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I J N R E

Study of the kinetics and isotherm adsorption of Red SRL dye on agricultural waste - Grapefruit peels

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Abstract:

The purpose of this research is to explore the possibility of using Grapefruit peels for the removal of red SRL dye from aqueous solutions. The process was studied as a function of contact time, initial dye concentration and pH. Adsorption process was attained to the equilibrium within 15 min for initial dye concentrations of 40 mg. L^{-1}. An acidic medium was the optimum condition for adsorption of dye at room temperature. The maximum dye removal was obtained in the range of pH 2 to 5 initial using adsorbent dosage of 2 g.L^{-1} and agitation rate of 600 rpm. The adsorption capacity was found to be about 16.534 mg g^{-1}. Experimental data were analyzed by the Langmuir , Freundlich and Redlich-Peterson isotherms, and isothermal constants were calculated using a linear regression analysis. The Freundlich isotherm showed the maximum value of adsorption capacity was 106.951 mg.g^{-1}, and the correlation coefficient (R^2) was 0,9936.The study revealed that Grapefruit peels could be used as an effective for the removal of red SRL dye from aqueous solution under a wide a wide range of experimental conditions.

Keywords: Dye, Agricultural waste, adsorption kinetic, adsorption isotherm.

Résumé:

Le but de cette recherche est d'explorer la possibilité d'utiliser les pelures de pamplemousse pour l'élimination du colorant rouge SRL des solutions aqueuses. Le processus a été étudié en fonction du temps de contact, de la concentration initiale du colorant et du pH. Le processus d'adsorption a atteint l'équilibre en 15 minutes pour des concentrations initiales en colorant de 40 mg. L^{-1}. Un milieu acide était la condition optimale pour l'adsorption du colorant à température ambiante. L'élimination maximale du colorant a été obtenue dans la gamme de pH 2 à 5 en utilisant une dose d'adsorbant de 2 g.L^{-1} et une vitesse d'agitation de 600 rpm. La capacité d'adsorption a été trouvée à environ 16,534 mg.g^{-1}. Les données expérimentales ont été analysées par les isothermes de Langmuir, Freundlich et Redlich-Peterson, et les constantes isothermes ont été calculées en utilisant une analyse de régression linéaire. L'isotherme de Freundlich a montré que la valeur maximale de la capacité d'adsorption est de 106,951 mg.g^{-1}, avec un coefficient de corrélation (R^2) de 0,9936. L'étude a révélé que les pelures de pamplemousse pouvaient être utilisées comme un matériau efficace pour éliminer le colorant rouge SRL d'une solution aqueuse dans une large gamme de conditions expérimentales.

Mots clés: Colorant, déchets agricoles, cinétique d'adsorption, isotherme d'adsorption.

1. Introduction

Environmental pollution increases with increasing of various industries that use synthetic dyes for different kinds of applications. Most of pollutant and dyes or their degradation products are become toxic for aquatic and terrestrial environment. For this reason, treatment of wastewaters is one of the most important environmental issues.

Dye containing in wastewater produced in large volume from textile industries cannot be freely released into the surrounding aquatic systems without proper treatment because of its toxicity, which can endanger the living organisms and the flora. For this reason, several techniques are proposed to remove from polluted waters. The conventional ones include lime precipitation, adsorption onto activated carbon and ion exchange [1], [2].

Separation based on ion-exchanging resin and adsorption on active coal are known for their efficiency in the final treatment of heavy metals, but the elevated cost of these methods as well as some operating parameters limits their use for the low heavy metal concentrations [3].

Furthermore, some of these technologies have significant disadvantages, including incomplete dye removal, regeneration of other waste that require disposal and production of chemical sludge which can't be recovered [4], [5]. To overcome this limitation, Attention has been focused on natural agricultural waste materials such as seeds, fruit peel, nut shells, crop residues and fruit shells as low-cost and environmentally friendly adsorbents which are highly efficient and generally available in large quantities [6], [7].

Therefore, in this research Grapefruit peel (GFP= was used as adsorbent to eliminate lead ions from aqueous solution.

2. Materials and methods

2.1. Biosorbent material

GFP used as adsorbent in this study was collected in the region of Oued Sly -CHLEF (ALGERIA) during the period (from February to March) in the form of large chips. The GFP was washed with deionized water and dried in an oven at 120 °C for 24 h to remove the moisture content. The dried sample was crushed and sieved to a particle size range of 0.5–1.0 mm.

