ADSORPTION OF MALATHION ON THERMALLY TREATED EGG SHELL MATERIAL

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ABSTRACT

Thermally treated egg shell materials were prepared at different temperatures. The samples were investigated by means of FT-IR and thermogravimetric analysis (TGA). The adsorption behavior of malathion on egg shell and its thermally treated samples was studied using batch method and gave uptake capacities up to 0.964 mmol/g. Adsorption kinetics as well as the adsorption isotherms were discussed. Regeneration of the loaded resin towards the successive resin was also clarified. The adsorption of malathion is maintained untill the third cycle without a significant activity loss.

Keywords: Malathion; Adsorption; Egg shell; Isotherm; Kinetics

1. INTRODUCTION

Treatment of industrial wastewater is more necessary in the near future due to international regulations which mandate the reduction of different compounds in the cleaned water. In this respect, pesticides threaten the human being and environment due to their toxic and carcinogenic effects. Large quantities of pesticides (not only herbicides and insecticides, but also fungicides, rodenticides, etc.) enter the environment through agricultural, domestic and industrial activities (Martínez et al., 2000; Xu et al., 2005 and Hernández-Soriano et al., 2007). In addition, increasingly stringent pesticide regulations are being enforced by regulatory bodies to prevent the presence of pesticides in effluent and finally in receiving water courses. Thus, it is necessary to reduce and eliminate these life threatening compounds from wastewater before it is discharged. So, their removal from water becomes a very important task (Gupta and Ali, 2001; Gupta et al., 2002; Gupta et al., 2006; Ali and Gupta, 2007; Gupta and Ali, 2008). Adsorption techniques have proved to be an excellent method to treat effluents, offering advantages over conventional processes, especially from an environmental point of view (Ravikumar et al., 2007). Adsorption is considered to be relatively superior to other techniques because of low cost, simplicity of design, availability and ability to treat wastes in more concentrated form (Kannan and Sundaram, 2001; Meshko et al., 2001).

Chicken egg is one of most common food articles and utilized all over the globe. Egg shell membrane is a novel substrate, robust, cost effective and easily available. The by-product egg shell represents approximately 11% of the total egg weight (Stadelman, 2000; Pundir et al., 2009). It was also reported that about 28% of all eggs produced were sent to commercial breaking operations for manufacturing egg products (Poland and Sheldon, 2001). In Taiwan, for example, the annual generation of egg shell waste from the food processors was estimated to be over 1.3×10^4 ton on the basis of 7.1×10^9 of pieces of hen eggs (Tsai et al., 2006). The byproduct egg shell from these breaking operations represents a significant waste for the processor because it is traditionally useless after the production of eggs and its derivatives. Most of the egg waste was commonly disposed of for landfill without any pretreatment (Tsai et al., 2006). It is obvious that these approaches are not desirable practices in view of the odor from biodegradation (Poland and Sheldon, 2001). Egg shell can be also used as a fertilizer or soil conditioner because of its high nutrition contents such as calcium, magnesium and phosphorus (Tacon, 1982). In addition, the egg shell membrane contains high amounts of minerals and amino acids (Tsai et al., 2006).There are many distinctive properties associated with egg shell like high porosity, antibacterial or anti-inflammatory characteristics (Pundir et al., 2009; Arami et al., 2006; Tembe et al., 2008). Due to its large porous surface and porous structure, egg shell was chosen as good adsorbent (Allen et al., 2000, Tsai et al., 2008). Due to these properties egg shell membranes have multiple applications in therapeutic, nutraceutical, metallurgy or bioremediation areas, either as such or after processing (Pundir et al., 2009).

