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PREPARING OF EGG SHELLS ADSORBENT FOR REMOVING RED REACTIVE DYE FROM WASTEWATER

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Abstract: In this study, egg-shells were prepared as an adsorbent for the removal of red reactive (RR)dye from simulated aqueous solution by sorbent process. All parameters as; pH; dosage of egg-shells (sorbent), contact time, initial concentration of RR dye was effective on the removal efficiency of the dye. From this search it was found that Freundlich isotherm fitted well to the sorption data. Maximum removal was observed at above pH 6.0. The efficiency of egg shells for the removal of RR dyes was 91.78%. Also the kinetic-study was in good-concordance with pseudo-second-order-model. The results appeared that RR dyes is considerably adsorbed on egg shells and it could be and economic method for the removal of RR dyes from aqueous solutions.

Keywords: *Egg-shells; RR dye; kinetic; isotherm; Sorption.*

تحضيرممتزات قشور البيض لإزالة الصبغة الحمراء الفعالة من مياه الصرف

الخلاصة: في هذه الدراسة، تم تحضير قشور البيض كمادة مازة لإزالة الصبغة الحمراء الفعالة بعملية الأمتزاز من محلول مائي مُحضر مختبرياً. تم دراسة تأثيرجميع المُتغيرات على نسبة الأزالة كالدالة الحامضية، كمية قشور البيض، زمن التماس،و التركيز الأولي للصبغة الحمراء.تم اكتشاف ان النتائج العملية تنطبق بصورة جيدة جداً مع النموذج الرياضي فريندلج. وأن أعلى نسبة إزالة تم الحصول عليها عند قيمة الدالة الحامضية 6 حيث بلغت الأزالة 91.78%. نتائج الامتزازتم تطبيقها على موديلات الحركة من الدرجة الاولى،الثانية وقد وُجد أنها تتلائم مع موديل الحركة من الدرجة الثانية. ان النتائج أظهرت امكانية امتزاز الصبغة الحمراء الفعالة بإستعمال قشور البيض وعليه من الممكن إستعمالها كوسط ماز غير مُكلف إقتصادياً.

1. Introduction

Industry of textile is one of the distinguished contaminants producing high effluent concentration through the environment. Over 7 x 10^5 tones and about10,000 special varieties of dye and pigment are resulted worldwide yearly and the volume is gradually increasing [1].Reactive-dyes are synthetic fragrant water soluble and dispersible organic compounds [2]. Dyes are the maximum without difficulty diagnosed contaminant because they are able to seen by human eye. They are proof against to light and while drainage to the water body, they prevent the sun light from penetrating through also reduce the beauty quality of water [3],[4].

Discharge of dyes can destroy the total ecosystem and jeopardy health of human as it is consist of compounds that are resistant to biological transformation. Add to that,

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several types of dyes have been classified as having the potential to cause cancer [5]. The dyes elimination from wastewater is environmental importance, and it is not only necessary to protect human health but to protect water-resources.

Adsorption is a physical and chemical technicality that includes mass transfer from liquid to solid phase to elimination or reduces chemical deposit in wastewater [6, 7, 8]. Activated-carbon is most-widely used as an adsorbent in treatment of wastewater. Though of its activity in adsorption process, this adsorbent has costlier that cause it not being as attractive to use in small industry; because of this problem, in recently years researches have to produce other alternative-low-cost-adsorbents that can substitute activated-carbon in wastewater-treatment. This type of low cost adsorbents derives from agriculture residual; industrial byproducts or natural materials [9].

Egg-shell from operations of egg fraction is a major problem for waste disposal to the food industries, therefore the values development which added by products from this waste is greeting [6]. Natural porosity of egg-shell makes it a good material for utilized as a sorbent. Many researchers have determined the ability to absorb the egg-shell as inexpensive-sorbent, in simulated-wastewater with one or multi-compounds. These researches focused on the effect of this sorbent in elimination of heavy metals [10, 11], phenol- components [12], dyes [13] and pesticides [14], and etc. Main objective of this research is to study the bio-adsorption of RRdye from aqueous solution using biomass of egg-shells.

