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LEMON PEEL AS NATURAL BIOSORBENT TO REMOVE PHOSPHATE FROM SIMULATED WASTEWATER

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Abstract: Lemon peel, a discarded agro-waste, was used as a biosorbent for removal of phosphate from simulated wastewater by sorption process. The characteristics of this adsorbent were tested by using FTIR in order to study the chemical compounds and oxidizing compounds, also to know the functional groups of organic compounds such as amino groups, carboxyl, hydroxyl and carbonyl. The influence of various practical factors such as pH; adsorbent dosage, contact time, initial concentrations of phosphate and temperature have been investigated through a set of batch experiments on the removal process efficiency. Equilibrium isotherm and kinetic study models of phosphate sorption onto adsorbents were also studied, Langmuir isotherm was found to be the appropriate equation and a second-order kinetic model was used to calculate the kinetic constants of inclusive adsorption rate. The results indicated that adsorption is an endothermic process for phosphate removal.

Keywords: *Lemon peel; adsorption; phosphate; isotherms; temperature.*

قشور الليمون كوسط طبيعي ماز لأزالة الفوسفات من المياه الملوثة المُصنعة

الخلاصة: أجري هذا البحث لدراسة إمكانية استخدام قشورالفاكهة كوسط ماز لإزالة الفوسفات من المياه الملوثة. و تم اختيار قشرة ثمرة الليمون كوسط طبيعي لأمتزاز الفوسفات من مياه الصرف الصحي المحاكاة، و قد تم أولا اجراء فحص التحليل الكيفي لقشرة ثمرة الليمون باستخدام جهاز الأشعة تحت الحمراء لغرض دراسة المركبات الكيميائية و المركبات المؤكسدة و معرفة المجموعات الفعالة للمركبات العضوية مثل المجموعات الأمينية،الكربوكسيلية، الهيدروكسيل و الكربونيل. كم تمت دراسة العوامل المؤثرة على عملية الأمتزاز مثل قيمة الدالة الحامضية ، كمية القشور المستعملة, زمن التماس بين المادة الممتزة و السطح الماز, التركيز الأولي للعناصر الملوثة و تأثير تغير درجة الحرارة. تم تحليل البيانات الناتجة من عملية الأمتزاز بواسطة موديلات لانكمير و فريندلج و اختبار البيانات الحركية من الدرجة الاولى و الثانية و قد أظهرت النتائج أن موديل لانكمير هو المفضل أكثر و ملائمتها مع الدرجة الثانية. وكانت نسبة الأزالة تزداد بزيادة الحرارة وذات طابع ماص للحرارة وفقا لنتائج الحرارية.

الكلمات الدالة: قشور الليمون، الأمتزاز، الفوسفات، الايسوثرم، درجة الحرارة.

1. Introduction

Phosphorus is a vital component, which has a main contribution in the agricultural and industrial development [1]. Non- point source of phosphate is an igneous rocks phosphorous where these rocks are exposed to factors of weathering and erosion in addition to exploration and therefore phosphorus liberated in phosphate into the soil where absorbed by plant roots and this enters the live parts by eating these plants and

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when the plants die and animals decompose then back to the soil and water while the point sources include an industrial cleaning solvent, sewage processing and allowed industrial effluent [2].

An environmental effect of the presence of phosphates in the water is to stimulate plankton and water plants that supplied a nutritious substance for the other livings which lead to an increase in the overall biodiversity of the aquatic formation; but with continued phosphate loading and there is a accumulation of phosphate in the surface water ecosystem, the state of growing old process of lake or superficial water ecosystem will be rushed. Treatment processes for phosphate have been investigated in previous studies such as ion exchange, dissolved air flotation, and membrane filtration [3]. Generally the most suitable to remove the phosphate output in the industrial wastewater is adsorption technique. This process will be an attractive technology whether adsorbents are available and cheap.

Many researchers have utilized many of the fruit peel as an alternative to activated carbon for being expensive, the using of agricultural-residues as adsorbent is draw attention broadly because of their available in large quantities and low-costs in addition due to the fact that the particles are relatively high carbon content and the existence of porous structure [4]. The influence of sorbent depends up on a substantial extent on the omposition and biochemistry, especially on functional groups existing in cell wall polysaccharides. Carboxyl groups can acts as an active role in minerals sorption by algal sorbents [5]. Pectin, a cell wall polysaccharide of higher plants, is based mostly on galacturonic acid, and includes a large number of carboxyl groups; it has a familiar capability to preserve the cohesion of divalent cations. Thus, pectin-rich materials such as citrus peels, which are extracted pectin commercially, have a high natural ability for metal hooking. Numbers of pectin-rich by products were examined for their metal-binding capabilities, including an apple waste, sugar beet pulp, orange and banana peels, citrus and coffee husks, and various fruit materials, such as numerous kinds of citrus rinds [2].

