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کاربرد پوسته تخم‌مرغ به عنوان یک جاذب طبیعی برای حذف رنگ‌های ۱و۲ دی هیدروکسی آنتراکینون و ۲-آمینوآنتراکینون از محلول‌های آبی

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Application of Eggshell as a Natural Sorbent for the Removal of 1, 2-dihydroxyanthraquinone and 2-Aminoanthraquinone Dyes from Aqueous Solution

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چکیده
مطالعه حاضر نشان می‌دهد پوسته تخم‌مرغ می‌تواند به عنوان یک جاذب طبیعی برای حذف آلیزارین (۱و۲-دی هیدروکسی آنتراکینون) و ۲-آمینوآنتراکینون از محیط‌های آبی مورد استفاده قرارگیرد. آزمایش‌ها بر اساس زمان تماس، غلظت، دما، pH و میزان رنگ بررسی شد. مقدار رنگ حذف‌شده با افزایش pH محلول اولیه تغییر می‌کند و در pH=۷ به مقدار حداکثر می‌رسد. زمان به تعادل رسیدن۳۰ دقیقه بدست آمد. با افزایش غلظت رنگ و زمان تماس مقدار رنگ حذف‌شده (برحسب میلی‌گرم بر گرم جاذب) افزایش می‌یابد. درصد جذب با افزایش مقدار جاذب کاهش می‌یابد. داده‌های این آزمایش‌ها با معادلات لانگمیور-فراندلیچ توصیف‌کننده ایزوترم‌های تعادلی در تطابق است.

واژه‌های کلیدی
جاذب طبیعی؛ پودر پوسته تخم‌مرغ؛ آلیزارین؛ رنگ‌های آنتراکینون.

Abstract
The present study shows that the eggshell powder can be used as a natural adsorbent for the removal of alizarin (1,2-dihydroxyanthraquinone) and 2-aminoanthraquinone from aqueous solutions. Experiments were carried out as a function of contact time, concentration, temperature, pH and dosage. The amount of dye uptake was found to vary with increasing initial solution pH and maximum adsorption was observed at pH=7. The equilibrium was attained in 30 min. The amount of dye uptake (mg/g) was found to increase with increase in dye concentration and contact time. The percent of adsorption was found to decrease with increase in amount of adsorbent. The data were fitted with the Langmuir and Freundlich equations to describe the equilibrium isotherms.

Keywords
Natural Adsorbent; Eggshell Powder; Alizarin; Anthraquinone Dyes.

1. INTRODUCTION

Dye stuff is one of the largest industries all over the world, and its implications to economic and social conditions in many countries are quite important. Depending on several factors as fiber class, color or industrial procedure, there is a quite large variety of dye substances that might be highly pollutant if dumped. Over 50,000 tons of dyes are discharged into environmental effluent annually, so they are risky hazardous substances because they damage aquatic and vegetal life [1]. For many years, researchers have been working on several ways of removing dyes from wastewater and different procedures have been developed: adsorption onto materials such activated carbon [2], physical and chemical

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degradation [3-4] and a large number of other techniques: Fenton's oxidation, electrochemical degradation, ionization, etc [5-6].

Dyes may be classified into several different groups, according to their usage in dyestuff. Consequently, there are acidic, basic, disperse, direct dyes, etc. (family names that have to do with when and how dyes are used). Regarding, on the other hand, to their chemical structure, lots of compounds are included as dye. In the present work we have considered of alizarin dye and 2-aminoanthraquinone. Alizarin or 1, 2-dihydroxyanthraquinone (also known as Mordant Red 11 and Turkey Red) is an organic compound with formula $C_{14}H_8O_4$ that has been used throughout history as a prominent red dye, principally for dyeing textile fabrics. Historically it was derived from the roots of plants of the madder genus. In 1869, it became the first natural pigment to be duplicated synthetically [7-8].

Technical ways of solving environmental concerns and menaces such as the dumping of surfactants, dyes, pharmaceuticals and other hazards are available long time ago, but making them cheaper and sustainable is still a challenge. A possible source of low-cost materials that could provide a successful solution is natural raw materials [9]. A sorbent can be assumed as "low cost" if it requires little or none processing, or if it is considered as a by-product or waste material that could be obtained in abundance [10]. Recently several industrial and agronomical wastes like teakwood leaves, sewage sludge [11], waste apricot [12], saw dust [13], rice husk [14], pine wood saw dust [15], waste tires [16], coir pith and orange shell [17], wastage substances [18], TiO_2 catalyst [19], poultry feathers [20], and bottom ash and de oiled soya have been used for the removal of dyes from solutions [21].