2. Material and Methods

Egg-shell was collected as residua from house-held. Shells washed with distilled water; removed its membrane by hand. Next those shells have washed again and dried at 105C^o for 24hr. Egg shell milled; then set with standard sieves and screened to reach the desired size (sizes ≤0.6 mm). The characteristics of egg-shell were shown in Table 1 [15]. The selected quantity was stored in container at room-temperature for using in the biosorption-experiments.

Table 1. The characteristics of egg-shell powder

Parameters	Values
Particle size	≤0.6 mm
pH	6.6
Specific gravity	0.85
Moisture content (%)	1.173
Porosity (%)	25.3

Dissolving 1 g of dry-powdered-dye in 1000 ml distilled water to prepared the solution of RRdye then stored in glass container at the room-temperature. A commercial-grade of this dye with molecular-formula $C_{44}H_{24}O_{20}N_{14}Cl_2Na_6S_6$, molecular-weight 1496.98g/mol, wave-length(λmax) 540nm, and pH 6.2, was get from factory of Hilla textile(Iraq)(Origin: SIGMA-ALDRICH Company). Fig.1 appears the RRdye chemical structure utilized in this search [16].

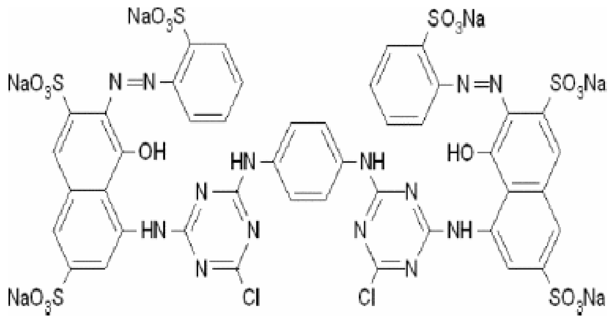

Figure 1.The chemical structure of RR dye.

Effect of pH, dosage of egg-shells, and initial concentration of RR dye and influence of contact-time on the biosorption-capacity were studied in a batch system. All batch experiments were conducted at room-temperature. The amount of removal of RRdye (q_e in mgg^{-1}) was identified by [17]:

$$q_e = \frac{V(C0-Ce)}{m} \qquad (1)$$

Where, q_e is the ability of the quantity sorption in mg/g (contaminated /sorbent), C_o is concentration of the initial dye in solution; C_e is the concentration of dye in solution after equilibrium, V is the volume of the solution that is adsorbent mass is exposed, and M is mass of sorbent.

Batch experiments of a sorption were executed aliquots of 250ml of RRdye solution of (50ppm) spilled into conical flasks having rightly weigh of mounts of egg-shell(1.0-4.0gm-range). Conical flasks were shaken over experiments with 200rpm shaker set. After shaking for time of equilibrium, the mixes were distilled by filters papers to remove all suspended a sorbent. Final concentrations of RRdye set by UV spectrophotometer in laboratory in college of engineering, Al-Mustansiriyah University.

A time of contact of 2h was chosen for the whole stability trial. pH solution adjusted by adding a amount of HCl and NaOH solutions(0.1N), that calculated by pHmeter.

3. Results and Discussion

3.1 Effect of pH

Aqueous solutions pH is major key for process of sorption. It’s function of hydrogen and hydroxyl ions concentrations [18]. pH of RRdye solution was set as (4, 6, 8, 10) values at concentration of dye (50mg/L) with initial amount of egg shells as 1g at room temperature. The influence of solution pH on RRdye adsorption using egg-shell was achieved and the results are explained at Fig.2, display the rise of pH cause to increase in the efficiency of removal pollutant (RR dye) on egg-shell.

