ORIGINAL RESEARCH PAPER

THE TREATED EGGSHELLS AS A NEW BIOSORBENT FOR ELIMINATION OF CARBARYL PESTICIDE FROM AQUEOUS SOLUTIONS: KINETICS, THERMODYNAMICS AND ISOTHERMS

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Abstract: The efficiency of treated eggshells (TES) for removing the carbaryl pesticide from aqueous solutions was examined by biosorption process. Batch mode experiments were conducted using various parameters such as contact time, temperature, biosorbent amount, carbaryl concentration and *p*H. Removal efficiency of carbaryl by the TES attained 87.35 % after 60 min of contact time, using 10 mg·L^{-1} of pesticide and 1.5 g·L^{-1} of biosorbent. The results indicate that Freundlich equation is well described with the carbaryl adsorption, with correlation coefficient R^2 value of 0.99. They showed that the biosorption processes were spontaneous and exothermic. The Gibbs energy ΔG increased with increase in temperature indicating an increase in feasibility of biosorption at low temperature. These results show that treated eggshells can be employed as an alternative to commercial adsorbents in the removal of pesticides from aqueous solutions.

Keywords: *batch, biosorption, isotherm models, treated eggshells, water treatment, wastewater*

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INTRODUCTION

In modern agriculture, pesticides are widely used. Following this heavy application, there have been serious problems generated by pesticide wastes, which could subsequently threaten water resources and human health [1].

Carbaryl(1-Naphthalene-*N*-methylcarbamate) is a carbamate insecticide used in the fight against moths, beetles, and other sucking and chewing insects in a wide range of domestic and agricultural situations, it is used also as an animal ectoparasiticide. Stable in neutral and mildly acidic conditions, carbaryl not responds to light and heat. It hydrolyzed in alkaline medium at 1-naphthol.

Under certain conditions, carbaryl can react with nitrite to form *N*-nitrosocarbaryl. Nitrosocarbaryl has been shown a high mutagenic effect at the low concentrations in laboratory tests. This can concern humans because there is a probability that nitrite - which is a substance found in saliva and in food additives - reacts with carbaryl in the stomach to give rise to Nitrosocarbaryl [2].

Since carbaryl has potential harm to human beings, many countries develop guideline levels for it in water. In Australia, the guideline for carbaryl in drinking water has recommended the health value (HV) to be 0.03 mg·L^{-1}. The environmental quality standards in Japan are established the level for carbaryl as 0.05 mg·L^{-1} in public water. Canadian drinking water quality maximum acceptable concentration (MAC) value is 0.09 mg·L^{-1} [3].

Most of analytical methods employed for quantification of pesticides are based on a separation by chromatographic technique such as thin-layer chromatography (TLC), gas chromatography (GC), high pressure liquid chromatography (HPLC) with detectors of ultraviolet (UV), diode array detector (DAD) and mass spectrometry (MS) [4] or by liquid chromatography tandem mass spectrometry (LC-MS/MS) [5].

Several technologies are valid with different success degrees to control the water pollution. Some of them are coagulation [6], filtration [7], foam flotation [8], ion exchange [9], advanced oxidation processes [10], solvent extraction [11], electrolysis [12], microbial reduction [13], activated sludge [14], aerobic and anaerobic treatment [15] and adsorption [16]. Most of them require a high financial input and their use is restricted. However, adsorption has remained as the most suitable technique [17] and activated carbon is the most widely used adsorbent for pesticides removal [18], but it is very expensive. As consequence, many studies have been under taken to investigate the use of low cost adsorbent [19].

This work was intended to remove the carbaryl, which is a pesticide widely used in the Souss-Massa's agriculture, from aqueous solutions, using treated eggshell (TES) as a new low cost, eco-friendly and a very efficient adsorbent. Batch adsorption experiments were achieved out like adsorbent dosage, contact time, initial concentration of pesticide, temperature and *p*H. The Langmuir and Freundlich isotherms models, kinetics and equilibrium studies have been investigated.