Hen eggshell usuallay contains ceramic materials formed by a three-layered structure, namely the cuticle on the outer surface, a spongy (calcareous) layer and an inner lamellar (or mammillary) layer. The spongy and mammillary layers form a matrix composed of protein fibers bonded to calcite (calcium carbonate) crystal. The two layers are also built in such a manner that there are multiple circular openings (pores). This structure allows gaseous exchange through the shell. The outer surface of the eggshell is covered with a mucin protein that acts as a soluble plug for the pores in the shell. The cuticle is also penetrable to gas transmission. The chemical compound (by weight) of by-product eggshell has been stated as follows: calcium carbonate (94%), magnesium carbonate (1%), calcium phosphate (1%) and organic matter (4%) [22].

This study present eggshell powder can be used as a potential adsorbent for removal of alizarin and 2-aminoanthraquinone dyes from aqueous solutions. In the optimal condition, it was verified adsorption kinetic. The effects of factors such as contact time, concentration, temperature, pH and dosage on adsorption capacity were investigated.

2. EXPERIMENTAL

2.1 Preparation

Stock solution of dye at a concentration of 100.0 mg L^{-1} was prepared by dissolving appropriate amount of Alizarin (1,2-dihydroxyanthraquinone) or 2-Aminoanthraquinone (SIGMA-ALDRICH) in water. Working reference solutions (10, 20, 30, 40 mg L^{-1}) were obtained daily by stepwise dilution from stock solution. A Perkin Elmer lambda 25 Ultraviolet–visible spectrophotometer was used. A Metrohm 691 pH meter was employed for pH measurements. The concentrations of the dyes solution were obtained from standard calibration curve. The hen eggshell was manually stripped from eggshell membrane after cleaning of the raw material. Eggshell rinsing in distill water and finally dried in oven (45 ^oC) for three hours. The eggshell was further ground to prepare powder particles. The eggshell was milled for preparing powder particles. The results of mean diameter, median diameter of eggshell particles are 6.9, 5.83 µm. (Fig. 1).

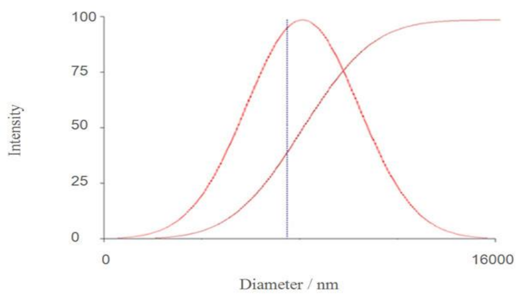

Fig. 1. Particles size of eggshell powder.

2.2 Adsorption experiments

Batch experiments of adsorption were performed in 250 mL Erlenmeyer flasks. Flasks were being agitated on an IKA shaker model KS 130 basic at 400 rpm for identified time intervals. The effect of contact time, concentration, temperature, pH and dosage of anthraquinonic was studied. Each experiment was carried out by suspending 0.7 g of sorbent in 100 mL of sorbate solution taken in Erlenmeyer flask under the optimum conditions set out for the experiment. Finally, the supernatant liquids were filtered and dye concentration was determined by using absorption Ultraviolet–visible spectrophotometer (Wave length analysis (260 nm)).

The effect of pH and contact time on the adsorption of alizarin and 2-Aminoanthraquinone (2-A) by eggshell powder at different pHs and time points were studied using 100 mL of dyes 10 mg L^{-1} at room temperature. The optimum pH and time for the adsorption process was confirmed from above experiments.

The uptake of dye in solution was calculated by differences in their initial and final concentrations. The obtained data were employed to calculate the equilibrium dye uptake capacity according to Eq. (1).

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

Where qe (mg g^{-1}) is the equilibrium amount of dye in the adsorbed phase, C0 and Ce are the initial and equilibrium concentrations of dye (mg L^{-1}) in the aqueous solution, v is volume of the solution (L) and m is the sorbent dose (g) in the mixture. Isotherm studies were performed using different concentrations of alizarin and 2-A (10–40 mg L^{-1}) at room temperature.

Removal percent (Re%) in solution was calculated using Eq. (2).

$$Re\% = \frac{C_0 - C_e}{C_0} \times 100 \qquad (2)$$

3. RESULTS AND DISCUSSIONS

3.1 Effect of pH

The pH of aqueous solution is an important factor and influences as well as the surface properties of adsorbent and therefore can affect the extent of adsorption. Thus, the adsorption behavior of dyes on the eggshell surface has been investigated over a pH range of 7.0–9.0 at room temperature (Fig. 2 and 3). Eggshell is destroyed at pH less than 7.

