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POMEGRANATE PEEL AS A SORBENT IN THE REMOVAL OF Pb (II) FROM WASTEWATER

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Abstract: Pomegranate peels were chosen for the ability to adsorption of lead ions from the simulated wastewater. It has been tested under various experimental parameters such as pH, contact time, weight of sorbent, and concentration of metal and effect of temperature. The outcomes indicated that adsorption of Pb (II) ions on the pomegranate peels can be appropriated with the Langmuir adsorption model and pseudo-second-order kinetic model. Result showed that the Pomegranate peel was found to be low-cost adsorbent for the removal of contaminates. A good efficiency to remove toxic metal ions was achieved by usage of such by- product.

Keywords: *Pomegranate peels; Lead; Sorption; Isotherms; Kinetics; Wastewater*

قشور الرمان كوسط ماز في إزالة ايونات الرصاص من المياه الملوثة المُصنعة

الخلاصة: تم إختيار قشر الرمان لأختبار كفاءته في إمتزاز أيونات الرصاص من المياه الصناعية المُحاكاة. و تم اختبار عدة عوامل لبيان تأثيرها على عملية المعالجة منها الدالة الحامضية و وقت التماس و وزن المادة المازة و كذلك تركيز الملوث كما تم اختبار تأثير درجة الحرارة.قد تم تحليل البيانات المختبرية بواسطة معادلات Langmuir و Freundlichو قد بينت النتائج التحليلية توافقها مع موديل لانكمير ولقد تم دراسة حركيات (kinetics) عملية الأمتزاز وان البيانات المستحصلة تم اختبارها بواسطة معادلات تفاعل الدرجة الاولى والثانية و قد توافقت مع الدرجة الثانية.و ان قشر الرمان اثبت اداءه الجيد في ازالة معدن الرصاص.

الكلمات الدالة: *قشور الرمان، الرصاص، امتزاز، ايسوثيرم، الحركية، المياه الصناعية.*

1. Introduction

The existence of heavy metal ions of the transition chain, namely: Cu, Fe, Ni, Pb, etc. in an environment is a major concern because of their toxicity for many forms of life. Contrary to organic pollutants, most of which are exposed to biological decomposition, the metal ions do not degrade to innocuousterminating products [1]. Lead is highly toxic heavy metal, and is aimed organs such as bones, brain, blood, kidney, and thyroid gland

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[2]. Existence of lead in leakage and Poisonous cause the other negative impacts on the receiving waters in water regime. Even the concentration of heavy metals is very low; it has toxic effect on aquatic life. Major source of lead and cadmium in water is from Industrial Processes i.e. electroplating, paint, pigment, the steel industry, textile industry, the metal finishing and manufacturing and assembling batteries [3].

Traditional ways to remove metals involve chemical precipitation, chemical oxidation and reduction, ion exchange filtration, electrochemical treatment, reverse osmosis, membrane technologies and evaporation. The main drawback of the traditional treatment techniques is production of the toxic chemical sludge and discarded/treatment becomes expensive and not environmentally-friendly. Thus removing toxic heavy metals to an ecologically secure manner in a cost effective and in a friendly way suppose considerable importance, [4][5]. In the last period, the researchers interested to find low-cost adsorbents that have metal binding capabilities. Agricultural residues have been fully considered for the removal of metals from wastewater. Which involve peat, wood, pine bark, banana pith, soybean and cotton seed hulls, peanut shells, hazelnut shell, rice husk, saw dust, wool, orange peel, compost and leaves [6].

The consumption of Pomegranate fruit is widely as fresh and in various products like a juice, jams and wine. Pomegranate peel is full with ellagitannins (ETs) such as punicalagin and its isomers, in addition to fewer quantities of punicalin (4,6-gallagylglucose), gallagic acid, ellagic acid (EA) and EA-glycosides [7]. It is a substance consist of many components, involving polyphenols, ellagictannis and Gallic and ellagic acids[8]. In the present study, the capability of pomegranate peel to remove Pb (II) from aqueous solutions has been investigated in a batch process. The impacts of various parameters such as pH of the aqueous solution, contact time of biosorbent, and different biomass quantity have been studied. Isotherm parameters were conclusion by using biosorption measurements.

