Experimental investigation and thermodynamic study of heavy metal removal from industrial wastewater using pomegranate peel

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Abstract. The objective of the study is to treat industrial wastewater and perform a thermodynamic experimental study for more economical and efficient adsorption process. This has been done by biosorption and chemisorption of chromium ions from synthetic wastewater into already prepared pomegranate peel as a natural adsorbent. Pomegranate peel proved to be an economic solution since it is available locally and it has an elevated adsorption capacity. Adsorption has been done in a fixed bed column (10 cm inside diameter, and 30 cm height) with continuous flow rate of 1 ml/min. The characteristic properties of adsorption for the pomegranate peel, analyzed by FTIR and SEM, proved that pomegranate peel is a good adsorbent because of its effective combinations and holes on its exterior. Also, comparing between adsorption ability of pomegranate peel together with Langmuir and Freundlich models indicates that Langmuir is preferable in fitting the experimental data. However, the elimination efficiency of the pomegranate peel was 90%, and the greatest adsorption capability was 9.45 mg/g. While, thermodynamic study results showed that endothermic adsorption was approved from positive values of ΔH° , also the negative values of ΔG° proved that the adsorption is unprompted and convenient.

1 Introduction

Water pollution with poisonous heavy metals by industrial wastewater discharge is an environmental problem through the world [1]. Fast manufacturing and growth sent out heavy metals into the water. Industries like mining, metal plating and battery manufacturing result into a release of heavy metals into aquatic ecosystem [2,3]. Biosorption is an environment friendly process for metal removal since it can be considered as cost effective and efficient adsorbents for heavy metal removal. Many biomasses can be used as biosorbent like waste agriculture materials, and different processes have been utilized in the treatment, this includes biological method through biosorption. Biosorption advantages are: low cost, high efficiency and availability during most of the year [4]. Local fruit wastes are successfully applied for the treatment of wastewater polluted with heavy metals, but it needs a further understanding of biosorption mechanism [5]. Pomegranate is a common fruit; it includes an edible part, seed, and peel. The pomegranate peel (PP) forms 5

% to 15% of its total weight [6]. Laterally, several researches were achieved for employing a pomegranate peel to eliminate Cr(VI), Ni(II), Pb(II), and Cu(II) from water samples [7, and 8]. Thermodynamic study was performed using adsorption measurements [9]. The aim of the present work is to remove chromium ions from synthetic wastewater using pomegranate peels as a natural biomass with an efficient, low cost, and environmental friendly adsorption process. In addition to performing a thermodynamic study to explain the impact of temperature on feasibility of the adsorption process, the characterization of PP with FTIR and SEM are done to present the impact of chromium ion binding with the functional combinations in the exterior surface of PP as natural adsorbent. Also, the adsorption isotherms study is performed.

2 Materials and method

2.1 Adsorbent preparation

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The pomegranate peels bought locally from a marketing center, washing it using tap water and distilled water. After that peels were cut off to small portions then dried by sun light for three days. The dried portions were dried again using an oven at 80°C for 36 hrs. The dried materials were grinded and sieved to give 1 mm particle size.

2.2 Cr (VI) solution preparation

Cr (VI) solution was prepared by dissolving the nitrates salts in deionized water and diluted to a desired metal concentration.

2.3 Analysis method

Atomic absorption instrument type (AA250, China) used to find Cr(VI) concentration.

2.4 Thermodynamic experiments

Thermodynamic experiments were done using 25 ml of chromium solution of 10 mg/L concentration, PP dose of 0.01 g/25 ml at different temperatures (30, 40, 50 °C) for contact time of (1hr). The amount of Cr(VI) adsorbed per unit of pomegranate peel (PP) and removal percentages were calculated according to mass balance of chromium concentration as:

$$q_e = \frac{(C_i - C_f)V}{m} \dots\dots\dots(1)$$

$$\% Removal = \frac{C_i - C_f}{C_i} \times 100 \dots\dots\dots(2)$$

2.5 Column tests

In this experiment 25 gm of PP powder were placed in 30 cm high, 10 cm i.d. glass column as shown in Fig. 1. After that 100 ml of the heavy metal solution were inserted into the column. The out flowing samples of 5.0 ml were assembled, labeled and analyzed. The samples were filtered using filter paper No. 40 and the quantity of chromium ions was found by atomic absorption.

Fig. 1. Experimental apparatus used in the experiments.