The percentage of dye adsorption on egg shell powder decreased with increasing pH, therefore the optimal pH was determined in range 7.0. Titrasol buffers are used for pH adjustment.

3.2 Effect of contact time

Effect of contact time on the adsorbed amount of dye by eggshell powder was studied in the range of 20 to 90 min and 30 to 180 min, respectively, for alizarin and 2-A. The effect of contact time on the adsorbed amount of alizarin and 2-A by eggshell powder from 10 mg L^{-1} solution for alizarin and 40 mg L^{-1} solution for 2-A was studied at room temperature. The results are shown in Fig. 4 and 5. It can be seen that the adsorption yield of alizarin or 2-A increased sharply with contact time until the equilibrium was attained. The equilibrium times for alizarin and 2-A were 30 and 60 min, respectively. After they reached the equilibrium, there were no significance changes in dyes concentration in the solution .

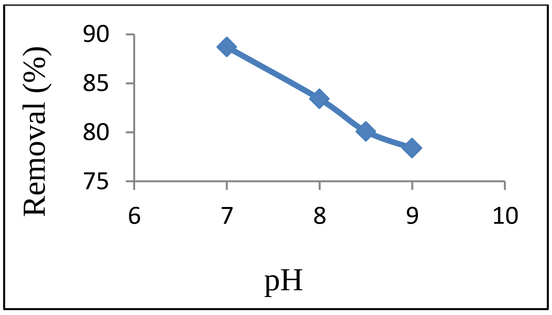

Fig. 2. The effect of pH on the adsorption of alizarin onto eggshell powder.

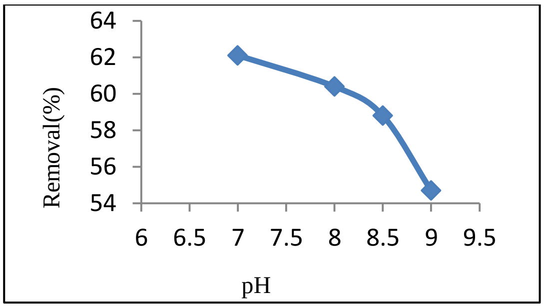

Fig. 3. The effect of pH on the adsorption of 2-aminoanthraquinon onto eggshell powder.

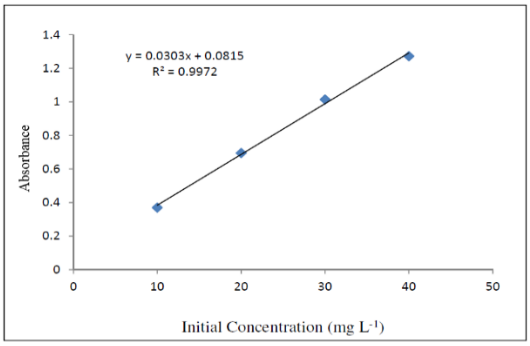

Fig. 4. The effect of contact time on adsorption alizarin onto eggshell powder.

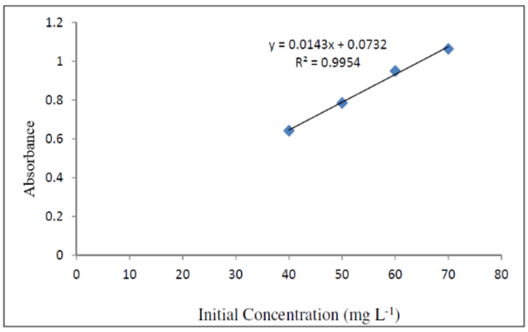

Fig. 5. The effect of contact time on adsorption 2-aminoanthraquinon onto eggshell powder.

3.3 Initial concentration
Dependency of the process of dyes adsorption from different initial concentrations (10 and 40 mg L^{-1}, respectively, for alizarin and 2-A) by the adsorbents is illustrated Fig. 6 and 7. The examination of data reveals that the amount of adsorbed dye increases with concentration of the solution, but the percentage of adsorption decreases. These data suggests that the removals of dyes are highly concentration dependent. At lower concentrations the number of dye molecules which are available in the solution is less as compared to the available sites on the adsorbent. However, at higher concentrations the available sites for adsorption become fewer and the percentage removal of dye depends on the initial concentration.

3.4 Temperature influence
During our investigation, a series of assays were performed to observe effect of temperatures. Temperature was varied between 25 and 55 ˚C, with a pH level of 7 and a dye initial concentration of alizarin and 2-A. No significant variations in treatment efficiency were observed. The results are shown in Fig. 8 and 9.