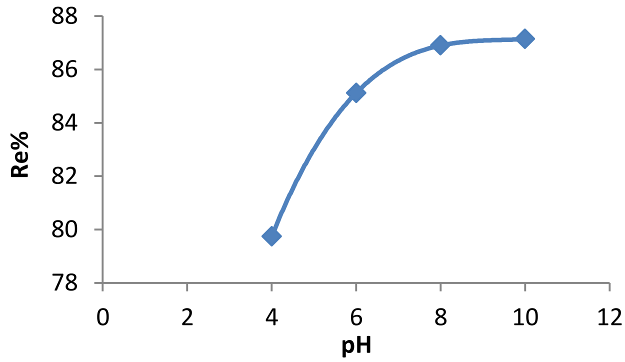

Figure 2. Effect of pH

A higher removal percentage of RRdye from solution was observed at pH(6, 8, 10). These outcomes maybe assigned to influence of pH solution on the charge of reactive groups during egg-shell membrane, thereby becoming it further active to adsorb dye in alkaline pH and raise the ability of ionized sites. Egg-shell membrane consisting of protein and polysaccharides that include functional-groups like a hydroxyl, amine and sulfonic groups (based on the aqueous solution pH) can interact with dye [19, 20]. So the optimum pH chosen for this study was 8.

3.2 Effect of Dosage of Egg Shells

Quantity of sorbent is one of the significant parameters to get quantitative uptake of RRdye. Dose effect was examined by variable the quantity of egg-shell (1.0- 4.0 g) by shaking 200rpm with 50 mg/L of RR dye concentration for 1hr, at room temp. (Fig.3). Sorption of RRdye was increased as the sorbent quantity increased this is generally due to an increase in the sportive surface area and the availability of more active sorption sites; after more increase in weights of sorbent than 3g we notice that no more change in removal rate because of the adsorbent was sufficient to adsorb [21, 22]. The optimum amount used in other tests was 3gm.

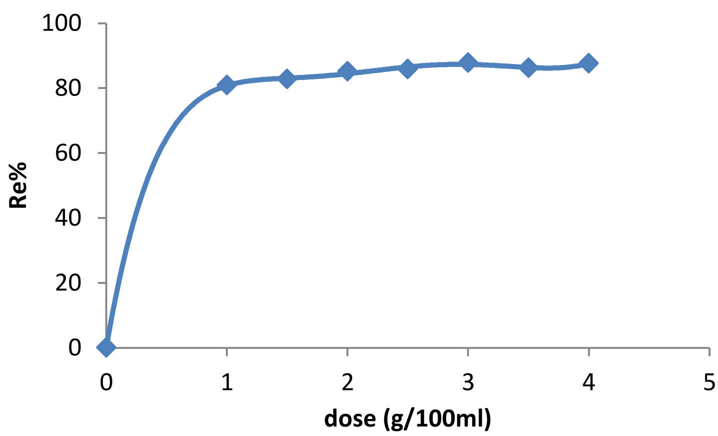

Figure 3. Effect of dosage and egg-shells

3.3 Effect of Contact Time

It is very necessary to understand the desired time to reach equilibrium sorption conditions. (Fig.4) offers the results of RRdye sorption-capacity vs. contact-time. The results revealed a rapid sorption of RRdye at the initial time. Equilibrium metal concentrations were obtained after 90min contact time. Moreover increase in contact time over 2hr didn't improve the capacity of sorption. The condition of equilibrium was almost achieved at first hour contact time and a comparatively slow phase was noticed beyond this time period. The fast initial-sorption is happen on exterior surface and this may be assigned to high provider of surface binding sites on the egg-shell, after that dye-molecules enter into pores(interior surface), comparatively slow process because of slow pore spread ions solute within a bulk of biosorbent [23, 24].

