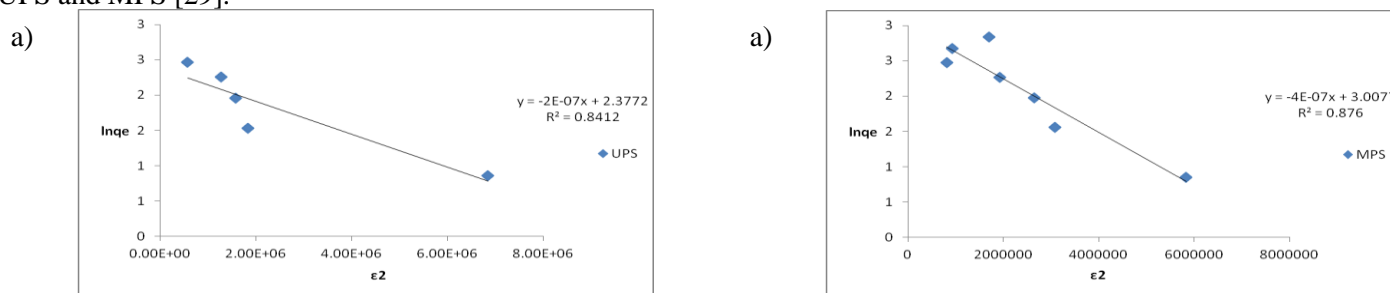
D-R studies results are given in Figure 8 (a and b) for UPS and MPS respectively. These results show that this model is not applicable. The (D-R) isotherm model is represented by an equation [27] that is given as:

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \text{ ----- (13)}$$

$q_m$  ( $\text{mg g}^{-1}$ ) theoretical saturation capacity, ( $\text{mol}^2 \text{kJ}^{-2}$ ) is a constant linked with mean free energy of adsorption per mole of the adsorbate and  $\varepsilon$  is the Polanyi potential [28], that is given as;

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \text{----- (14)}$$

Values of  $q_m$  and  $\beta$  can be calculated from intercept and slope respectively of graph given in Figure 8 (a and b) which is plotted between  $\ln q_e$  and  $\varepsilon^2$ . Dubinin-Radushkevich (D-R) equation indicates the heterogeneity of the surface of the UPS and MPS [29].



**Fig. 8:** Dubinin-Radushkevich (D-R) Isotherm for Biosorption of Cr (VI) on a) UPS and b) MPS

#### 4. CONCLUSION

The agricultural by-product peanut shells were successfully used as biosorbent. A little chemical treatment has done with peanut shells that increase its removal efficiency for Cr (VI). It was concluded from the present study that this biosorbent can be used for effective removal of Cr (VI) from aqueous solution. The percentage removal depends upon pH, temperature, adsorbent dose and contact time. The adsorption data is better fitted by the Langmuir model. The adsorption capacity, calculated by Langmuir model, increases twice due to chemical treatment of peanut shell powder.

#### REFERENCES

1. S. Ata, F.H. Wattoo, I. Qasim, M.H.S. Wattoo, S.A. Tirmizi, I. Mohsin, M.A. Qadir. *Turk. J. Biochem.* 38(1):25-30. (2013).
2. S.E. Manahan. Taylor & Francis/CRC Press, Boca Raton, FL. (2007).
3. M. Dakiky M. Khamis, A. Manassra, M. Mer'eb. *Advances in Environmental Research.* 6 (4): 533-540. (2002).
4. P.C. Grevatt. Environmental Protection Agency Washington, DC. (1998).
5. M.H.S. Wattoo, J. Iqbal, T.G. Kazi, M.A. Jakhrani. *Pak. J. Biolog. Scis.* 3 (6): 960 – 962. (2000).
6. Wattoo MHS, F.H. Wattoo, S.A. Tirmizi, T.G. Kazi, M.I. Bhangar, J. Iqbal. *J. Chem. Soc. Pak.* 28 (2): 136 –143. (2006).
7. H. Ohtake, E. Fujii, K. Toda. *Environl. Technol.* 11 (7): 663-668. (1990).
8. A. Bhattacharya, T. Naiya, S. Mandal, S. Das. *Cheml Engin. J.* 137 (3): 529-541. (2008).
9. M. Gholipour, H. Hashemipour, M. Mollashahi. *J. of Engin. Applied Sci.* 6 (9): 10-18. (2011).
10. R.H. Vieira, B. Volesky. *Internl. Microbio.* 3 (1): 17-24. (2010).
11. A. Witek-Krowiak, R.G. Szafran, S. Modelski. *Desalination.* 265 (1): 126-134. (2011).
12. U.K. Garg, M. Kaur, V. Garg, D. Sud. *J. Hazar Materials.* 140 (1): 60-68. (2007).
13. X.S. Wang, Z. Z. Li. *Desalination.* 249 (1): 175-181. (2009).
14. A.S. Sartape, P.D. Raut, S.S. Kolekar. *Adsorp. Sci. Technol.* 28 (6): 547-560. (2010).
15. X. Jing, Y. Cao, X. Zhang, D. Wang, X. Wu, H. Xu. *Desalination.* 269 (1): 120-127. (2011).
16. S. Gopalakrishnan, T. Kannadasan, S. Velmurugan, S. Muthu. Vinoth Kumar, P. *Res. J. Chem. Sci.*, 3 (4): 49. (2013).
17. B. Zhao, W. Xiao, Y. Shang, H. Zhu, R. Han. *Arabian J. Chem.* 10, S3595-S3602. (2014).
18. R.N. Bishnoi, M. Bajaj, N. Sharma, A. Gupta. *Bioresource technology.* 91 (3): 305-307. (2004).
19. H. Uzun, Y.K. Bayhan, Y. Kaya, A. Cakici, O. Faruk-Algur. *Bioresource Technol.* 85 (2): 155-158. (2002).
20. R.S. Bai, T.E. Abraham. *Bioresource Ttechnol.* 79 (1): 73-81. (2001).
21. G. Blázquez, F. Hernáinz, M. Calero, M. Martín-Lara, G. Tenorio. *Cheml Engin. J.* 148 (2): 473-479. (2009).
22. K. Selvi, S. Pattabhi, K. Kadirvelu. *Bioresource Technl.* 80 (1): 87-89. (2001).
23. Z. Al-Qodah. *Water Research.* 34 (17): 4295-4303. (2000).

24. K. Foo, B. Hameed. *Cheml Engin. J.* 156 (1): 2-10. **(2010)**.
25. M. Sekar, V. Sakthi, S. Rengaraj. *J. Colloid Interface Sci.* 279 (2): 307-313. **(2004)**.
26. O. Hamdaoui, E. Naffrechoux. *J. Hazardous Materials.* 147 (1): 381-394. **(2007)**.
27. M.M. Montazer-Rahmati, P. Rabbani, A. Abdolali, A.R. Keshtkar. *J. Hazardous Materials.* 185 (1): 401-407. **(2011)**.
28. R.A. Sari, M. Tuzen. *Cheml Engin. J.* 151 (1): 255-261. **(2009)**.
29. P. Mourao, P. Carrott, M. Ribeiro-Carrott. *Carbon.* 44 (12): 2422-2429. **(2006)**.

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