MATERIALS AND METHODS

Biosorbate

The carbaryl was selected in the present study as a representative carbamate pesticide; it was obtained from Sigma-Aldrich Company at Casablanca (Morocco) with a technical purity of 99.9 %. The chemical structure of carbaryl is given respectively in Figure 1.
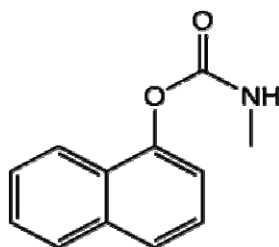

Figure 1. Chemical structure of carbaryl

Preparation and characterization of biosorbent

The eggshells employed in this study were collected from a popular restaurant near Agadir in Morocco. The eggshells were washed several times with tap water and treated with HCl acid 0.1 M for 10 min. The sample was rinsed, dried overnight at 373 K and powdered to small grains. The powder was undergoing a basic treatment with NaOH 50 % for 5 h at 343 K, and then treatment temperature was increased to 373 K and was kept for 1 h. The resulting powder was rinsed with distilled water to reduce the pH to 7 and was dried in oven at 333 K for 24 h. The TES biosorbent is identified by elemental analysis (PANalytical's WD-XRF spectrometers), X-ray diffraction (Philips X'Pert PRO), analysis of Infrared spectroscopy (ATI Mattson Genesis series FTIR_UNICAM instrument), and scanning electron microscopy (SEM) (FEI Quanta 200).

Experimental protocol

Batch adsorption tests were conducted in a series of Erlenmeyer flasks (50 mL). An amount of 37 mg of TES was mixed with 25 mL pesticide solution of appropriate concentration (5 - 20 mg·L^{-1}) and securely capped immediately. The suspensions were shaken under speed of 120 rpm at 295 K and allowed to equilibrate. The samples were then retired from the batch at predetermined times intervals and the suspensions were centrifuged for 15 min at 3600 rpm. Each batch of the experiment was duplicated under identical conditions. Every sample was filtered before analysis in order to reduce interference of the carbon fines with the analysis. The concentrations of carbaryl in the solution before and after adsorption were determined using a liquid chromatography coupled with tandem mass spectrometry LC/MS-MS (API 3200 System, AB SCIEX/USA). For LC/MS-MS analysis, the samples were transferred after filtration to an HPLC bulb. Every solvent used for LC/MS-MS was HPLC grade. In the autosampler, the samples were kept at 298 K and 20 µL of subsamples were injected. A gradient elution A-phase/B-Phase was used to elute analytes through a column Gemini-

NX C 18 (100 mm x 2 mm i.d, 3 μm) where A-phase is the ammonium formate in ultra-pure water at 5 mmol·L^{-1} and B-phase is the ammonium formate in methanol at 5 mmol·L^{-1}. Identification of carbaryl was carried out by MRM (Multiple Reaction Monitoring) method. The MRM method is a mass spectrometric technique for quantifying one or more target molecules in a complex sample. The mass spectrometer measures the ratio Mass/Charge (m/z) of ionized molecules. The analytical specificity of the MRM method is afforded by the combination of the value of m/z of the molecule to be assayed (precursor) and the value of m/z of the fragment. Together, these two parameters intended to be specific for the molecule to be assayed is called a transition.

Kinetic studies

Biosorption tests were conducted in a range of Erlenmeyer flasks (50 mL) where each 25 mL of carbaryl solutions with initial concentrations of 0.5 - 2 mg·L^{-1} were prepared. 37 mg of the TES was added into each flask, capped immediately and the suspensions were shaken under speed of 120 rpm at 295 K and allowed to equilibrate. Samples were taken at predetermined time interval, and the concentration of carbaryl was determined. The amount of biosorption at any time t, Q_t (mg·g^{-1}), was calculated using the formula (1):

$$Q_t = \frac{C_0 - C_t}{W} V \tag{1}$$

where C_0 and C_t (mg·L^{-1}) are respectively, the liquid phase concentrations of carbaryl at initial and any time t, V is the solution volume (L) and W is the TES mass (g).

The amount of equilibrium adsorption Q_e (mg·g^{-1}) was calculated using the equation (2):

$$Q_e = \frac{C_0 - C_e}{W} V \tag{2}$$

where C_e (mg·L^{-1}) is the liquid concentrations of pesticide at equilibrium.