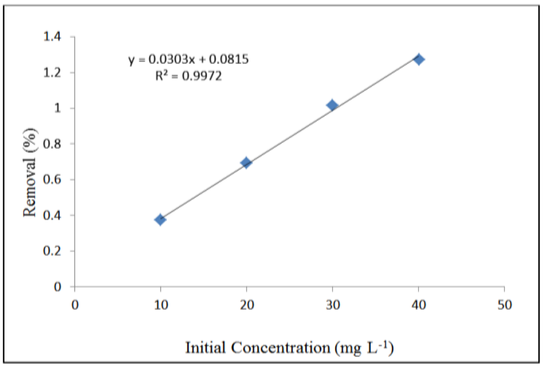

Fig. 6. The effect of initial concentration of alizarin onto eggshell powder.

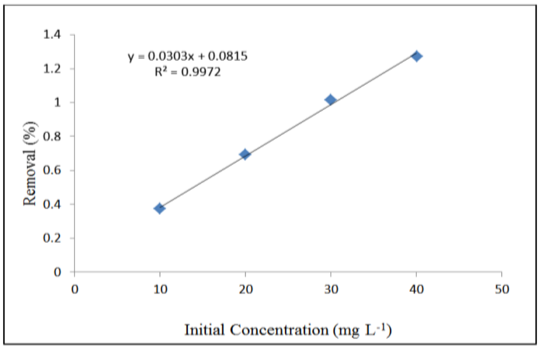

Fig. 7. The effect of initial concentration of 2-aminoanthraquinon onto eggshell powder.

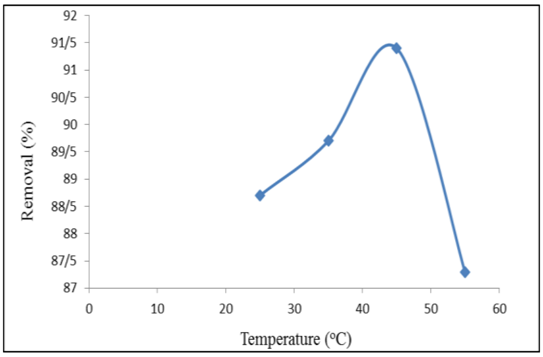

Fig. 8. The effect of temperature on adsorption alizarin onto eggshell powder.

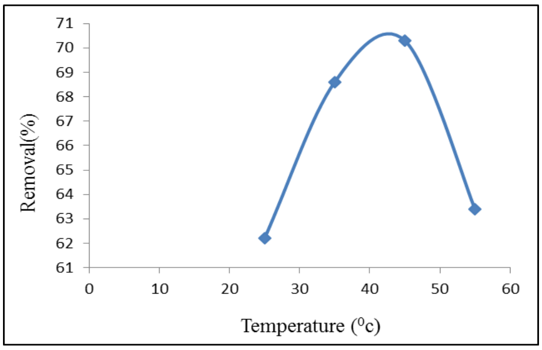

Fig. 9. The effect of temperature on adsorption 2-aminoanthraquinon onto eggshell powder.

3.5 Effect of adsorbent dosage
One of the parameters that strongly affect the sorption capacity is the amount of the adsorbents. With fixed dye concentration, it can be easily inferred that the percent removal of dye increases with increasing amount of the adsorbents (0.3–0.9 g) as shown in Table. 1. This is due to greater availability of the exchangeable sites or surface area at higher concentration of the adsorbent.

Table 1. Effects of eggshell powder dosages for alizarin and 2-aminoanthraquinon adsorption

Entry	Adsorbent dosage (g)	Removal (%)	
		Alizarin	2-Amino anthraquinon
1	0.3	84.0	55.3
2	0.5	85.7	58.0
3	0.7	88.7	62.1
4	0.9	89.4	62.7

3.6 Adsorption isotherms
Several models have been published in the literature to describe experimental data of adsorption isotherms. The Langmuir and Freundlich models are the most frequently employed models [23-25]. In this work, both models were used to describe the relationship between the amount of dye adsorbed and its equilibrium concentration in solution at room temperature for 30 min for alizarin or 60 min for 2-A (Fig. 10-13).

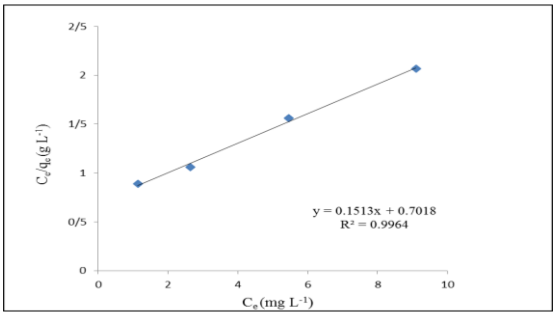

Fig. 10. Langmuir adsorption isotherms of alizarin onto eggshell powder.