2.2. Physicochemical data of dye

The adsorbate SRL dye (was procured from the manufacture of the textile industry located in the city of Oran (West Algeria). To provide dye wastewater for use in adsorption studies, each basic dye was dried in an oven at 105 °C for 2 h. A total of 1000 mg was dissolved in 1 liter of double-distilled water (stock solution). From this stock solution (conserved at 4 °C), diluted solutions were prepared to conduct the different experiments.

2.3. Batch adsorption studies

Batch adsorption experiments were conducted in stoppered 250 mL Erlenmeyer flasks containing 0.2 g of GFP and 200 mL of SRL solutions with different initial dye concentrations (50, 100, 150, 200, 300 and 400 mg L^{-1}). The flasks were agitated at 600 rpm in a thermostatic water bath shaker at 20 °C. The final concentrations of SRL were determined at predetermined time intervals until the equilibrium was reached. The samples were periodically withdrawn and centrifuged at 3000 rpm for 20 min and the supernatant liquid was separated and analyzed for residual dye concentration.

2.4. Biosorbent material

The residual concentrations of SRL were analyzed by absorbance measurements using a double beam UV-Visible spectrophotometer (OPTIZEN 2010 type) at 630 nm, pH measures are done on a pH-meter (HANNA 120). The removal efficiency (E) of each tested system and the SRL uptake at equilibrium, Q_e (mg g^{-1}), was determined by the following equations:

$$E\ (\%) = \frac{C_0 - C_t}{C_0} \times 100 \qquad (01)$$

$$Q_t(mg\ g^{-1}) = (C_0 - C_t)\frac{V}{m} \qquad (02)$$

Where:

Q_t (mg g^{-1}) is the amount of dye sorbed by adsorbent, C_0 and Ct are the initial and final concentrations (mg L^{-1})of the dye, respectively; V is the volume of solution (mL), and m is the mass (g) of the adsorbents used. Each experiment was performed twice at least under identical conditions.

3. Results and Discussions

3.1. Effect of contact time

The effects of contact time on the amount of SRL adsorbed per unit mass of adsorbent were investigated under all experiment conditions, that is, concentration, temperature, and pH. It is seen that a rapid adsorption takes places at 10 min and thereafter the gradual increase in adsorption occurs with increasing contact time up to 30 min. After this time, the amount of dye removal was not significant and therefore the time of 30 min was fixed as the optimum contact time. A similar result has been recorded for the removal of dye by biosolid in a work done by [8].

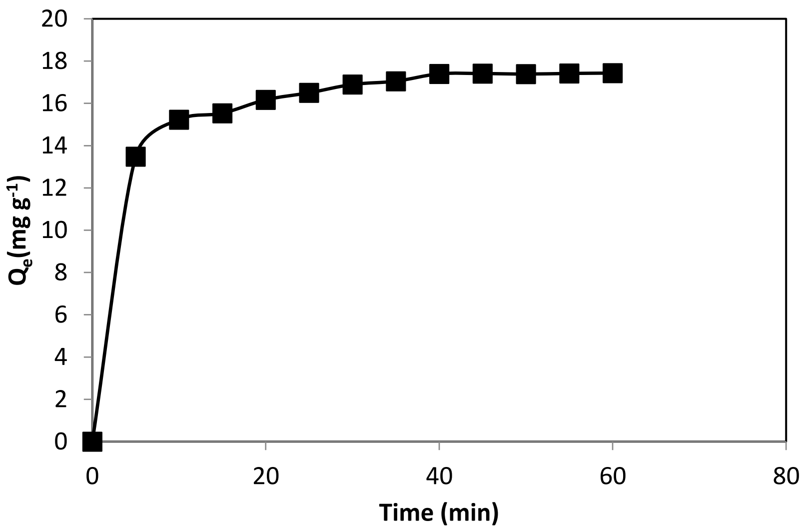

Fig.1. Effect of contact time on SRL dye adsorption onto GFP.
Conditions: initial dye concentration 40 mg L^{-1}; pH = 6; biosorbent content 3 g L^{-1}; T = 22°C.

3.1. Effect of initial concentration on the adsorption process

The effect of contact time was investigated with the initial SRL Dye concentrations of 40,60, 80, 100, 120, 150 and 200 mg L^{-1} at 22°C. Fig. 2 depicts the adsorption capacity as a function of contact time and initial concentration. The adsorption increased rapidly in the first 30 min, and thereafter gradually increased till the equilibrium. The adsorption capacity of GFP for SRL increased from 19 to 55 mg.g^{-1} as the initial dye concentration increased from 40 to 200 mg L^{-1}, indicative of the suitability of GFP for the adsorptive treatment of textile effluents.