Lemon peel is one of the citrus fruit peels that considered as a natural sorbent in this study to eliminate phosphate from simulated wastewater. Lemon is one of the important agricultural crops because it used as a constituents for cooking, as decoration, and as in juice in lemonade, carbonated beverages, and others [6].

1. The experimental approach

2.1 The reagents and Materials

Solutions have been prepared by melting KH_2PO_4 salt with distilled water and then diluted to get the required concentrations of phosphate. Utilized all reagents were from analytic reagent category.

2.2 Lemon peel as biosorbent

Citrus peels utilized in this study were gathered from the domestic fruit market in Baghdad, Iraq. It was washed with tap water, then by distilled water; dried by sunlight for few days, after that in a furnaceat 80 ^oC for one day. These dried peels were grinded and sieved to get particle size of 0.6 mm diameter.

2.3 Batch phosphate sorption experiments

Different parameters were investigated for removal of phosphate by sorption onto lemon peel such as pH, amount of adsorbent, phosphate concentration, and temperature. 100 ml water volume with desired phosphate concentration mixed with lemon peel (as adsorbent) in 250 ml Erlenmeyer flask was taken for all tests. After the equilibrium, liquidation samples by using 70 mm filters (Whatman) and the remaining phosphate concentration was measured using Spectrophotometer (thermo-genesys 10 UV, USA). The quantity of phosphate removed (q_e in mgg^{-1}) was specific as follows [7]:

$$q_e = \frac{V(C_0 - C_e)}{m} \qquad (1)$$

Where, q_e is the quantitative ability of adsorption in mg/g (pollutant/adsorbent), C_o is the initial phosphate concentration in solution; C_e is the phosphate concentration in solution after equilibrium has been reached, V is the volume of the solution that is adsorbent mass is exposed, and m is adsorbent mass.

3. Results and Discussion

3.1 FT-IR spectrogram

FTIR spectrogram of lemon peel before and after phosphate sorption is proved in "Fig.1". It suggested that functional groups such as amide, hydroxyl, methyl, and carboxyl were available in significant capacity in each samples of biosorbent. From FTIR spectrogram of phosphate loaded biosorbent it has seen that there was a change in wave number of prominent peaks related to the phosphate loading. This change in the wavelength appeared that there was a phosphate binding action occurring on the surface of lemon peel. This analysis shows that functional groups such as carboxyl, hydroxyl, carbonyl and other aromatic was participant in phosphate ion adsorption on the surface of biomass. The involvement of each functional group is briefed in Table 1.

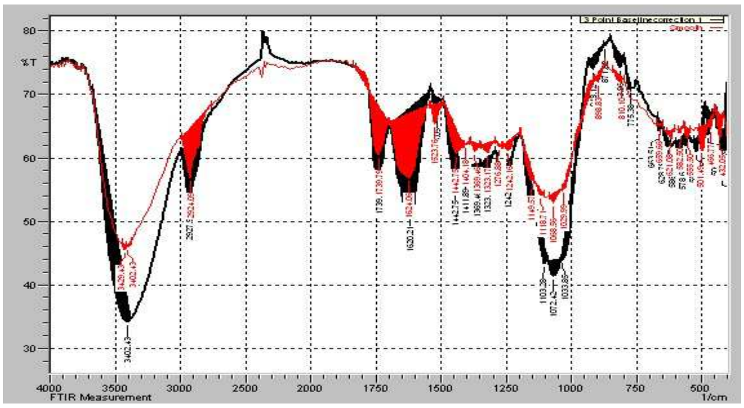

Figure 1: FTIR spectrogram of lemon peel before and after phosphate ion adsorption

Table 1. Functional groups in control of Phosphate sorption by Lemon peel.