2. Materials and approaches

2.1. The preparation of sorbent

Biosorbent were prepared from Pomegranate peel to remove Pb^{+2} ions. These peels collected from the juice market; washed and then dried by using oven at the temperature of 110 °C for one day, then crushed and sieved to obtain particles with size 0.5 mm.

2.2. The preparation of Lead solution

Artificial wastewater used in this experiment containing the required concentration of lead was being prepared by dissolving the calculated quantity of the Pb $(NO_3)_2$ in distilled water. pH of solution was adjusted to desired value by adding 0.1 M HNO_3 or NaOH as required. The mass these metals required to achieve the required concentration was calculated according to equation (1) assuming complete dissolution [4]:

$$W = V \times C_i \times \frac{M.wt}{At.wt} \quad (1)$$

Where:
W= weight of the heavy metal salt (mg).
V= the solution volume (L).
C_i= initial concentration of metal ion in solution (mg/L).
M.wt= molecular weight of a metal salt (g/mole).
At.wt= atomic weight of the metal ion (g/mole).

2.3. Batch experiments

The sorption of Pb (II) on pomegranate peel sorbent was studied by batch method. In each experiment 100 ml of metal solution with concentration of (50 mg/L) was adopted in 250 ml Erlenmeyer flask. Weighed a desired dose quantity of sorbent (0.15-0.55 g) and added to every conical flask; were agitated throughout the orbital shaking incubator with speed of 200 rpm for 2 hours. The samples were taken at various periods of time, and then separated the supernatant by filtration and measured by Atomic Absorption Spectrometer (AAS) for remaining heavy metal content.

3. Results and discussion

3.1 The impact of pH

Usually, the pH of solution plays a significant role in the sorption process. For the purpose of study the impact of pH on the removal of lead by using Pomegranate peel as sorbent; 100 mL of 50 mg/L metal solution was used. Experiments were performed in pH of 2, 4, 6, and 8. Hydrochloric acid (HCl) and sodium hydroxide (NaOH) were used for pH adjustment. "Fig.1" indicated that more than 4 pH value the sorption capacity impact was important for Pb^{+2} ions. At the pH 6.0 precipitations will happen to heavy metals, because of the insoluble metal hydroxides begin precipitating from the solutions at higher values of pH and lead to the real sorption studies very difficult. This situation should be avoided through the sorption tests that distinguish between the sorption and precipitation metal removal becomes difficult [9]. At low value of pH, the competition would be between the proton and metal ions on the active binding sites. The protonation of active sites therefore prefers to reduce the metal sorption. At low value of pH about 2 each the binding sites can be Protonated, and thus desorbing all the originally bound metals from the biomass. pH dependence by the metal uptake could be relatedto a large extent to the different functional groups on the biomass surfaces and also the chemistry of metal solution [10].Therefore optimum lead biosorption process will be at pH 4.

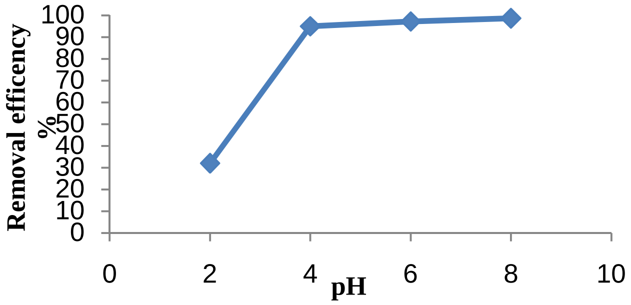

Figure 1.Impact of the pH on Pb (II) removal by using Pomegranate peel.

3.2 Impact of sorbent dose

Quantity of sorbent is one of the important parameters used to get the quantities removal of metal ion. Sorbent amount was studied by varying the quantity of Pomegranate peel (0.15- 0.55 g) in volume of 100 mL and about 50 mg/L of metal solution. Sorption of metal ions was increased as the sorbent amount increased. Result was expected due to a constant initial concentration of metal which increases the amount of adsorbent that supply larger surface area or adsorption site[11].The higher removal efficiency was achieved by using 0.5 g/100 ml sorbent dosages "Fig.2".