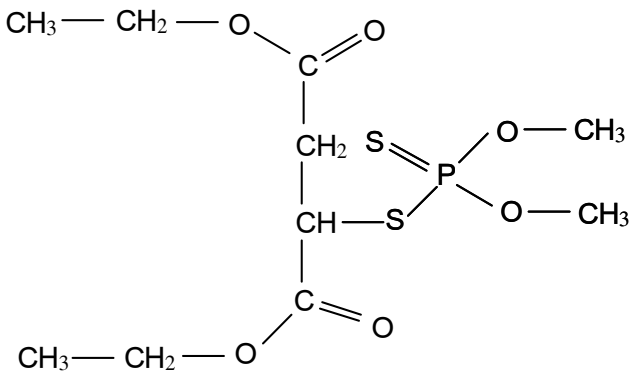
Malathion is a pesticide, commonly used by Egyptian farmers, so its removal from water sources can become a very important issue. Malathion was studied on bagasse fly ash (Gupta et al., 2002) and found to be 0.006 umol/g. Tire rubber granules were used for removing atrazine from aqueous solution (Alam et al., 2005). Porous polymeric adsorbents like Amberlite XAD-4(polystyrene-divinyl benzene copolymer) and XAD-7(non-ionic aliphatic acrylic polymer) were used for the adsorption of herbicides such as alachlor, amitrole, trifluralin and prometryn (Kyriakopoulos et al., 2005).

The present work aims to study the adsorption characteristics of malathion on natural and thermally treated egg shell material. The adsorption isotherms as well as the kinetics of the adsorption reaction will also be studied. The study will shed some light on the mechanism of adsorbent/adsorbate interaction and the efficiency of the regeneration method.

2. MATERIALS AND METHODS

2.1. Materials

Malathion [s-1,2-bis(ethoxycarbonyl)ethy-*o,o*-dimethyl phosphoro- dithioate] with molecular formula $C_{10}H_{19}O_6PS_2$ and formula weight of 330 g/mol was obtained from ADWIA, Egypt. The solubility in water was found to be 145 mg/L.



Malathion

The egg shells, collected from local shops, were vigorously mixed and rinsed with distilled water for the preparation of the egg shell material. The washed egg shells were dried at a temperature of 40°C for 24 h. The dried membrane was ground and sieved to the required particle size of < 0.125 mm (E1). Calcined egg shell samples were obtained from thermal treatment of the bulk egg shell sample (E1) for 2 h in a muffle furnace at 200°C and 400°C to give samples E2 and E3, respectively.

2.2. Instruments

Thermogravimetric analysis (TGA) of E1 was carried out in a nitrogen atmosphere using Shimadzu DTA/TGA-50, Japan with a heating rate of 10°C min^{-1}. The flow rate of N_2 was adjusted to 20 cm^3 min^{-1}.

Infra red spectra were performed using Nicolet IR200 FT-IR Spectrometer.

Elemental analyses (C/H/O/N/S) of the samples (1–3 mg) were made at the micro analytical center of Cairo University. For each analysis, the standard sample (i.e., sulfanilic acid) was analyzed for checking the experimental error within ±1%. All measurements were carried out in triplicate.

2.3. Estimation of malathion

The concentration of malathion was measured spectrophotometrically at λ = 195 nm (in distilled water) and at λ = 200 nm (in methanol) using JENWAY Spectrophotometer 6405 UV/Vis. A blank of the sorbent without insecticide was done and considered in the calculations. The Calibration curves of malathion in distilled water (MeOH) were constructed according to the above method of measurement (Pal and Vanjara, 2001).

2.4. Adsorption studies

2.4.1. Effect of adsorbent dose

The mass of the dry adsorbent (E1, E2 or E3) was varied from 0.05 to 0.35 mg. The desired mass was placed in a flask with 100 mL of 300 ppm (0.909 mmol/L) aqueous solution of malathion at pH 6 for 6 hours. The mixture was shaken using Vibromatic–384 shaker at 300 rpm and 25°C. The uptake of malathion was calculated by determining the residual concentration of malathion in the supernatant according to the above method and according the following equation:

$$q_e = \frac{(C_o - C_e) \times 100}{m} \quad (1)$$

where q_e (mmol/g) is the uptake of malathion at equilibrium, C_o and C_e (mmol/L) are the concentration of malathion at initial and equilibrium, respectively, m (g) is the mass of the used egg shell material.