The carbaryl removal percentage can be calculated by the equation (3):

$$\% \ Biosorption \ efficiency = \frac{C_0 - C_t}{C_0} \times 100 \tag{3}$$

The pseudo first order model was proposed by Lagergren [20]. The integrated form of the model is:

$$log(Q_e - Q_t) = \log Q_e - \frac{k_1}{2.303} t \tag{4}$$

where k_1 is the equilibrium rate constant of pseudo first order kinetics (min^{-1}) and t is time (min).

The pseudo second order equation is often used with success to describe the kinetics of the binding reaction of the pollutants on the adsorbent [21]. This model allows characterizing the adsorption kinetics, taking into account the fast fixing of solutes on the most reactive sites and the slow binding to low energy sites. The linearized form of the pseudo second order model is given by equation (5):

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{1}{Q_e} t \tag{5}$$

where k_2 is the pseudo second order rate constant (g·mg^{-1}·min^{-1}).

Biosorption isotherm

Among the several existing models, Langmuir and Freundlich isotherms were employed to investigate the biosorption behavior. The sorption data collected at different temperatures were subjected to these commonly used models. Langmuir isotherm [22] is a model for monolayer localized physical adsorption on homogeneous surface; it is based on the following hypotheses: uniformly energetic adsorption sites, monolayer coverage, and no lateral interaction between adsorbed molecules. The linear form of Langmuir equation is:

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{K_L}{Q_m} \qquad (6)$$

where Q_m (mg·g^{-1}) is the maximum monolayer adsorption capacity and K_L is the constant related to the free energy of adsorption.
The Freundlich equilibrium isotherm equation [23] was also used to describe experimental adsorption data. It proves the heterogeneity of the surface and assumes that the adsorption occurs at sites with different energies of adsorption. These energies vary with the surface coverage. The Freundlich mathematical formula is purely empirical for microporous and heterogeneous adsorbates. The Freundlich linear form equation is:

$$logQ_e = \frac{1}{n}logC_e + logK_f \qquad (7)$$

where K_f (Freundlich constant) is the maximum multilayer adsorption capacity (mg^{1-n}·L^n·g^{-1}) and n is a characteristic constant which measures the adsorption intensity.

Biosorption thermodynamics

The thermodynamic parameters can be estimated by the change of equilibrium constants with temperature. These parameters reflect the feasibility and favorability of the adsorption. In this study, we have carried out a determination of these parameters. Indeed, the change in free energy is given by equation (8):

$$\Delta G°(kJ·mol^{-1}) = -RTlnK_c \qquad (8)$$

where T is the temperature expressed in Kelvin and R is the gas constant (8.314 J·mol^{-1}·K^{-1}).
The enthalpy ΔH^0 (kJ·mol^{-1}) and the entropy ΔS^0 (kJ·K^{-1}·mol^{-1}) are determined using the Van't Hoff equation:

$$lnK_c = -\frac{\Delta H^0}{R} \times \frac{1}{T} + \frac{\Delta S^0}{R} \qquad (9)$$

where K_c is the equilibrium constant ($K_c = Q_e/C_e$), ΔH^0 and ΔS^0 are found by plotting lnK_c = f (1/T).