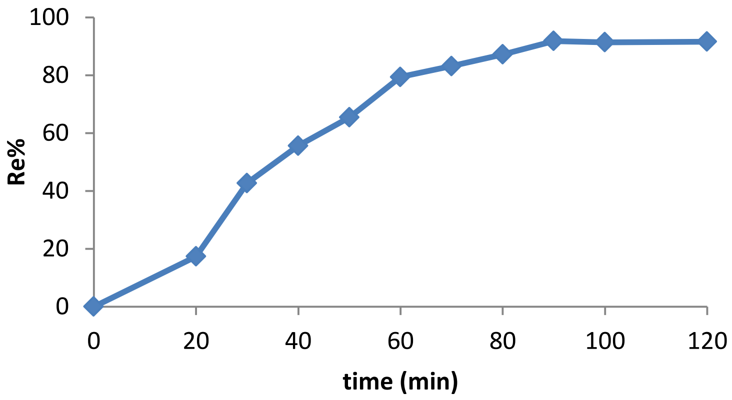

Figure 4. Effect of contact time

3.4 Effect of Initial Concentration of Dye

Fig.5 appears the variation of a sorption-removal as a function of initial RRdye concentration. Using the optimum pH8 and sorbent dose 3g at room temperature. The percentage removal of RR increased 60.45% to 91.56%, with decrease in initial concentration from 100mg/L to 25mg/L. In accordance to Kumar *et al*., 2010[25], when concentration is lower, the uptake ratio was higher because of larger surface area of sorbent which are expected to be available for sorption. When the concentration became higher, the percentage removal decreased since of adsorption sites became less because sites of sorption were saturation. By higher concentration the ratio of initial number of moles of RR to the availability sites of sorption was higher, which produce the lower sorption ratio [25, 26].

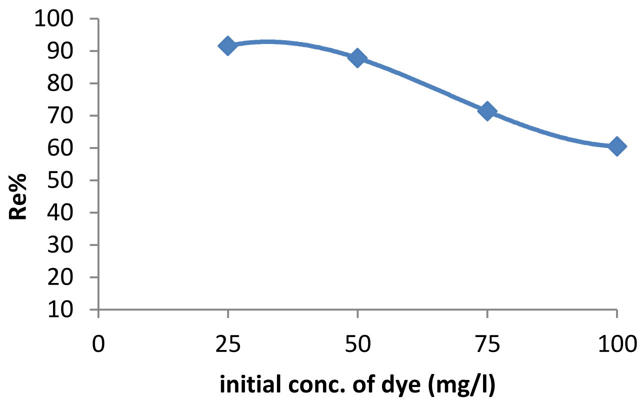

Figure 5.Effect of initial concentration of dye.

4. Isotherm Models

Models of Langmuir and Freundlich were utilized to evaluate activity of sorption. Isotherms sorption was assessment the relation between the pressure stability or concentration and amount of adsorbate adsorbed by the unit mass of adsorbent at a constant temperature. Langmuir model is [17]:

$$q_e = \frac{q_{m}\, bC_e}{1+bC_e} \qquad (2)$$

Where: q_e is the sorbed metal ions on the biomass (mg/g), q_m is the highest sorption capability of monolayer coverage (mg/g), b is constant related to binding site attraction (L/mg), and C_e is concentration of metal ions in the solution at balance (mg /L). Freundlich model is [17]:

$$\text{Log } q_e = \log K + \frac{1}{n}\log C_e \qquad \text{(linear form)} \qquad (3)$$

Where: $K_=$ constant indicate that proportional sorption capability of sorbent (mg/g), 1/n = constant expressing the sorption potential (K and n are expressed range of sorption and at grade of nonlinearity between solution and concentration, consecutively). The results of both models are presented in Fig.6 and Table 2, Of K and n are expressed in the adsorption range and in the degree of nonlinearity between solution and concentration, consecutively.