Wave number (cm^{-1})	Functional groups	After sorption of phosphate (cm^{-1})
3402.43	Carboxylic acid, Amides, Alcohols, Amines	3429.43
2427.94	Alkanes, Carboxylic acid	2924.09
1620.21	Amides	1624.06
1516.05	Carboxylic acid	1523.76
1404.18	Carboxylic acid	1411.89
1238.30	Ketones, alcohols, Alkyl halides	1242.16
1103.28	Ketones, alcohols	1118.71
1068.56	Ketones, alcohols	1072.42
1029.99	Ketones, alcohols	1033.85
898.83	Aromatics	918.12
810.10	Aromatics	813.96
659.66	Alkyl halides	663.51
621.08	Alkyl halides	628.79
555.50	Alkyl halides	578.64
466.77	Alkyl halides	474.49

3.2 Influence of various pH values

The pH dependent experiments were conducted between 3.5 to 7.5 in 100 ml with 50 mg/l initial concentration of phosphate and 1.0 g lemon peel; these values of pH were selected in order to avoid the direct precipitation of phosphate. The tests were carried out at 150 rpm for 60 min at room temperature. The removal efficiency by using various value of pH is shown in "Fig 2". It was found that the maximum removal occurs at pH 5.5 and stabilizes from pH 6 to pH 8.

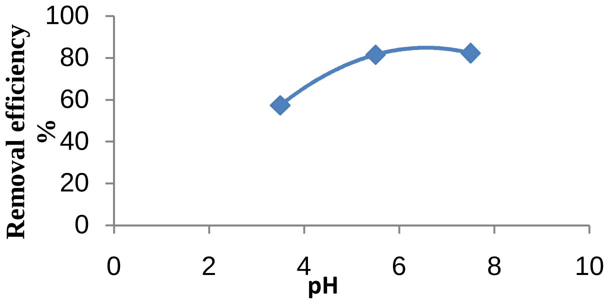

Figure 2. Influence of various pH value on Phosphate Adsorption

There are three forms of phosphate: $H_2PO_4^-$ (dehydrogenate phosphate anion), HPO_4^{2-} (hydrogen phosphate anion), or PO_4^{3-}(orthophosphate anion) "Fig.3", the form of phosphate in the solution is dependent on the .pH as described in "Fig.4" [8] ·and equation 2, 3, 4 [9]. There are $H_2PO_4^-$and HPO_4^{2-} types in the pH range between 4 and 10. The concentration of $H_2PO_4^-$ types is higher for pH lower than 7 whereas HPO_4^{2-} types occupy for pH range 7-10. When the pH is between 10 and 12 HPO_4^{2-} dominatesthe types of PO_4^{3-} while at pH is higher than 12.5 the concentration of PO_4^{3-}

types becomes considerable. Moreover, the $pK_a$of propyl amine (grafted on SBA-15) is known to be 10.6 [9].

$$H_3PO_4 \longleftrightarrow H_2PO_4^- + H^+, \quad pK1= 2.15 \tag{2}$$

$$H_3PO_4^- \longleftrightarrow H2PO_4^{2-} + H^+, \quad pK2= 7.20 \tag{3}$$

$$H_3PO_4^{2-} \longleftrightarrow PO_4^{3-} + H+, \quad pK3= 12.33 \tag{4}$$

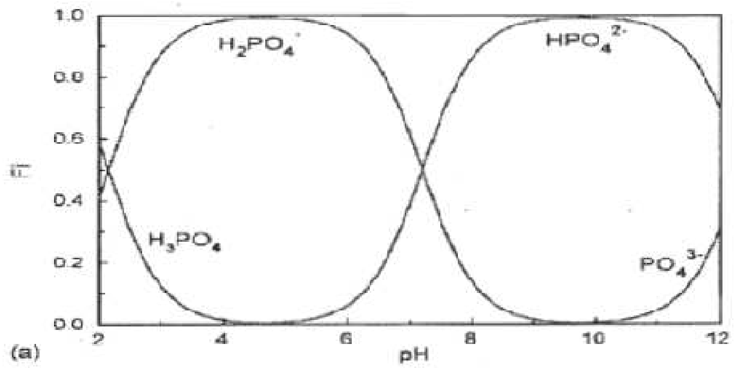

Figure 3.Forms of phosphate species in the solution.