RESULTS AND DISCUSSION

Characterization of biosorbent

The chemical composition of TES (Figure 2) shows a high proportion of Ca (95.96 %), however, small amounts of Mg (1.94 %), Si (0.37 %), Na (1.17 %) and P (0.57 %) have been revealed. The analysis by XRD represented in Figure 3 shows the presence of calcite. A major peak appeared at 2θ = 29.28° while several other small peaks were appeared at 2θ = 23.01°; 36.06°; 39.26°; 43.19°; 47.44°; 48.39°; 57.42°; 60.50° and 64.65°. Analysis of IR spectrum of TES shown in Figure 4 reveals three bands at 712 cm^{-1}, 871 cm^{-1} and 1402 cm^{-1}. These bands are attributed to stretching and folding of carbonate group. The Scanning electron microscope (SEM) photograph shown in Figure 2 reveals clearly the calcite crystals and suggests a presence of fine particles with a porous and regular surface morphology.
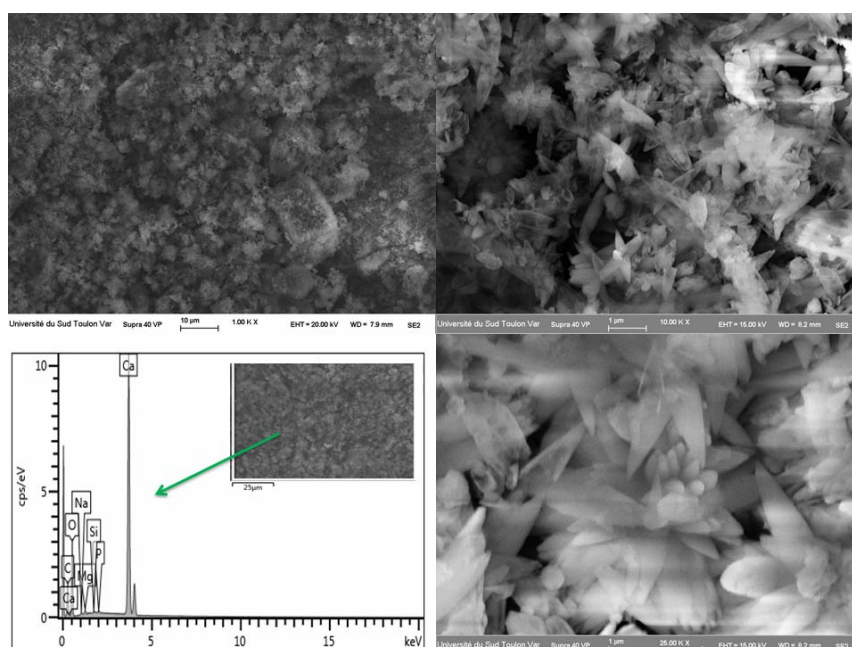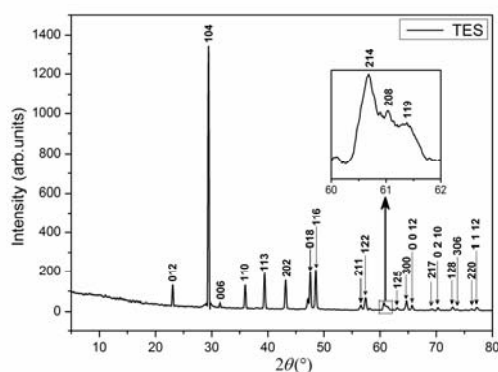

Figure 2. *SEM photograph and EDS of TES*
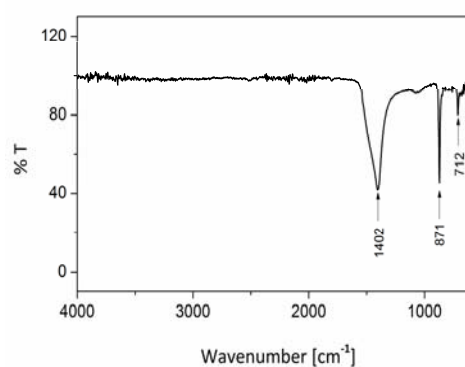

Figure 3. *X-ray diffraction of TES*   **Figure 4.** *FT-IR of TES*

Determination of pH zero charge point

The zero point charge pH (pH$_{ZPC}$) of the TES biosorbent has been determined by the pH drift method [24]. Indeed, to obtain pH$_{ZPC}$, 20 mL of 0.05 mol·L^{-1} NaCl were added to several polystyrene flasks. A range of initial pH (pH$_i$) values of the NaCl solutions were adjusted (by JENCO Model 6173, USA pH-meter) from 2 to 12 by the addition of 0.1 mol·L^{-1} of HCl and NaOH. The volume was completed in each flask to 30 mL by supplementary addition of 0.05 mol·L^{-1} NaCl solution. After having noted the pH$_i$ values of the solutions, 50 mg of TES were added to each flask, which was immediately covered for more security. The suspensions were placed on a shaker at 298 °K for two days to equilibrate, and then centrifuged at 3600 rpm for 15 min. The final pH (pH$_f$) values of the supernatant were registered. The value of pH$_{ZPC}$ was determined by plotting the curve of ΔpH (pH$_f - p$H$_i$) versus pH$_i$, which was corresponded to the point where the curve crossed the line abscissa (Figure 5). The value of pH$_i$ for TES was found equal to 8.8.
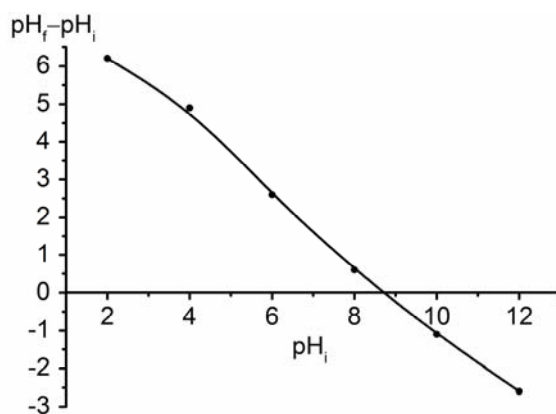