2.4.2. Effect of contact time

The effect of conditioning time on the adsorption of malathion by the dry adsorbent (E1, E2 or E3) was investigated. A 0.06 g portion of dry adsorbent was placed in flasks containing 100 mL of 300 ppm (0.909 mmol/L) aqueous solution of malathion at pH 6. The contents of the flasks were equilibrated on the shaker at 300 rpm and 25°C. Five mL of the solution (free from adsorbent particles obtained by filtration) were taken at different time intervals (from 4 min to 6 hours) and the residual concentration of malathion was determined. The adsorbed amount of malathion per unit weight of the adsorbent beads q_t (mmol/g), at time t was calculated from the mass balance equation as:

$$q_t = \frac{\sum_{i=1}^{n} (C_{t(i-1)} - C_{ti}) V_{t(i-1)}}{m} \quad (2)$$

where C_{ti} (mmol/L) is the measured concentration of the drawed sample number i at time t and $C_{t0} = (C_0)$, V_{ti} (mL) is the volume of the solution in the flask at sample number i and time t, and m is the weight of the adsorbent beads added into the flask.

The data obtained was treated according to the pseudo-first (Eq. 3) and pseudo-second (Eq. 4) order kinetics (Malik, 2004):

$$\log (q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303}\right) t \quad (3)$$

$$\frac{t}{q_t} = \left(\frac{1}{k_2 q_e^2}\right) + \left(\frac{t}{q_e}\right) \quad (4)$$

where q_e and q_t (m mol g^{-1}) refer to the amount of malathion adsorbed at equilibrium and at time t (min), respectively; K_1 and K_2 (g $mmol^{-1}$ min^{-1}) are the overall rate constant of pseudo-first and pseudo-second order reaction, respectively. The values of K_1, K_2 and q_e were obtained from the straight line plots of log ($q_e - q_t$) or (t/q_t) vs. t (min).

The uptake/time data was treated according to Fickian diffusion low (Chang and Juang, 2004):

$$q_t = K_i t^{0.5} + X \quad (5)$$

where q_t (m mol g^{-1}) is the amounts of malathion adsorbed at time t (min) and K_i is intraparticle diffusion rate (mmol/g $min^{-0.5}$).

2.4.3. Effect of initial concentration and sorption isotherms of malathion

Portions of 0.06 g of dry sample of the same adsorbent (E1, E2 or E3) were placed in a series of flasks containing 100 mL of malathion solution with different initial concentrations of 50, 100, 200, 300 and 500 ppm at pH 6. The contents of the flasks were shaken at 300 rpm and 25°C for 6 h. After equilibrium, the residual concentration of malathion was estimated and then the adsorbed amount was calculated.

The adsorption isotherms of malathion using E1, E2 and E3 were also studied following the above method. The adsorption data were treated according to Langmuir model (Eq. 6) (Langmuir, 1918):

$$\frac{C_e}{q_e} = \frac{C_e}{Q_{max}} + \frac{1}{K_L Q_{max}} \quad (6)$$

where C_e is the equilibrium concentration of malathion in solution (mmol/L), q_e the adsorbed value of malathion at equilibrium concentration (mmol/g), Q_{max} is the maximum adsorption capacity (mmol/g) and K_L is the Langmuir binding constant which is related to the energy of adsorption (L/mmol). Plotting C_e/q_e against C_e gives a straight line with slope and intercept equal to $1/Q_{max}$ and $1/K_L Q_{max}$, respectively.