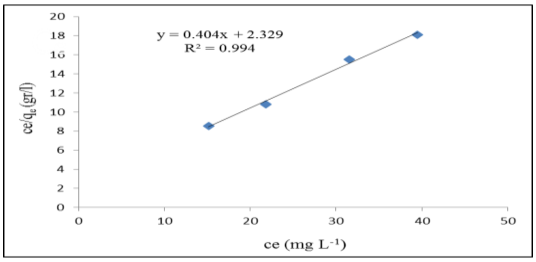

Fig. 11. Langmuir adsorption isotherms of 2-aminoanthraqiunon onto eggshell powder.

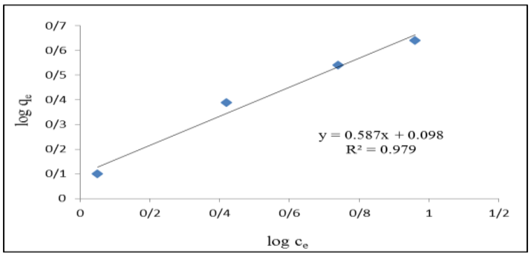

Fig. 12. Freundlich adsorption isotherms of alizarin onto eggshell powder.

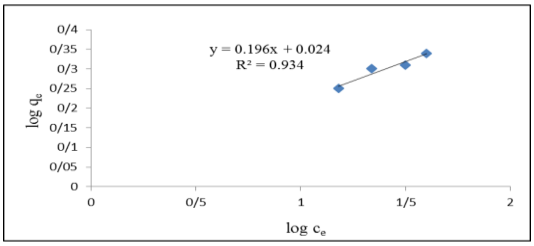

Fig 13. freundlich adsorption isotherms of 2-aminoanthraqiunon onto eggshell powder.

The sorption isotherms were determined at room temperature for a concentration range of 10–40 mg L^{-1} and 40-70 mg L^{-1} respectively, for alizarin and 2-A. In all experiments 0.7 g of adsorbent was used.

3.6.1 Langmuir isotherm

The main assumption of the Langmuir method is that adsorption occurs uniformly on the active part of the surface, and when a molecule is adsorbed on an active site, the other molecules could not be interacted with this active.

The Langmuir equation may be written as:

$$q_e = \frac{Q^0 b C_e}{1 + bC_e} \quad \text{(Non – linear form)} \qquad (3)$$

$$\frac{C_e}{q_e} = \frac{1}{Q^0 b} + \frac{C_e}{Q^0} \quad \text{(Linear form)} \qquad (4)$$

Where q_e is the amount of solute adsorbed per unit weight of adsorbent (mg g^{-1}) and C_e is the equilibrium concentration of solute in the bulk solution (mg L^{-1}) while Q^0 is the monolayer adsorption capacity (mg g^{-1}) and b is the constant related to the free energy of adsorption ($b \propto \exp(-\Delta G/RT)$). The constants of the Langmuir isotherm are obtained by plotting $\frac{C_e}{q_e}$ versus C_e.

3.6.2 Freundlich isotherm

The Freundlich isotherm may be written as:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \qquad (5)$$

Where K_f is the constant indicative of the relative adsorption capacity of the adsorbent (mg g^{-1}) and 1/n is the constant indicative of the intensity of the adsorption. The constants of the Freundlich isotherm are obtained by plotting log q_e versus log C_e. Freundlich and Langmuir constants are given in Table 2.

4. CONCLUSIONS

The present study shows that the prepared eggshell powder can be used as a potential adsorbent for the removal of alizarin (1,2-dihydroxyanthraquinone) and 2-aminoanthra-quinone dyes from aqueous solutions. The equilibrium data are described satisfactory by the Langmuir and Freundlich isotherm models and the maximum adsorption capacity of alizarin and 2-aminoanthraquinone on eggshell powder were 6.6. Low cost, rapid adsorptive ability and natural waste of these adsorbents would offer a promising technique for industrial wastewater cleanup.

Table 2. Freundlich and Langmuir isotherm constants for 2-aminoanthraquinon and alizarin adsorption on the Eggshell powder.

Dye	Langmuir			Freundlich		
	Q^0	b	R^2	K_f	1/n	R^2
2-Amioanthraquinon	2.470	0.171	0.994	1.061	0.196	0.934
Alizarin	6.603	0.226	0996	1.252	0.587	0.979

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