Figure 5. *Determination of pH$_{ZPC}$ of TES*

Effect of biosorbent dose on the sorption of carbaryl

To assess the effect of adsorbent dose on the removal of carbaryl, several equilibrium experiments have been conducted by contacting different amounts of TES from the range of 6.25 to 100 mg with 25 mL of a pesticide solution at 10 mg·L^{-1} as initial concentration, at fixed temperature of 295 K and under agitation for 24 h (Figure 6).
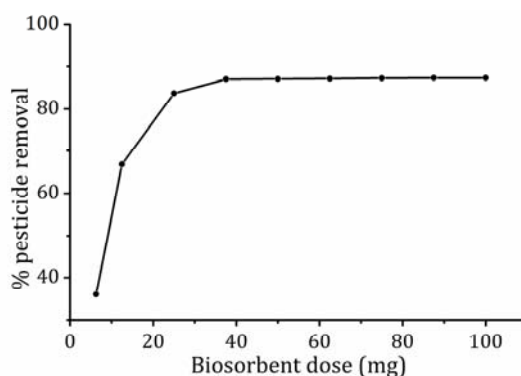

Figure 6. *Effect of adsorbent dose on the carbaryl biosorption*

Figure 6 showed the variation of the amount of pesticide adsorbed versus adsorbent dose. The removal percentage of carbaryl was increased from 35.95 % to 87.35 % with increasing of biosorbent dosage and that the maximum pesticide removal was achieved within the amount 1.5 g·L^{-1}. These results may be explained by the creation of several fixation sites with increasing adsorbent dose.

Effect of contact time and initial carbaryl concentrations

The effect of contact time and initial concentration on the adsorption of carbaryl onto TES surface is shown in Figure 7. The experiments were carried out at a range of 5 - 20 mg·L^{-1} as initial pesticide concentrations, using 1.5 g·L^{-1} adsorbent dose and at ambient temperature. The amount of pesticide adsorbed increased with increase in contact time at all initial concentrations and reached equilibrium after 60 min. Moreover, the amount of pesticide adsorbed was increased with the increase in initial concentration. For the first 15 min of experience, the uptake was rapid then it was slowed down and finally it attains saturation at 60 min. The results depicted in Figure 7 reveal that the initial carbaryl concentration has no effect on the required time for equilibrium. While, the curves show that the higher adsorption amount occurred in the first rapid stadium. It may be due, on one hand to the increased number of vacant sites available at this stadium, and on the other hand to the existed increase in the concentration gradients between carbaryl in solution and carbaryl on the adsorbent surface. As time passes, the pesticide concentration is reduced due to the accumulation of pesticide particles in the vacant sites, leading to a decrease in the adsorption rate at later stadium. The same results have been observed in adsorption of dye molecules [25]. Furthermore, the amount adsorbed is increased with the increase in initial pesticide concentration. That is because, at low concentrations, the ratio of the initial number of pesticide molecules to the available surface area is low. Therefore, the fractional adsorption becomes independent of initial concentration. Nevertheless, at high concentration, the ratio is higher because the available sites become fewer, so the removal rate of pesticide depends upon concentration.
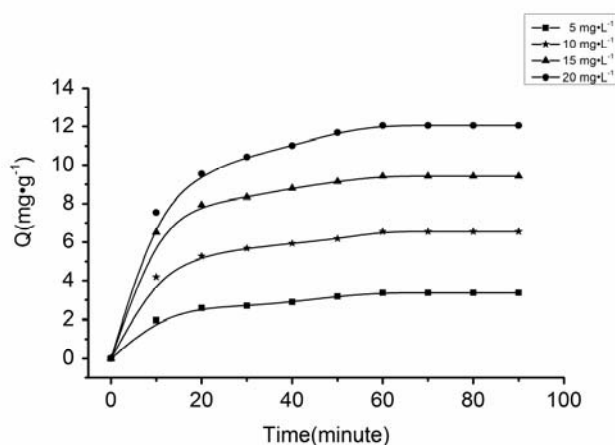