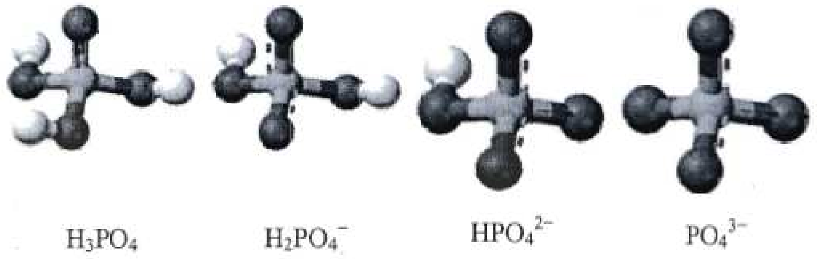

Figure 4. The distribution graphic of phosphate types as a function of pH

Boujelben et al: (2008) [4] mentioned that the highest removal efficiency of PO_4^{3-} was at around pH 5 (0.25 mg/g) on iron coated natural and engineered sorbent. Similar observations have been found by Anirudhan et al. (2006) [1], Das et al. (2006) [3] and Saad et al.(2007) [7] who that the higher adsorption of phosphate ions happen in pH 5 with using the DMAHP (98.7%), LDHs (91.7%) and ammonium functionalized MCM-48 (34 mg/g). In the case of iron coated natural, DMAHP and LDHs, the higher pH value decreases the adsorption of phosphate because of the increasing of competitive influence of OH^- for adsorption on these adsorbents. While Saad et al. (2007) [7] explain the decreasing of phosphate adsorption into ammonium functionalized MCM-48 above the pH 8 to the neutral charge on the adsorbent which loses the electrostatic attraction toward the accruing negatively charged phosphate anions HPO_4^{2-} and PO_4^{3-} in the solution [5].

3.3 Influence of various amount of sorbent

The influences of sorbent doses on equilibrium uptake of phosphate was studied with masses of lemon peels between 0.5- 2.0 g per 100 ml of water contained 50 mg/l of phosphate with pH 5.5, 150 rpm for 60 min at room temperature. "Fig.5" is illustrated the results. Based on these results 1.5g was taken as optimum adsorbent dose for the rest experiments.

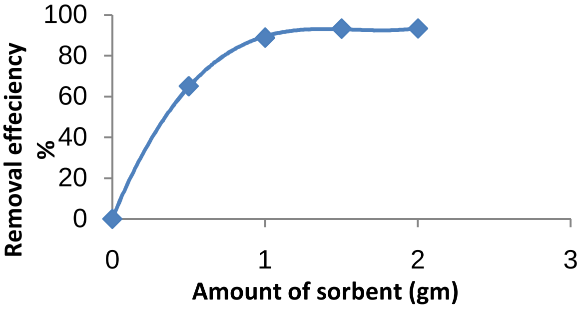

Figure 5. Influence of various amount of sorbent on the removal efficiency of phosphate

3.4 Impact of contact time

The impact of contact time of lemon peels for the removal of phosphate was studied at room temperature; the experiments work out at 120 min. It is observed that "Fig.6" the removal efficiency was higher in the starting till 50 min and, after that, the adsorption rate become practical very slow and after 60 min. it starts unchanged. The variance in the grade of adsorption possibly is due to the reality that in the beginning all the sites on the surface of the adsorbent were empty and the solute concentration gradient was comparatively high. As a result, the range of phosphate elimination reduced to increase the duration of exposure, which based on the number of empty sites on the surface of dose [10]. Because of these results 60 min was taken for as the optimum time for the remaining experiments.

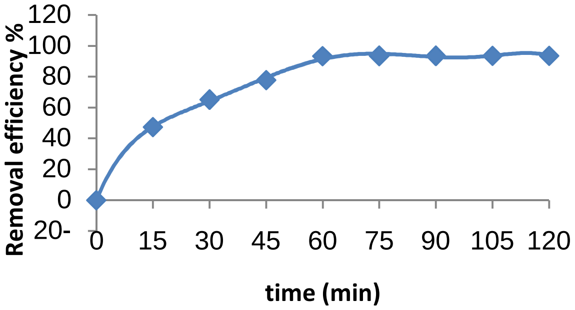

Figure 6. Influence of contact time on the removal efficiency of phosphate

3.5 Influence of different concentrations of phosphate

The influence of varying concentrations of phosphate (50-100-200 mg/l) in the existence of lemon peel as an adsorbent was investigated; all tests were conducted at room temperature and 150 rpm agitation speed. The result shown in "Fig.7", from this figure, it is found that an increase in initial phosphate concentrations decreased the removal percentage of phosphate for the same adsorbent loading. This has been attributed to the higher initial concentration ratio of phosphate molecules to the space available; therefore sorption is influenced by beginning concentration [5].