2.5. Desorption studies

A 0.6 g portion of the adsorbent (E1, E2 or E3) was mixed with a malathion solution through shaking in malathion solution (300 ppm) for 2 h. The loaded adsorbents were filtered off, washed by distilled water and then dried at 40°C for 2 h. The sorbed pesticide amount was calculated. The loaded samples were heated at different temperatures (150°C, 250°C, 350°C, 500°C and 600°C) for 2 h. The sorption/desorption process was repeated at 500°C for several cycles.

3. RESULTS AND DISCUSSION

FT-IR spectrum of E1 (Figure 1) shows some peaks positioned at 3411, 1648, 1528, 1308 and 1168 cm^{-1}. The bands at 3411 cm^{-1} can be attributed to the presence of O–H and N–H groups, while the bands at 1648 and 1528 cm^{-1} reflect the carbonyl group stretching (amide) and N–H bending respectively. Bands at 1308.03 and 1168.70 cm^{-1} correspond to C–H bending and C–O stretching respectively (Tsai et al., 2006).

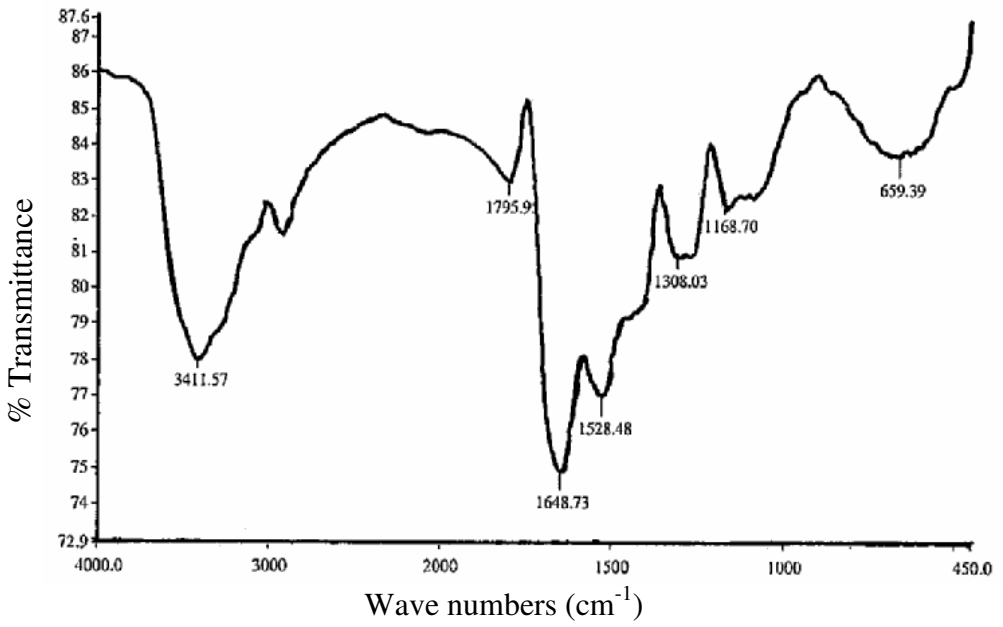


Figure 1. Fourier transform infra-red (FTIR) spectrum of E1

The TGA analysis of egg shell indicates thermal stability up to 630°C with a mass loss of $\Delta m = 2.6\%$ referring to volatile material. The thermal decomposition process occurs at the temperature range from 636 to 795°C with mass loss $\Delta m = 42.5\%$, which corresponds to carbon dioxide release, in a single step, in a defined way.

Elemental analysis was used as a means of examining the remaining residues in the preparation of the egg shell products. The results of ultimate analysis of egg shell material (E1) are given in Table (1). The residual contents (i.e., H, N and S) of egg shell material (E1) are relatively low, showing that the egg shell particle should be almost composed of carbonate minerals (e.g., calcite).