Figure 7. *Effect of carbaryl concentration and contact time on the removal pesticide by TES at 25 °C*

Effect of *p*H for the removal efficiency of carbaryl

In order to investigate the effect of this factor on adsorption of carbaryl onto treated eggshell, experiments were performed in the *p*H range of 2 - 12. The mean of the duplicated experimental results is plotted in Figure 8, indicating that *p*H considerably affected adsorption. The Figure 8 shows that uptake decreases slightly from 12.05 to 10.66 mg·g^{-1} for an increase in *p*H from 2.0 to 6.0 than decreases quickly to reach the value of 5.15 mg·g^{-1} at *p*H equal to 10. The curve continues to decrease lightly to arrive at 3.78 mg·g^{-1} in the *p*H 12. The same results are shown for adsorption of pesticides from aqueous solution onto banana stalk activated carbon [26]. The *p*H$_{ZPC}$ of the TES is determined to be 8.8. For *p*H values higher than 8.8 the surface of TES exhibits a negative charge and yields a positive charge at a *p*H less than 8.8. carbaryl is a negatively charged molecule, this charge comes on one hand from the electron cloud of the two aromatic nuclei, which allows the approximation of the pesticide molecule from the adsorbent surface, and on the other hand from mesomeric effect directed from oxygen to nitrogen atoms enhanced by inducing effect of CH$_3$ producing an important electronic density on the oxygen atom allows to fix carbaryl on the adsorbent. It observed from Figure 8 that the amount of pesticide adsorbed on the TES is high for acidic *p*H, which indicates that the positive form of TES is responsible for adsorption in this range. In fact, the H$^+$ ions react with CO$_3^{2-}$ and allow carbaryl to be fixed by the Ca^{2+} ions incorporate in the adsorbent surface. In alkaline medium, the electrostatic forces of repulsion existing between CO$_3^{2-}$ on TES surface and the carbaryl prevent the attachment and cause the decrease of the adsorption (Figure 9).
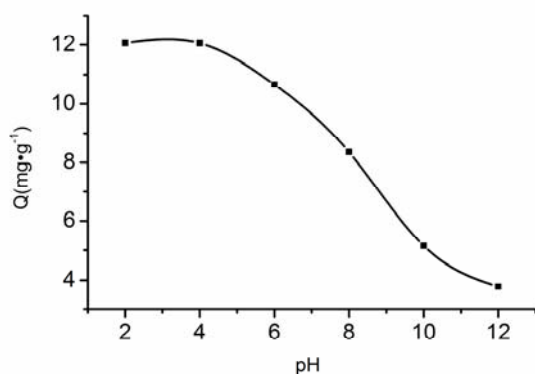

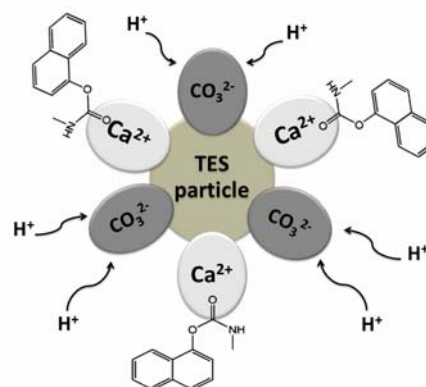*Figure 8.* *Effect of pH on the TES biosorption*