3 Results and discussion

3.1 SEM test of pomegranate peel

The porous composition of (50 µm) particle size of pomegranate peel was noticed with 500X resolution (Figs. 2, and 3). The test display several holes in the surface that are able to uptake chromium ions. The test result showed that there is a noticeable variation in surface structure of PP before and after Cr(VI) adsorption.

Fig. 2, SEM image of pomegranate peel before adsorption.

Fig. 3, SEM image of pomegranate peel after adsorption.

3.2 FTIR characterization of pomegranate peel

The FTIR analysis of PP before and after Cr (VI) binding is offered by Figure 4. FTIR analysis was utilized to show the variation in the functional groups before and after adsorption. The test demonstrates several peaks, the peak at 2360.67 and 2341.7 cm^{-1} has been seen which could be as a result of chromium ion binding and adsorbing in the surface of the pomegranate peel.

Fig.4. FTIR analysis of pomegranate peel before and after adsorption (blue color is PP before adsorption, and red color is PP after adsorption).

3.3 Thermodynamic analysis

The thermodynamic properties like change in free energy ΔG° , enthalpy ΔH° , and entropy ΔS° have been obtained using:

$$K_c = \frac{C_{AC}}{C_e} \quad \dots\dots\dots(3)$$

$$\Delta G^\circ = -RT \ln K_c \quad \dots\dots\dots(4)$$

$$\log K_c = \frac{\Delta S^\circ}{2.303R} - \frac{\Delta H^\circ}{2.303RT} \quad \dots\dots\dots(5)$$

Vant Hoff equation (No.5) was utilized to evaluate ΔH° and ΔS° . From the intercept and slope for $\log K_c$ vs. $1/T$ as shown in Fig.5, the results are available in Table 1.

Fig. 5. Aplot of Vant Hoff equation for Cr(VI) adsorption onto PP at different Cr(VI) concentrations.

The values of ΔH° lie between 4.65 to 15.26 kJmol⁻¹ which proved the biosorption, the results indicate that biosorption is most effective. The positive values of ΔH° indicate the endothermic type of adsorption and it

decides the potential of physical adsorption. Since in the adsorption process the rising of system temperature tends to enhance adsorption of Cr (VI), these principles are different from chemisorption. ΔG° values are gained from Eq. 4, the negative values of ΔG° shown in Table 1, suggest it is highly appropriate and unprompted. Furthermore, it was noticed that negative values of ΔG° increased as the system temperature was increased, which indicates that the adsorption is more superior at high temperatures. The positive values of ΔS° are shown in Table 1, proved the rising in disturbance at the interface of chromium ion with PP.

Table 1. Thermodynamic properties of Cr(II) adsorption on Pomegranate Peels.

Cr(VI) conc.	ΔH°	ΔS°	ΔG° kJ/mol				
mg/l	kJ/mol	J/mol	20°C	30°C	40°C	50°C	R ²
10	4.65	18.86	-1.56	-1.73	-1.85	-2.11	0.998
20	7.32	26.38	-1.34	-1.43	-1.75	-1.93	0.978
30	14.42	48.53	-0.83	-0.99	-1.55	-2.21	0.954
40	15.26	49.49	-0.06	-0.68	-1.31	-1.43	0.943

3.4 Adsorption isotherms for the adsorption of Cr(VI) onto PP

The adsorption results were tested using Freundlich and Langmuir models at different temperatures. The parameters of each adsorption isotherm were obtained. The linear form of Langmuir isotherm is given by Eq. 6 [11]:

$$1/q_e = (1/q_m) \times (1/b) \times (1/C_e) + (1/q_m) \quad \dots(6)$$

It was demonstrated that the plot of $1/q_e$ versus $1/C_e$ displays a straight line (Fig.6), and the values of b and q_m are documented in Table 2. Also, the values of q_e estimated from the model as $q_e(cal.)$ is quite around the experimental values as $q_e(exp.)$. Thus, the Langmuir isotherm fits well the experimental data. The linear form of Freundlich isotherm is given by Eq. 7 [11].

$$\log q_e = \log K + (1/n) \log C_e \quad \dots\dots\dots(7)$$

It is observed that the $\log q_e$ versus $\log C_e$ gives a straight line relation as shown in Fig.7. The values of Freundlich constants are given in Table 2, the Freundlich isotherm is also complied because $q_e(exp.)$ values are near $q_e(cal.)$. In addition to that, the high correlation coefficient (R^2) for Cr (VI) adsorption by PP refers that the system undergoes both Langmuir and Freundlich models, with better fitted to Langmuir model.