Table (1) Elemental analysis of egg shell material (E1)

Egg shell material	Elemental analysis				
	C% (wt%)	H% (wt%)	N% (wt%)	O% (wt%)	S% (wt%)
E1	13.83	0.55	1.97	28.31	0.12
E2	15.56	0.54	1.92	27.07	0.12
E3	16.98	0.47	1.84	26.04	0.11

3.1. Adsorption studies

3.1.1. Effect of adsorbent dose

Adsorption of malathion as a function of adsorbent dose is shown in Figure 2. As the adsorbent dose increases, the removal efficiency of malathion decreases. The maximum uptake (about 95% removal efficiency) was obtained at adsorbent dose of 0.05 g while the minimum was at 0.3 g. The observed decrease in uptake as the dose increases may be attributed to the agglomeration of the adsorbent particles through the adsorption. On the other hand, the uptake of malathion by the investigated egg shell follows the order E3 > E2 > E1. This order may be related to the increase in the hydrophobicity of egg shell as a result of thermal treatment. The increase in the hydrophobicity leads to (i) less competition from water molecules to the substrate sites, (ii) strong intermolecular interaction between malathion molecules, causing them to pack flat in the adsorbed layer and (Bojemueller et al., 2001; Chandrasekhar and Ramaswamy, 2002).

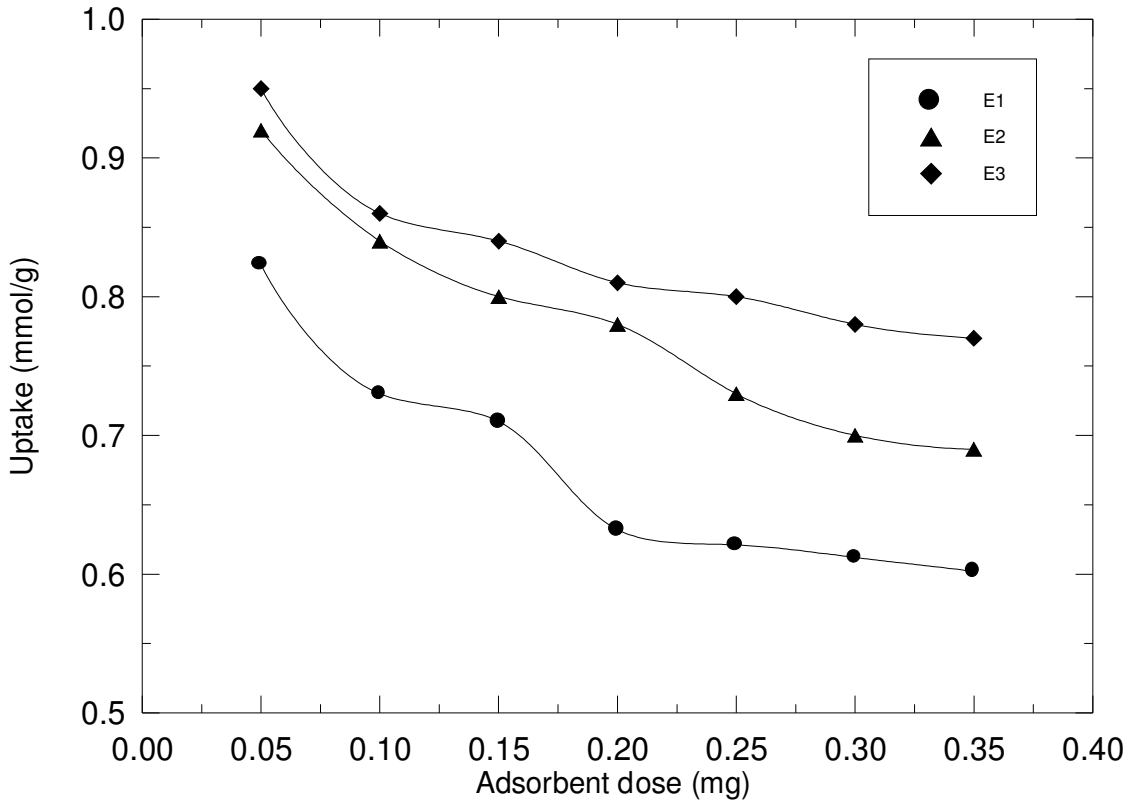


Figure 2. Uptake of malathion as a function of adsorbent dose at initial concentration of 300 mg/L