Figure 9. *Schematic interaction between carbaryl and TES functional group*

Effect of temperature

The effect of temperature on carbaryl adsorption onto TES from aqueous solution was studied at 295, 303 and 313 K, at *p*H 4.0, 300 rpm agitation speed, 1.5 g·L^{-1} as adsorbent dosage and 10 mg·L^{-1} as initial pesticide concentration. Figure 10 shows that adsorption decrease from 12.84 mg·g^{-1} to 6.93 mg·g^{-1} with increasing temperature from 295 K to 313 K. The fact that the equilibrium uptake of the pesticide decreased with

increasing temperature suggests that the process between pesticide and TES is exothermic. The lower removal due to increasing temperature may be attributed to stronger bonds being formed at lower temperature [26, 27]. Furthermore, with increase in temperature, the solubility of the pesticide increases and this makes it more soluble, therefore, the pesticide exhibit lower tendency to go to the adsorbent surface and get adsorbed, so it becomes less retained by the adsorbent.
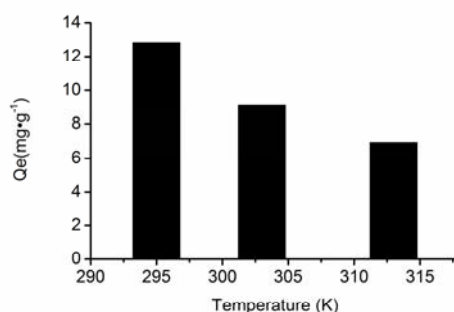

Figure 10. Effect of temperature on the adsorption of carbaryl onto TES

Biosorption kinetics

Two kinetic models were used to investigate the mechanism of pesticide biosorption. Generally, the biosorption process on a porous biosorbent involves several transport stages; external diffusion, internal diffusion, and actual adsorption. The conformity of the predicted model is investigated by the determination of correlation coefficient (R^2 values close or equal to 1). A relatively high R^2 value indicates that the model successfully describes the kinetics of pesticide biosorption.

Pseudo-first-order kinetic model
The pseudo first order model parameters are obtained by plotting the curve corresponding to $log(Q_e$-$Q_t)$ versus t. The values of k_1 and Q_e can be determined respectively from the slope and intercept. The results at variable initial pesticide concentrations are given in Table 1. The calculated and experimental equilibrium biosorption capacity Q_e(cal) and Q_e(exp) values have shown large gap at various initial pesticide concentrations. These results show that the equation of Lagergren is not applicable in the case of carbaryl retention onto TES support.

Pseudo-second-order kinetic model
The values of Q_e and k_2 can be calculated respectively from the slope and intercept of the plot obtained by plotting t/Q_t versus t. The curve is shown in Figure 11. The results of pseudo second order parameters at various initial pesticide concentrations are depicted in Table 1. From these results it is clear that the Q_e(exp) and Q_e(cal) values are in good agreement at various concentrations. Indeed, the highest correlation coefficient values show that the biosorption of carbaryl onto TES is properly explained by the pseudo second order model kinetics.
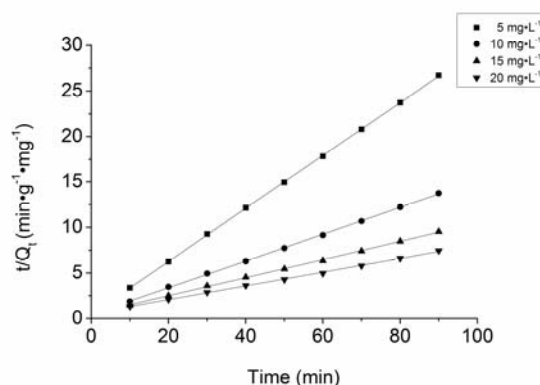
Figure 11. *Pseudo second order kinetics plots for removal of carbaryl
pesticide by TES at different initial pesticide concentrations*

Table 1. *Kinetic parameters for the removal of carbaryl by TES*

Carbaryl concentration [mg·L^{-1}]	Q$_e$(exp) [mg·g^{-1}]	Pseudo – first order			Pseudo – second order		
		K$_1$x10^2 [min^{-1}]	Q$_e$(cal) [mg·g^{-1}]	R^2	K$_2$x10^2 [min^{-1}]	Q$_e$(cal) [mg·g^{-1}]	R^2
5	3.37	2.214	3.287	0.8962	18.373	3.44	0.9999
10	6.55	2.366	11.455	0.9260	4.730	6.82	0.9997
15	9.44	2.418	39.893	0.8005	1.931	10.05	0.9994
20	12.49	2.127	76.683	0.4899	1.022	13.21	0.9989