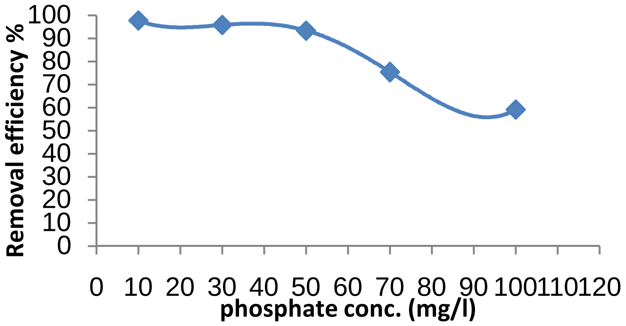

Figure 7. Influence of phosphate concentration.

3.6 Isotherm model

Langmuir and Freundlich models were applied to establish sorption activity. Sorption isotherms evaluate the relation between the stability of pressure or concentration and quantity of adsorbate adsorbed by the unit mass of adsorbent at a constant temperature. The model of Langmuir is [11]:

$$q_e = \frac{q_m b C_e}{(1+bC_e)} \qquad (5)$$

Where: q_e is the sorbed phosphate ions on the biomass (mg/g), q_m is the maximum adsorption capacity for monolayer coverage (mg/g), b is the constant associated with attraction of binding site (L/mg), and C_e is phosphate ions concentration in the solution at equilibrium (mg /L).

And Freundlich model is [11]:

$$q_e = KC_e^{1/n} \qquad (6)$$

Where: $K_=$ constant indicative of the proportional adsorption ability of the adsorbent (mg/g), 1/n = constant expressive of the strength of the adsorption (both K and n are being expressive of the range of adsorption and the grade of non-linearity between solution and concentration, respectively). The results of both models are presented in Fig.8 and Table 2, respectively.

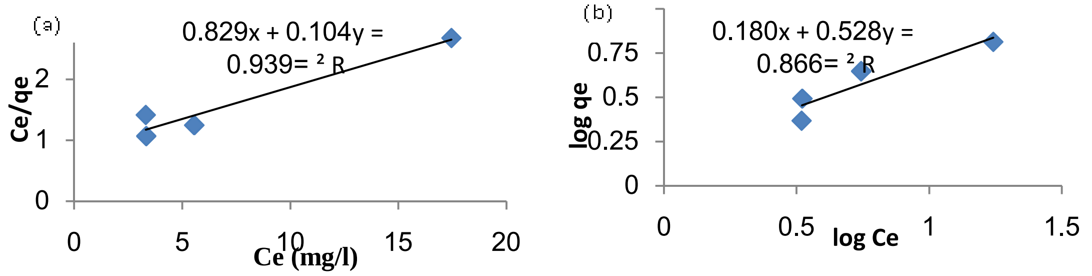

Figure 8. Isotherm models (a) Langmuir model, (b) Freundlich model

Table 2.Parameters of Isotherm forms

Langmuir coefficients	Value	Freundlich coefficients	Value
R^2	0.939	R^2	0.866
q_m	9.615	1/n	0.528
B	0.126	K	1.514

In comparison withthe experimental isotherms with the theoretical isotherm models appeared that the Langmuir equation acted as the richest suitable of the experimental data for lemon peel compared with other isotherm equations.

3.7 Adsorption kinetic

Adsorption mechanism of phosphate is explained by the adsorption kinetics models, which these are pseudo-first-order and pseudo-second-order. A study of adsorption kinetics plays an important role in the efficiency and field-deployment costs of a sorbent [12]. The pseudo-first-order and pseudo-second-order models, respectively, [13]:

$$\ln(q_{eq}-q_t)=\ln q_e - k_1 t(7)$$

$$\frac{t}{q_t}=\left(\frac{1}{k_2 q_{eq}^2}+\frac{t}{q_{eq}}\right) \qquad (8)$$

Where q_{eq} and q_t (both in mg g^{-1}) are the amount of phosphate adsorbed at equilibrium and at time correspondingly. K_1 (min^{-1}) and K_2 (g mg^{-1} min^{-1}) are the kinetics rate constants for the pseudo first- and second order models, correspondingly. "Fig.9" and Table 3 showed the results below:

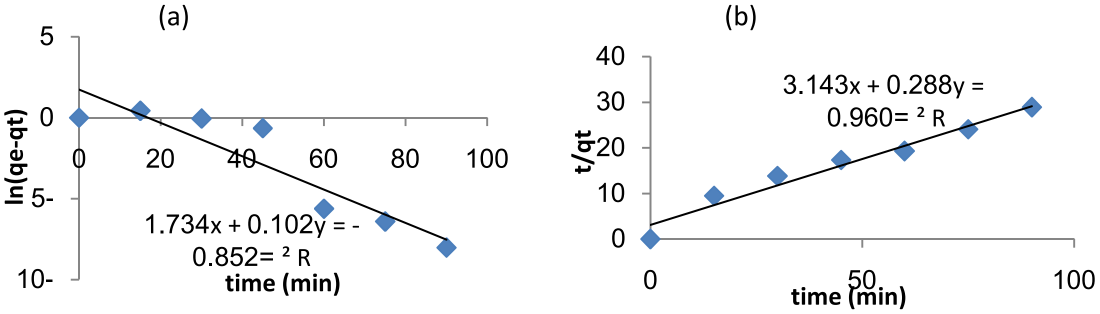

Figure 9. Kinetic models (a) Pseudo first order (b) Pseudo second order.

Table 3.Parameters of Kinetic Models

	$q_{e experimental}$	Pseudo-first-order			Pseudo-second-order		
		k_1 1/min	$q_{e calculated}$	R^2	k_2	$q_{e calculated}$	R^2
Phosphate	3.115	0.102	5.663	0.852	0.026	3.472	0.960

From Table 3 it found that the theoretic values of q_e(cal) accepted well with the experiential uptake values, q_e(exp.) in the case of pseudo-second-order model. Further, the coefficient of determination (R^2) was 0.960, suggesting that this sorption procedure can be described as well by using pseudo-second-order process.

3.8 Influence of temperature

The adsorption tests were realized to research the influence of temperature on the elimination of phosphate using lemon peels at different temperatures 20, 30 and 40 ^{0}C (293, 303 and 313 K) using phosphate solution having initial concentrations of 50 mg/l, agitation rate 150 rpm for 60 min and at constant adsorbent loading 1.5g. The thermodynamic parameters were studied application the next equations [10]

$$lnK_d = \left(\frac{\Delta S^\circ}{R}\right) - \left(\frac{\Delta H^\circ}{RT}\right) \qquad (9)$$

$$\Delta G^\circ = \Delta H^\circ - \Delta S^\circ T \qquad (10)$$

Where K_d is the distribution coefficient; ΔH, ΔS, and T the enthalpy, entropy, and temperature in Kelvin, respectively; R is the gas constant (8.314 J/mol K) and Gibbs free energy change ΔG^0. Influence of temperature change, the values of distribution coefficient and thermodynamic parameters are presented in "Fig.10", Tables 4 and 5, respectively.

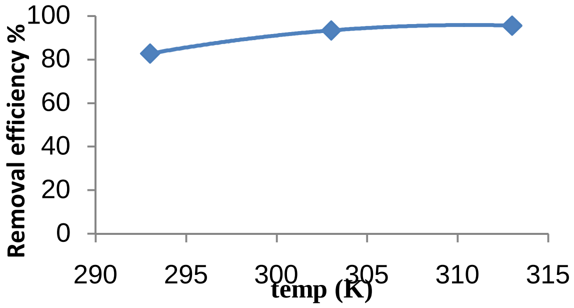

Figure 10. Influence of change in temperature on the removal efficiency of phosphate

Table 4: The distribution coefficients at various temperatures

Phosphate	k_d			R^2
	293 k	303 k	313 k	
	4.794	14.015	21.624	0.951

Table 5: The thermal parameters of Phosphate adsorption on the Lemon peel

Phosphate	ΔH(J/mol)	ΔS (J/mol K)	ΔG(kJ/mol)		
			293 K	303 K	313 K
	57.674	-210.677	-61.7283	-63.8351	-65.9418

From results it may be watched that the removal rate of phosphate on lemon peels increases with increasing the temperature. This indicates that the sorption of phosphate is favored at high temperatures and endothermic, so the adsorption extent increased with rising temperature.

4. Conclusions

Overall, the current search appears that:

- The lemon peel is effective biosorbent for phosphate ions removal from simulated wastewater when appropriate experimental provisions.
- Phosphate adsorption on lemon peel is extremely influenced by the value of pH. Best pH is found to be 5.5 and an adsorbent dosage of 1.5g/100 ml with removal efficiency of 93.34% at room temperature (approximately 25±5 ^{0}C).
- The most favorable exposure time is found to be 60 min.
- The adsorption isotherms of phosphate could be well described by Langmuir-model and Pseudo-second order kinetic model was found to be more suitable for the process.
- The removal efficiency and the capability of sorption were found to increase with rising temperature, showing the endothermic character of the process.

5. References

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