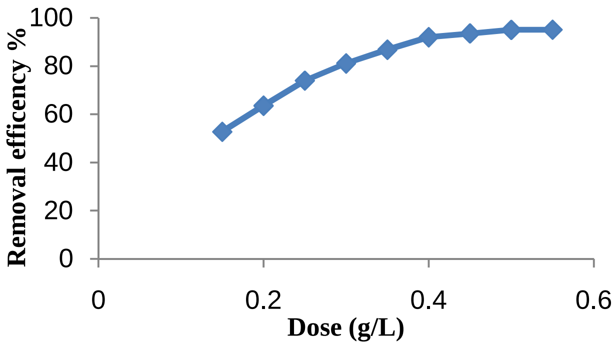

Figure 2.Impact of sorbent quantity on removal of Pb (II) using Pomegranate peel.

3.3 Impact of contact time

Plot of % efficiency of removal versus time is presented in "Fig.3". The result showed that the biosorption of Pb (II) has increased with the increase in time. In the beginning this increase was fast and then slow removal was noted until equilibrium. Equilibrium was founded after a 60 min. In the beginning, the rate of biosorption was speedy because of an adsorption of metal ion particles on the upside surface of an adsorbent. And then became slow because of the slow passage of metal ion particles in the internal structure of the adsorbent [12].

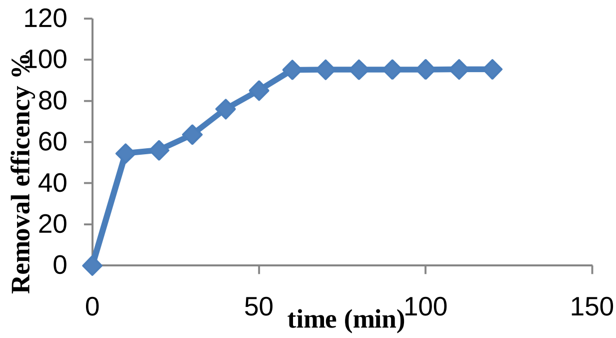

Figure 3.Effect of time on of Pb (II) uptake using Pomegranate peel.

3.4 Sorption isotherms

Adsorption data analysis is essential to develop the biosorption isotherms, and the interaction between adsorbent and sorbate may be identified by the sorption models. In this study the Langmuir, Freundlich isotherm models were investigated, [13].

3.4.1 Langmuir isotherm model

The Langmuir isotherm model implies that adsorption on a surface of adsorbent is compatible in quality. A saturated monolayer curve can be represented by the expression, [14]:

$$q_e = \frac{q_m b C_e}{(1 + bC_e)} \qquad (2)$$

where: q_e is the metal ions that sorbed on a biomass (mg/g), q_m is the maximum capacity of adsorption for monolayer coverage (mg/g), b is the constant relevant to affinity of a binding site (L/mg), and C_e is the concentration of metal ions in the solution at equilibrium (mg/L). The Langmuir model most often used to describe sorption isotherm which limited by the defaults of unified capacities of sorption on an adsorbent surface. Equilibrium constant of an adsorbate-adsorbent and the monolayer ability b and q_e have been identified by the slope- intercept from the Langmuir plot in "Fig.4".

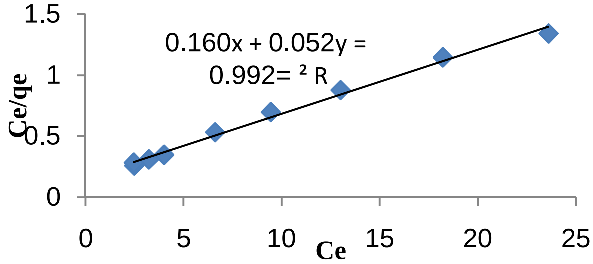

Figure 4.Langmuir plot of Pb (II) sorption on Pomegranate peel.

3.4.2 Freundlich isotherm model

The Freundlich isotherm is an experimental relation finding the interplay between adsorbate particles and diverse surfaces. The expression of linear equation is [15]:

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

Where: Kis the constant indicative of the relative sorption ability of adsorbent (mg/g). 1/n is the constant pointing to sorption intensity. Each of K and n are constants, and are being shows how the sorption and the degree of non-linear between solution and concentration, respectively. The plots of linear Freundlich are acquired by plotting log q_e vs. log C_e from which adsorption coefficients "Fig.5". All of the constants from Langmuir and Freundlich isotherms are shown in Table 1.