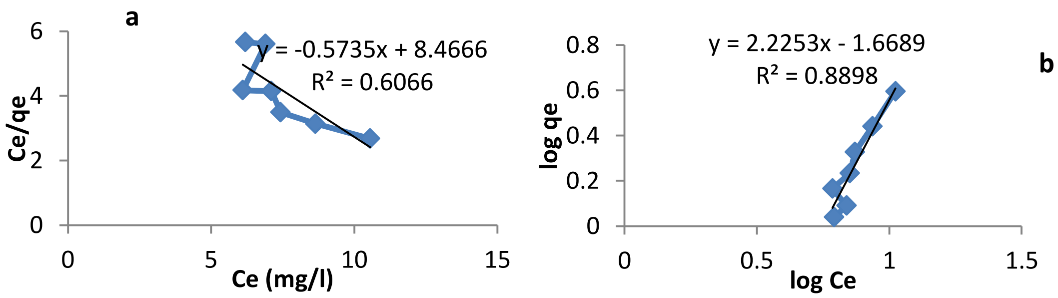

Figure 6. Isotherm Models: a. Langmuir and b. Freundlich

Tabel 2. Parameters of Isotherm forms.

Langmuir coefficients	Dye	Freundlich coefficients	Dye
R^2	0.606	R^2	0.889
q_m	-1.745	1/n	2.225
b	-0.0677	K	0.0215

Compared to the isotherms experiment with the theoretical isotherm models; it represented that Freundlich equation is suitable of the experiential-data for egg-shell.

5. Kinetic Models

Mechanism of dye sorption is clarified using the kinetics models of sorption; these are pseudo-first-order and pseudo-second-order. Utilizes of these models clarify the behavior of dye sorption on egg-shells. The pseudo-first order and pseudo-second order-models, consecutively [14, 15]:

$$\ln (q_{eq} - q_t) = \ln q_e - K_1 t \qquad (4)$$

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

Where q_{eq} and q_t (both in mg g^{-1}) are the quantity of adsorbed dye at equilibrium and at time, alternately. K_1 (min^{-1}) and K_2 (g mg^{-1} min^{-1}) are the rate constants of kinetics for the pseudo first- and second order-models, alternately. The results are offered in Fig.7 and Table 3 below:

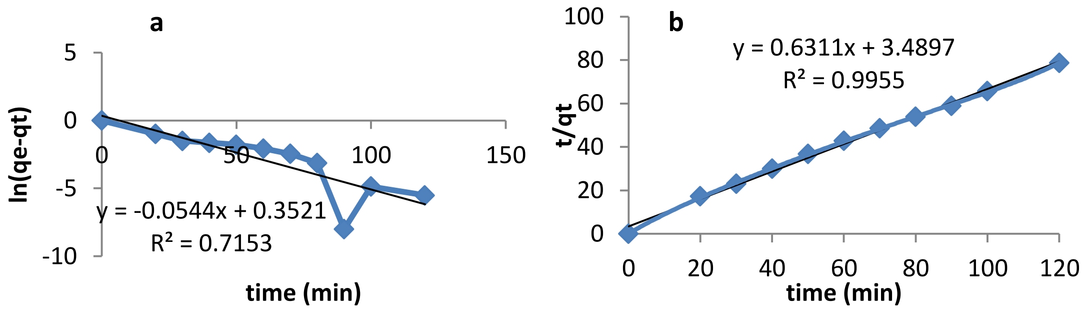

Figure 7. Kinetic Models: a. pseudo-first-order and b. pseudo-second-order.

Table 3. Parameters of Kinetic Models.

Dye	q_e experimental	Pseudo-first-order			Pseudo-second-order		
		k_1 1/min	$q_{ecalculated}$	R^2	k_2	$q_{ecalculated}$	R^2
	1.530	-0.054	1.422	0.715	0.1141	1.585	0.995

Table2; found that the theoretic values q_e (cal) are well accepted with the values of experiential uptake, q_e (exp) in case of pseudo-second-order model. In addition, the relation coefficient (R^2) was 0.995, indicating that this procedure of sorption may be described as well by pseudo-second-order process.

6. Conclusions

Based on of this study:

1. The egg-shell residue that easy and affordable available was utilizing as a perfect adsorbent to remove RRdye.
2. Egg-shell is inexpensive and available in large amount, thus no-regeneration is essential.
3. Results show Freundlich isotherm fit the sorption equilibrium data also a realistic description was provided to elimination of RRdye by Pseudo-second order reaction kinetic which closer experimental and calculated values of qe.

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