Adsorption isotherms

To assess the efficiency of the adsorbent for the removal of pesticide, the equilibrium adsorption of carbaryl was studied as a function of concentration on the TES. As was shown previously, the adsorption capacity increases with increasing the initial pesticide concentration. The parameters calculated according to the isotherm models studied are listed in Table 2. These results show that the correlation coefficients obtained from the Freundlich isotherm model (R^2 = 0.991) were higher than Langmuir model, which proves that the Freundlich model is more suitable to describe the adsorptive behavior of TES surface to uptake the carbaryl pesticide. Furthermore, the value of *n* > 1 indicates the favorable physisorption conditions.

Table 2. *Isotherm parameters for carbaryl biosorption onto TES*

Isotherm model	Parameters		
Langmuir	Q$_m$ = 13.18 mg·g^{-1}	K$_L$ = 0.223	R^2 = 0.971
Freundlich	K$_f$ = 9.58 mg^{1-n}·L^n·g^{-1}	n = 3.745	R^2 = 0.991

Thermodynamic studies

The calculated thermodynamic parameters are presented in Table 3. The negative values of *ΔG^0* show that the adsorption is highly favorable and spontaneous. The values of *ΔG^0* are within -20 and 0 kJ·mol^{-1} indicates that the dominating mechanism is the physical

adsorption. The negative value of ΔH^0 shows that the adsorption is exothermic process whereas negative ΔS^0 values reflect the decreasing randomness at the solid/liquid interface during the pesticide/adsorbent reaction.

Table 3. *Thermodynamic parameters of pesticide adsorption onto TES*

Temperature [K]	ΔG^0 [kJ·mol^{-1}]	ΔH^0 [kJ·mol^{-1}]	ΔS^0 [kJ·K^{-1}·mol^{-1}]
295	-5.347	-78.479	-0.248
303	-2.893		
313	-0.859		

Regeneration of TES biosorbent

The reusability of TES adsorbent has a capital effect on these environmental applications. In this fact, the adsorption/desorption process was repeated for five cycles using the same TES for each cycle. The spent biosorbent was calcinated at 400 °C for 60 min, and then treated with ethanol as regenerant solvent. Figure 12 shows the change in adsorption capacity as a function of cycle number. This capacity decreases from cycle to cycle and changes from 14.18 mg·g^{-1} for the first cycle to 4.69 mg·g^{-1} for the cycle 5. This result shows that the TES has a very good regeneration performance and its environmental applications can be prolonged to wastewater treatment.
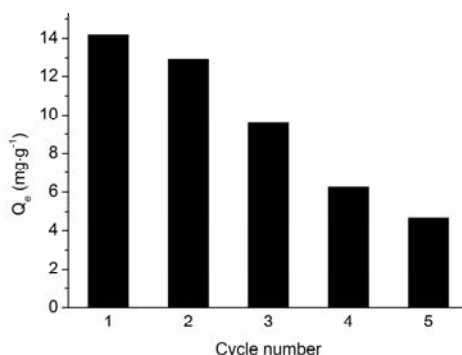

Figure 12. *Regeneration of TES*

CONCLUSIONS

According to the results of this study, treated eggshells were shown to be a very efficient, low cost and ecological biosorbent for removal pesticide from aqueous solutions. The kinetic studies of carbaryl adsorption onto TES indicate that the equilibrium data was obtained after 60 min, using 1.5 g·L^{-1} as adsorbent dosage and 10 mg·L^{-1} as initial pesticide concentration. Freundlich model is more appropriate to explain the nature of the biosorption with high correlation coefficient. Thermodynamic studies reveal that the pesticide adsorption is exothermic, spontaneous, and the adsorption mechanism was found to be physisorption. This study indicated that treated

eggshells could be used as an excellent and inexpensive adsorbent for pesticide effluent treatment.

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