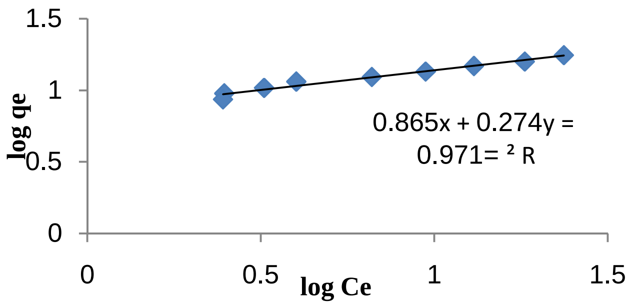

Figure 5.Freundlich plot of Pb (II) sorption on Pomegranate peel.

Table1. Langmuir, Freundlich isotherms Parameters for the Pb(II) sorption onto pomegranate peel.

Langmuir model	Lead (II)	Freundlich model	Lead (II)
R^2	0.992	R^2	0.971
q_m	19.231	1/n	0.274
B	0.325	k	7.328

3.5. Sorption kinetic models

Kinetic study is essential to improve the various operating conditions for the adsorption. Different kinetic models have been proposed to explain the system of reactions. The kinetics analysis of Pb (II) on the Pomegranate peels using pseudo-first order, pseudo-second order models; application of both kinetic models was specified by finding the coefficients of determination (R^2). At a high value of R^2, the model is better applied to the data[13].Pseudo-first order kinetic model is depending on the reality that the concentration change of Pb (II) with respect to time is fit to the power one. Differential equation described as, [16]:

$$\ln(q_{eq} - q_t) = \ln q_e - k_1 t \qquad (4)$$

While, the mechanism of adsorption over a full range of a contact time is described by the pseudo-second order kinetic model. The different equation is appeared as, [17]:

$$\frac{t}{q_t} = \left(\frac{1}{k_2 q_{eq}^2} + \frac{t}{q_{eq}}\right) \qquad (5)$$

Where q_{eq} is a quantity of metal sorbed at equilibrium (mg/g); q_t is a quantity of metal sorbed at time t (mg/g); and k_1 is the equilibrium rate constant of pseudo first sorption (1/min) and k_2 is the pseudo-second order rate constant (g/mg h). The slopes and intercept of ln (q_e-q_t) vs. t plot "Fig.6a" shown pseudo first order rate constants (k_1) and q_e. A plot of t/qt versus t “Fig.6b” was used to determine the pseudo-second-order rate.

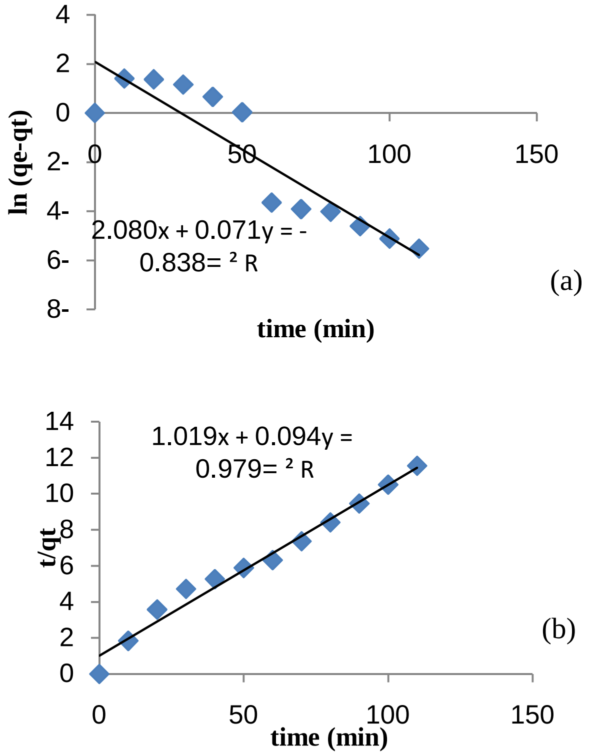

Figure 6. (a) Pseudo-first-order (b) Pseudo-second-order plots of Pb(II) on Pomegranate peel.

Table2. The sorption rate constants, practical and theoretical values q_e of the pseudo-first- and –second-order reaction kinetics for component systems.