Table 2 shows that n value of Cr (VI) is greater than 1; it is proved that adsorption is convenient for removal of Cr (VI) by pomegranate peel.

Table 2, Isotherms for Cr(II) removal by pomegranate peels.

Langmuir coefficients			Freundlich coefficients		
q_{max} (mg/g)	b (l/mg)	R^2	K (mg/g)	n	R^2
9.45	0.2	0.970	3.15	1.2	0.953

Fig. 6, Langmuir Isotherm for adsorption of Cr(VI) on PP.

Fig. 7, Freundlich Isotherm for adsorption of Cr(VI) on PP.

4 Conclusions

From the experimental results of this work, it can be concluded that pomegranate peel proved to be an efficient and economical natural adsorbent for remediation of Cr (VI) ions from industrial wastewater. The elimination efficiency of the pomegranate peel was 90%, and the highest possible adsorption capability was 9.45 mg/g. The FTIR and SEM analyses proved that pomegranate peel is a strong adsorbent because of complex structure and holes on its surface. Although, the adsorption capacity of pomegranate peel in comparison with Langmuir and Freundlich models refers that Langmuir is well fitted with the experimental data. Also, thermodynamic investigation demonstrates an endothermic adsorption as well as the process is unprompted and convenient.

List of symbols

Symbol	Definition (unit)
b	Constant (-)
C_{Ac}	Concentration of metal ion in the adsorbent (mg/L)
C_e	Equilibrium concentration of metal ion (mg/L)
C_i	Initial concentration (mg/L)
C_f	Final concentration (mg/L)
ΔG°	Change in Gibbs free energy (kJ/mol)
ΔH°	Change in enthalpy (kJ/mol)
K	Freundlich constant (-)
K_c	Equilibrium constant (-)
m	Mass of adsorbent (gm)
n	Freundlich constant (-)
q_e	Amount of adsorbed metal per unit weight (mg/g)
q_m	Maximum adsorption capacity (mg/g)
R	Gas constant (KJ/mol K)
ΔS°	Change in entropy (J/mol)
T	Temperature (K)
V	Volume of solution (mL)

References

1. N. Othman, S. Mohd-Asharuddin and Azizul-Rahman M-F-H. (2013).An Overview of fruit waste as sustainable adsorbent for heavy metal removal.
2. Masoudrohanimoghadam,NavidNasirizadeh, ZienabDashti and EsmeilBabanezhad. Removal of Fe(II)from aqueous solution using pomegranate peel carbon : equilibrium and kinetic studies.International journal of industrial chemistry (IJIC)a springeropen journal 2013 .4:19.
- 3.E.S.Z.ELAshtoukhy.,N.K.Amin,andO.Abdelwahab.(2008).Removal of lead (II)and copper(II)from aqueous solution using pomegranate peel as new adsorbant .Desalination.223,162-173.
4. T.V ,Ramachandra, N Ahalya., and R.D Kanamadi.(2008).Biosorption:Techniques and mechanisms .CES Technical Report 110.
5. K.Vijayaraghavan. and Y-S Yun.(2008).Bacterial biosorbent and biosorption.Biotechnology Advances.26,266-291.
6. H.K.Alluri.,S.R. Ronda.,S.SVigaya.,S.B Bondili.,V. Suryanarayana. And P Venkateshwar.(2007) Biosorption: An eco-friendly alternative for heavy metal removal .African journal of Biotechnology Vol.6(25) ,2924-2931.
7. EikaniMH,GolmohammadF,Homami SS (2012) Extraction of pomegranate (punica granatum l) seed oil using superheated hexane .Food Biprod process 91:32-36.
8. EL Nemr A (2009) Potential of pomegranate peel carbon for Cr(VI) removal from wastewater ,kinetic and isotherm studies ,J Hazard Mater 161:132-141.
9. Chandra Sekhra K, Kamala CT,Chary NSN ,Anjaneyulu Y (2003) Removal of heavy metals using a plant biomass with reference environmental control .Int J Miner Process 68:37-45.
10. Babel S ,kurniawan CT ,Chary NSN ,Anjaneyulu Y (2003) Removal of heavy Metals uptake from contaminatedwater: a review .J Hazard Mater 97:219-243.
11. Thamer J. Mohammed, and Raheek I. Ibrahim (2016), Remediation of Cu(II) from well water of Iraq using cortex of fruit and agriculture waste. Arabian J. for Sci. and Eng., 41:345–355.