3.2. Kinetics

Figure 3 shows the removal of malathion from aqueous solution by egg shell as a function of time. The uptake value increases as the contact time increases. About 91% of the maximum uptake value was reached after 100 min and the equilibrium was reached within 175 min. The thermally treated samples of egg shell (E2 and E3) display a higher uptake value than E1. This may be related to the increase of hydrophobicity of the thermally treated samples.

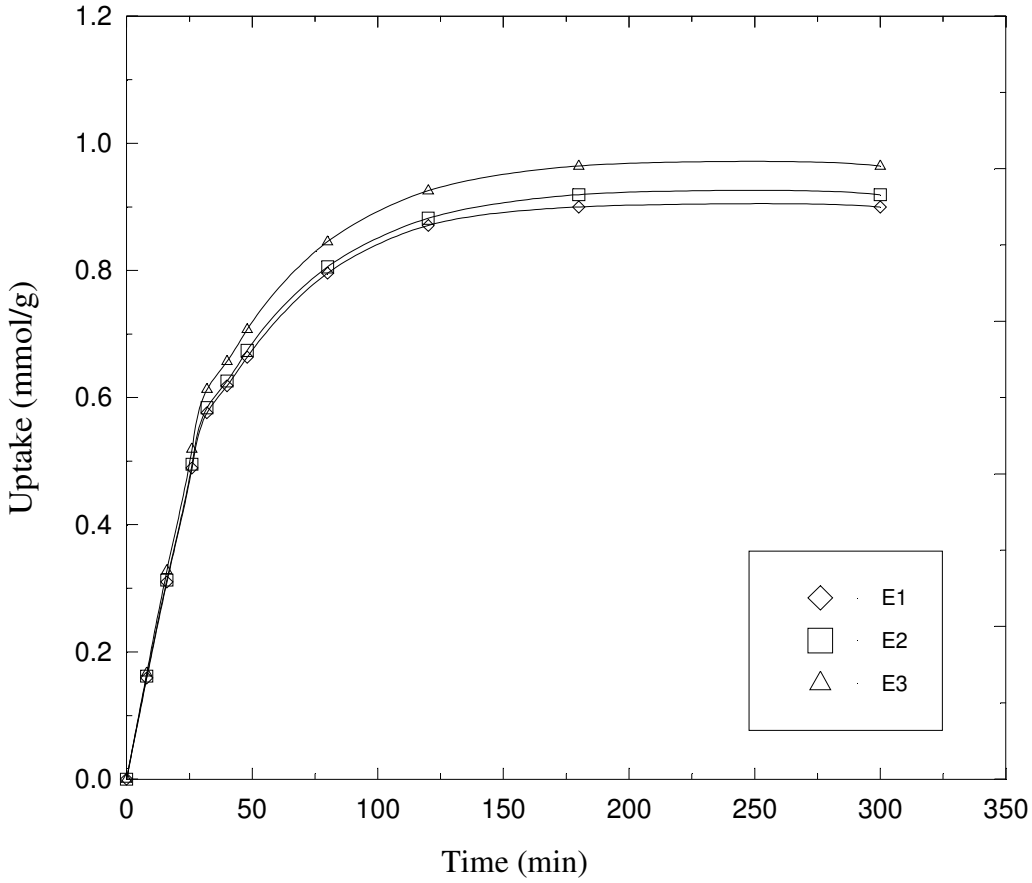


Figure 3. Effect of contact time on the adsorption of malathion from aqueous solution by studied adsorbents at initial concentration of 300 mg/L

The data presented in Figure 3 was treated according to the pseudo-first (Eq. 3) and pseudo-second (Eq. 4) order kinetics. The values of K_1, K_2 and q_e were reported in Table 2. As shown in Table 2, the values of q_e of pseudo-first order model are more comparable with the experimental ones. This indicates the validity of this model to describe the adsorption kinetics and the effect of the textural properties of the egg shell on the adsorption process.