Lead (II)	$q_{eexperimental}$ mg/g	Pseudo-first-order			Pseudo-second-order		
		k_1 1/min	$q_{ecalculated}$ mg/g	R^2	k_2g/mg.min	$q_{ecalculated}$ mg/g	R^2
	9.53	0.071	8.0045	0.838	0.00867	10.6383	0.979

3.6 Impact of Temperature and Thermal Study

The impact of temperature on removal of Pb (II) by using peels of Pomegranate was suggested by Implementation experiments of 50 mg/L initial concentration of metal ion at 298, 308, and 318 k. "Fig.7" showed that sorption decrease by rising temperature, which indicates that the process is exothermic in nature.Thermal parameters Gibb's free energy (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°) have been calculated by the next equations [18]:

$$\ln K_d = \left(\frac{\Delta S^\circ}{R}\right) - \left(\frac{\Delta H^\circ}{RT}\right) \qquad (6)$$

$$\Delta G^\circ = \Delta H^\circ - \Delta S^\circ T \qquad (7)$$

Where K_d is the distribution coefficient, ΔH°, ΔS° and ΔG° are change in enthalpy (kJ/ mol), entropy (J/ (mol K)) and free energy (kJ/ mol), respectively. R is the gas constant (8.314 J/mol K) and T is the temperature (K). The values of thermodynamic parameters are presented in Tables 3 and 4.

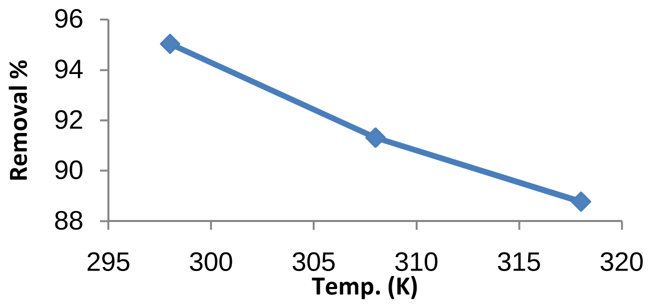

Figure7.Effect of Temperature on of Pb (II) removal using Pomegranate peel.

Table 3.The distribution coefficients at different temperature.

	k_d			R^2
	298k	308k	318k	
Lead (II)	19.16129	10.52074	7.912656	0.966

Table 4.The thermal parameters of Pb(II) ions removal on pomegranate peel.

	ΔH(J/mol)	ΔS (J/mol K)	ΔG(kJ/mol)		
			298K	308K	318K
Lead (II)	-34.9604	93.1168	-27.7838	-28.7149	-29.6461

The passive values for the ΔGin all examined temperatures showed the sorption is spontaneous. The passive value of ΔH, indicating the process is exothermic nature, and the positive value of ΔSshowsan increase in randomness in a solid/solution interface through a biosorption of Pb (II) ions Pomegranate peels.

4. Fourier-Transform Infrared Analysis (FTIR)

FTIR spectroscopy analysis offers excellent information on the nature of the functional groups present on the surface of the pomegranate peels. The FTIR spectra of loaded (Pb^{2+}) pomegranate in the range of 400–4000 cm^{-1} were performed to find out which functional groups were responsible of the adsorption process and are shown in figure 8. In figure (8), the unloaded pomegranate peel shows as the number of sorption peaks, appearing the complexity of the pomegranate peel. The spectrum pattern of loaded pomegranate peel occurred changes in the peak adsorption in comparison to unloaded pomegranate peel which caused by sorption process. The main roles of each functional group in this study are summed up in Table 5.