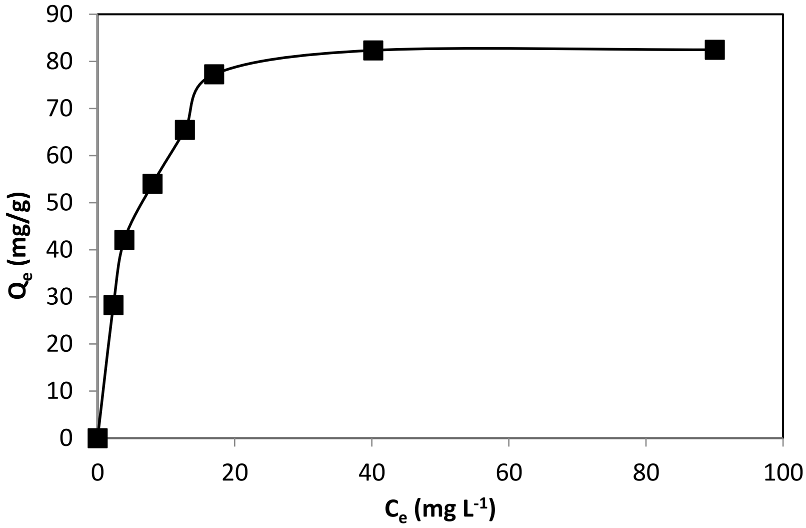

Fig.2. Effect of initial dye E5R concentration on adsorption.

3.2. Effect of solution pH on the adsorption process

The solution pH affects the surface charge as well as the degree of ionization and speciation of adsorbate. Fig. 3 shows the effect of solution pH on the removal efficiency of SRL onto GFP in the pH range of 2–12. From the figure, it was observed that the adsorption percent of SRL onto GFP increases from 70 to 85.04 while initial solution pH increases from 2 to 8. The maximum dye biosorption were observed at pH 8 and significantly decrease was observed in the removal efficiency thereafter. This behavior can be attributed to the interaction of cationic dye with more negatively functional groups (amine and carboxyl groups) in the structure of GFP. The decrease in adsorption capacity observed in alkaline pH could be due to the repulsion force between the negatively charged SRL molecules and hydroxide functional groups. At higher pH, the OH ions would compete with SRL anions for the binding sites, leading to the decrease of the removal efficiency. Similar observation has been reported in the adsorption of eosin yellow onto jute fiber carbon [9], [10].

3.3. Kinetic study

Experimental data related to the adsorption of E5R dye by DAS were applied to the Lagergreen pseudo-first-order equation, McKay pseudo-second-order equation and Weber and Morris intraparticle diffusion (Ho 1999, Weber 1963).

The pseudo-first-order equation is usually expressed as follows:

$$\log(Q_e - Q_t) = \log(Q_e) - \frac{k_1}{2,3}\, t \qquad (03)$$

The pseudo-second-order equation is expressed as:

$$\frac{t}{Q_t} = \frac{1}{k_2\,Q_e^2} - \frac{1}{Q_e}\,t \qquad (04)$$

Where:

Q_e and qt are the adsorbed amounts (mg g^{-1}) at equilibrium and at any time t, k_1 is the rate constant of pseudo-first-order adsorption (min^{-1}), k_2 (mg. g^{-1}. min^{-1}) is the rate constant of pseudo second-order sorption.

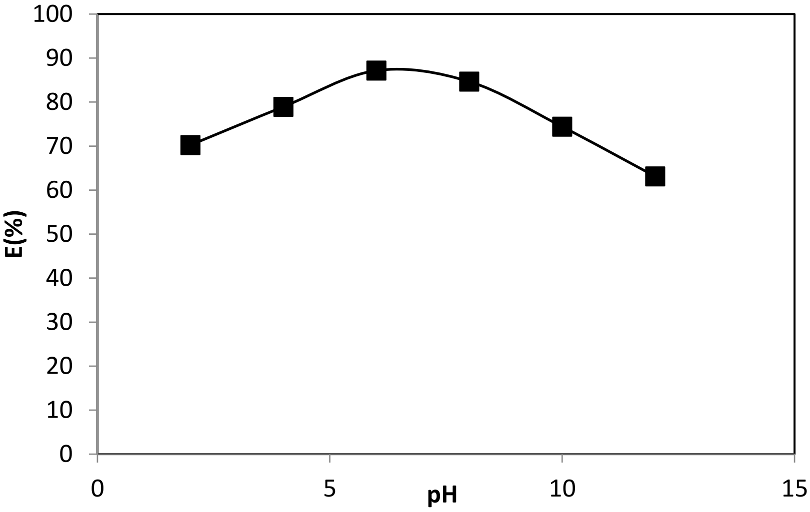

Fig.3. Effect of initial pH on adsorption of SRL onto GFP.