Table (2) Kinetic data for the adsorption of malathion by studied adsorbent at initial concentration of 300 ppm, natural pH and at 25°C

Adsorbent	Exp. q_e (mmol/g)	q_e (mmol/g)*	R^2	q_e (mmol/g)**	R^2
E1	0.8996	0.9048	0.9976	0.9361	0.9871
E2	0.9188	0.9283	0.9939	0.9516	0.9791
E3	0.9641	0.9749	0.9984	0.9905	0.9783

* Using pseudo-first order model

** Using pseudo-second order model

The uptake/time data (Figure 3) was treated according to Fickian diffusion low to determine if the intraparticle diffusion is the rate determining step or not. As the value of *X* decreases the effect of external diffusion on the reaction rate decreases. In our case, the plot of q_t against $t^{0.5}$ indicates that the adsorption is governed by intraparticle diffusion. The negative values of X (Table 3) indicate that the boundary layer (external film resistance) has no significant effect on the diffusion rate.

Table (3) Intraparticle diffusion parameters for the adsorption of malathion by studied adsorbents

Adsorbent	K_d (mmol g^{-1} $min^{-0.5}$)	X	R^2
E1	0.128357	-0.190439	0.98013
E2	0.130212	-0.193621	0.98069
E3	0.137263	-0.207031	0.98039

3.3. Isotherms

Adsorption isotherms of malathion in water by egg shell and its thermally treated samples were studied and depicted in Figure 4.

According to Gills' classification (Giles et al., 1960), the isotherms obtained in aqueous solutions (Figure 4) are S-type (according to the initial slope). This means that malathion is adsorbed as (i) a monofunctional (i.e. egg shell beads has a marked localization of the forces of attraction for the substrate over a short section and it is adsorbed as a single unit) through H-bonding with the O-H groups of the surface of egg shell beads, (ii) has moderate intermolecular interaction, causing it to pack vertically in a regular array in adsorbed layer and (iii) meets strong competition for substrate sites from the molecules of water.