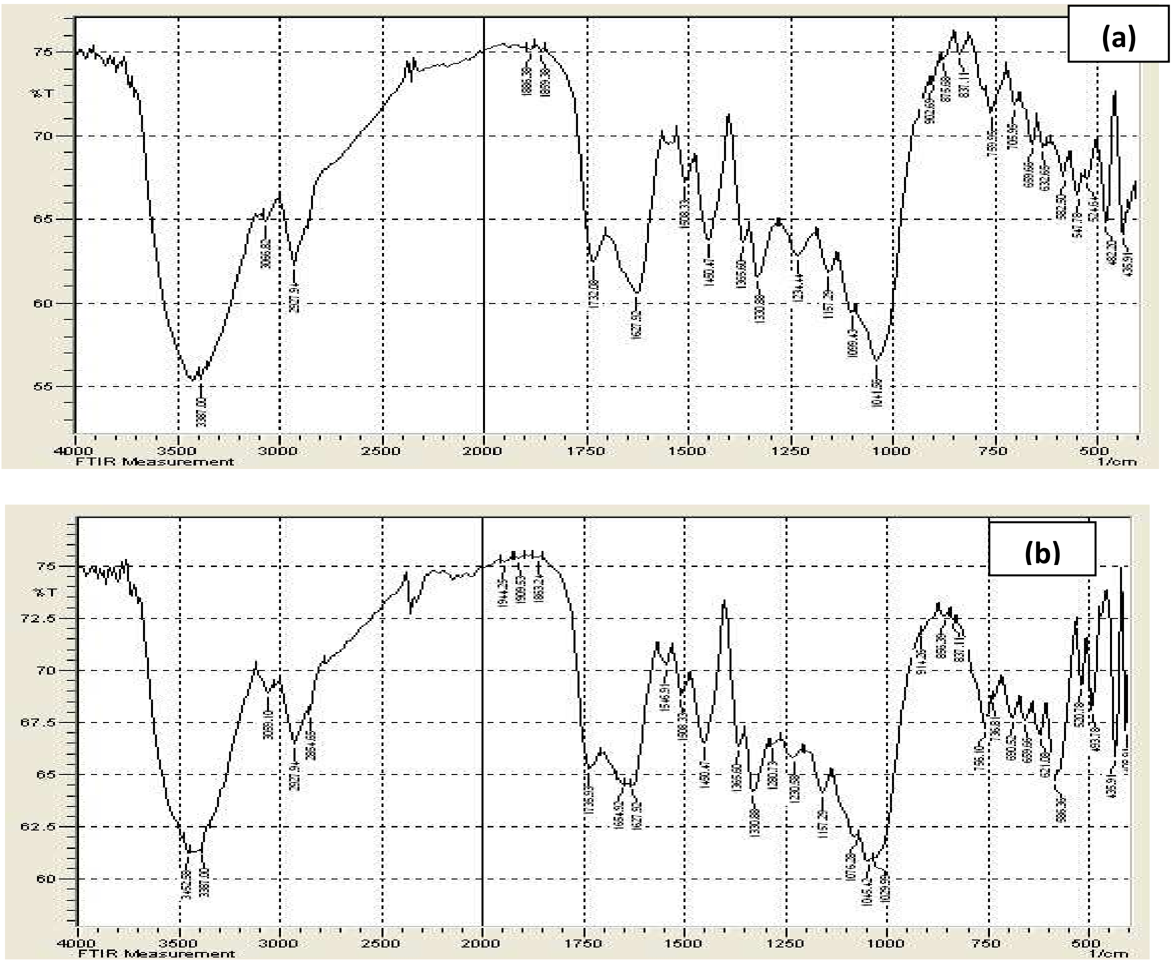

Figure 8: FT-IR of Pomegranate biosorbent (a) before and (b) after loaded of Pb (II)

Table 5.Function collections before and after PGP biosorbent with Pb (II)

Wave number (cm^{-1})	Assignment Groups	After adsorption (cm^{-1})
3406.00	Carboxylic, Amides, Amine,	3452.58
3066.82	Carboxylic acid, Hydroxyle, Alkenes	3059.10
1732.08	Carboxylic	1735.93
1234.44	Carboxylic acid	1236.58
1157.29	Carboxylic acid	1159.29
1041.56	Carboxylic acid	1045.42
865.86	Aromatic	875.39

5. Conclusions

From this search, it was found that the Pomegranate peel was used successfully as sorbent for sorption of Pb (II) from aqueous solution. The isotherm equilibrium examinations assured that the Langmuir form was the best model for the sorption process. The maximum adsorption potential of pomegranate peel adsorbent for Pb (II) removal was19.23 mg/g. Pseudo-second-order reaction kinetic has provided a factual description of removal of Pb (II) with suitable Practical and calculated values of qe.

Also correlation coefficients are higher in pseudo-second-order kinetics. The process was exothermic nature.

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