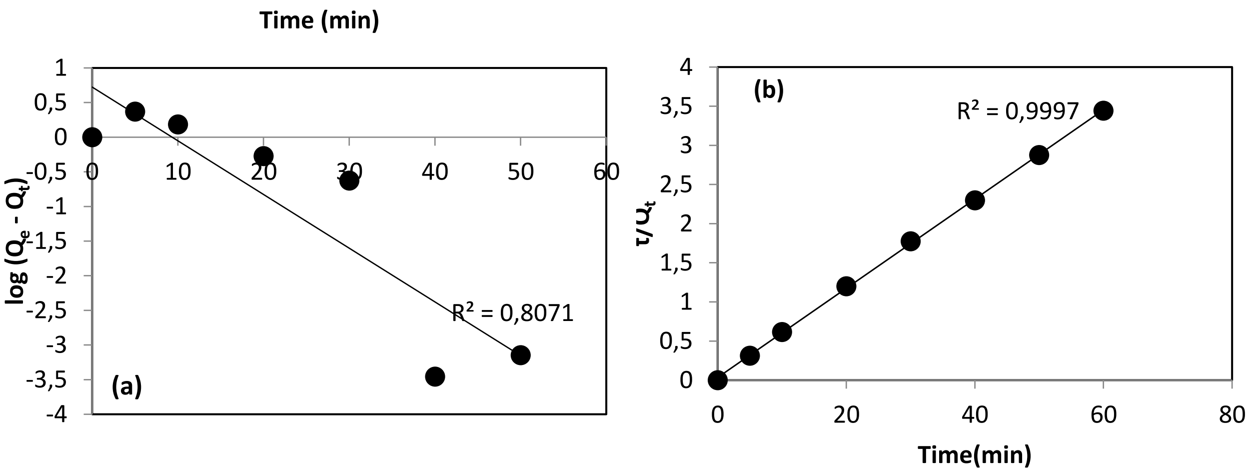

Fig.4. Kinetic study of SRL dye biosorption: (a) pseudo-first-order model; (b) pseudo-second-order model.

The kinetic parameters were obtained from the slopes and intercepts and are listed in Table 1. It is shown that, the pseudo -second-order kinetic model is more suitable to describe biosorption mechanisms of SRL dye onto GFP, due to highest values of correlation coefficients R2 = 0.999 and the good agreement of experimental equilibrium capacity values (Q_e^{exp}) with the theoretical values (Q_e^{cal}) calculated from Eq. (4).

Table 1. Kinetic parameters for biosorption of SRL dye by GFP.

Dried activated sludge	$Q_{exp.}$ (mg g^{-1})	Pseudo first-order			Pseudo second-order		
		Q_e^{cal} (mg g^{-1})	k_1 (min^{-1})	R^2	Q_e^{cal} (mg g^{-1})	k_2 (gmg^{-1} min^{-1})	R^2
	17.4	5.24	0.1771	0.80	17.54	0.09702	0.999

3.4. Biosorption isotherm

There are several mathematical models in the literature, can been used to describe biosorption isotherm. The Langmuir and Freundlich isotherm models are widely used for modeling equilibrium data.

The Langmuir model assumes uniform energies of adsorption onto the surface without transmigration of adsorbate in the plane of the surface. This model is valid for monolayer adsorption onto a surface containing a finite number of identical sites and it can describe by the following equation:

$$\frac{C_e}{Q_e} = \frac{1}{K_L\, Q_{max}} + \frac{1}{Q_{max}}\, t \qquad (05)$$

Where:

C_e is the equilibrium concentration (mg L^{-1}), Q_e is the amount adsorbed at equilibrium time (mg g^{-1}), and Q_{max} and K_L are Langmuir constants related to the adsorption capacity and energy, respectively.

The Langmuir model assumes uniform energies of adsorption onto the surface without transmigration of adsorbate in the plane of the surface. This model is valid for monolayer adsorption onto a surface containing a finite number of identical sites and it can describe by the following equation:

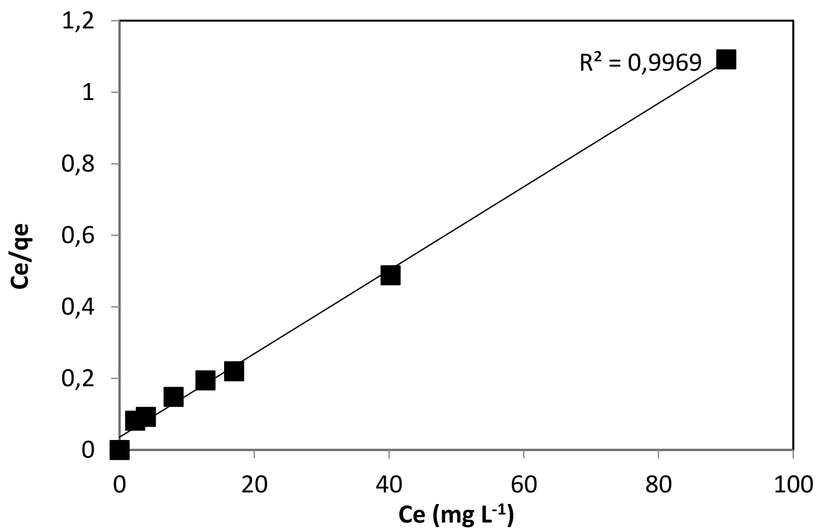

Fig.5. Langmuir isotherms adsorption of SRL onto GFP.

The results obtained from the Langmuir model for the removal of dyes onto CAS are shown in Table 2. The correlation coefficients showed strong positive evidence on the adsorption of dyes onto GFP follows the Langmuir isotherm. The applicability of the linear form of Langmuir model to GFP was proved by the high correlation coefficients $R^2 > 0.99$. This suggests that the Langmuir isotherm provides a good model of the sorption system. The maximum monolayer capacity Q_{max} obtained from the Langmuir is 85;84 mg g^{-1} this value, is in good agreement with Q_e founded experimentally.

The Freundlich adsorption isotherm is represented by the following equation:

$$\ln Q_e = \ln K_F + \frac{1}{n} C_e \qquad (06)$$

Where:
C_e is the equilibrium concentration (mg L^{-1}), Q_e is the amount of metal adsorbed at equilibrium time (mg g^{-1}), and K_F and n are Freundlich constants. n gives an indication of the favorability and K_F the capacity of adsorbent.

The obtained data from linear Freundlich isotherm plot for the adsorption of SRL onto CFP is presented also in Table 2. The correlation coefficients are lower than (0.85), indicating that Freundlich is not favorably to describe the adsorption of SRL onto GFP.

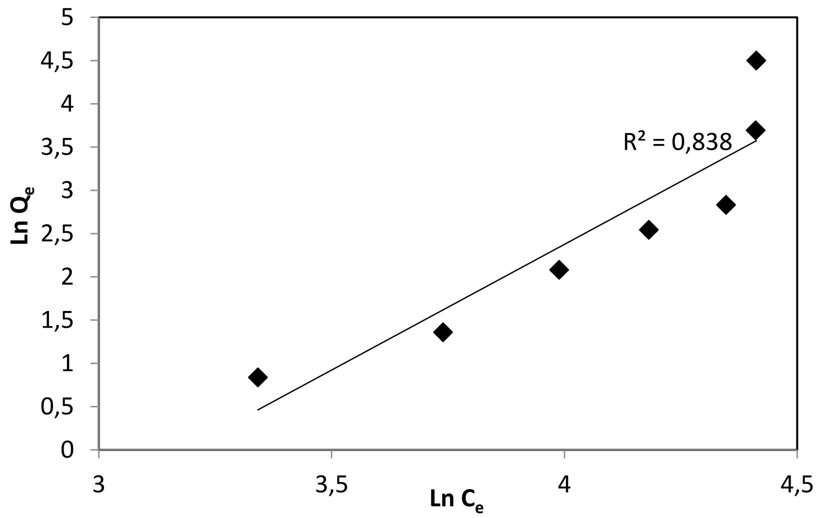

Fig.6. Freundlich isotherms adsorption of SRL onto GFP.

Table 2. Adsorption isotherm parameters for the adsorption of SRL onto GFP at temperature of 293 K.

Models	**Freundlich**			**Langmuir**		
Parameters	**K_F (mg g^{-1}.$L^{1/n}$.$mg^{-1/n}$)**	**n**	**R^2**	**K_L (L mg^{-1})**	**Q_{max} (mg g^{-1})**	**R^2**
	$9.63.10^{-5}$	0.334	0.85	0.327	85.47	0.996

4. Conclusion

The result shown that adsorption capacities are significantly influenced by the contact time, initial dye concentration and solution pH. The kinetic process fits well the pseudo-second-order reaction model and Langmuir isotherm model fitted best the adsorption process, dominated by electrostatic interaction between adsorbent and adsorbates.

The present investigation demonstrated that, the GFP is highly effective, economical, biodegradable, and environmentally clean adsorbent that can be used to remove dye from contaminated water. The main advantage of using raw agricultural waste materials as adsorbents is the ability to minimize the amount of chemicals added to the water during the water purification process.

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