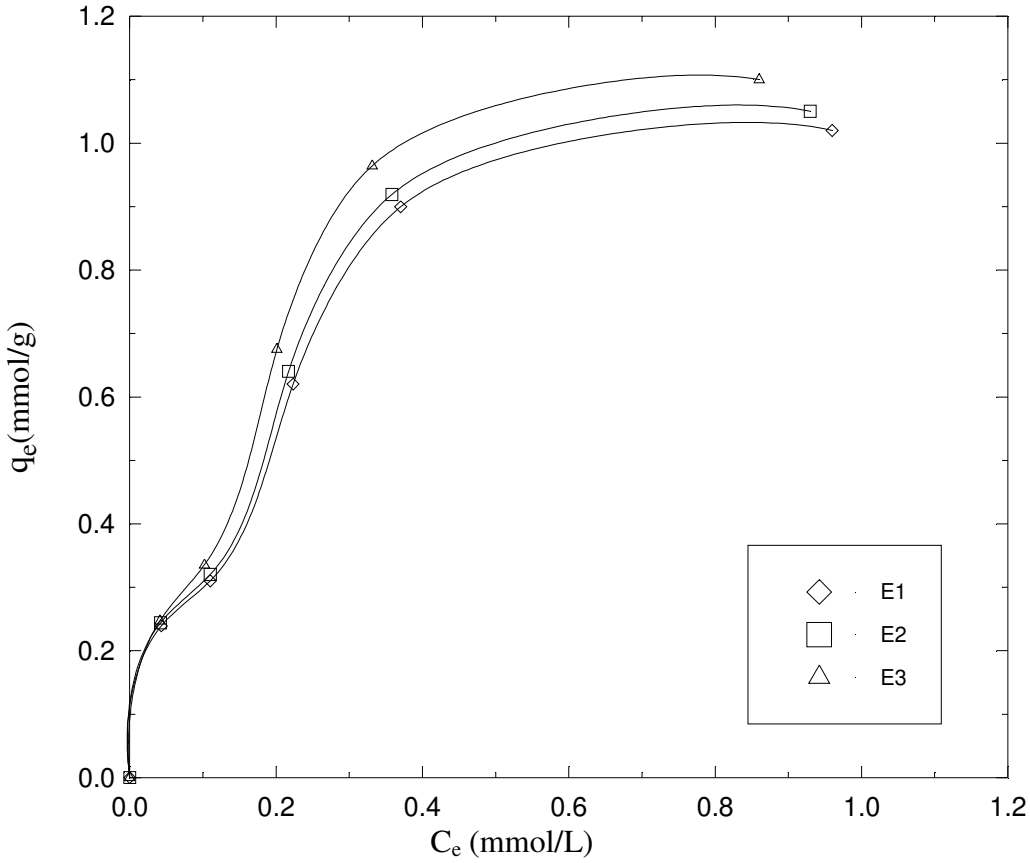


Figure 4. Effect of concentration on the adsorption of malathion from aqueous solution by studied adsorbents

The adsorption data in Figure 4 were treated according to Langmuir model (Eq. 6). The values of K_L and Q_{max} at different temperatures for adsorption of malathion were obtained and reported in Table (4). The values of (Q_{max}) follow the order E3 > E2 > E1. This order again confirms the effect of hydrophobicity on the uptake value. On the other hand, the thermally treated egg shell samples display similar values of K_L. This indicates the similar adsorbent/adsorbate interaction (Nennemann et al., 2001 and Lagaly, 2001). The isotherms (Figure 4) are also characterized by a multilayer adsorption with a short plateau (knee). This short plateau means that the adsorbate molecules have high affinity for the layer of adsorbate molecules (already adsorbed in the first degree of saturation). It is also seen that the point of inflection (knee) appears at lower concentration for thermally treated samples (E2 and E3) confirming their higher affinity for malathion.

Table (4) Langmuir parameters for malathion adsorption (mmol/g) by studied adsorbents from aqueous solution at 25°C

Adsorbent	K_L (L/mmol)	Q_{max} (mmol/g)	R^2
E1	3.549	1.354	0.969
E2	3.526	1.399	0.967
E3	3.556	1.506	0.964

3.4. Desorption studies

The regeneration data of E1, E2 and E3 for reuse is shown in Table 5. The temperature (500°C) was found to be the optimum temperature for regeneration of E3. This was attributed to the complete decomposition of malathion at 500°C (about 99% decomposition efficiency). The removal efficiency was noticed to decrease after the 3rd cycle.

Table (5) Regeneration of E1, E2 and E3 by thermal treatment at 500°C

	Exp. q_e (mmol/g)			
Adsorbent	1st Run of Regeneration	2nd Run of Regeneration	3rd Run of Regeneration	4th Run of Regeneration
E1	0.8996	0.8910	0.8805	0.7009
E2	0.9188	0.9105	0.9007	0.7406
E3	0.9641	0.9542	0.9410	0.7912

4. CONCLUSION

The adsorption behavior of malathion on egg shell and its thermally treated samples was clarified. The study indicates that the adsorption follows a pseudo-first order reaction with S-type isotherm. The medium of adsorption plays an effective role in the nature of adsorbent/adsorbate interaction and uptake capacity. The thermally treated samples display a slightly greater uptake capacity relative to untreated one. This behavior was related to the hydrophobicity of the thermally treated samples. Desorption of malathion from the loaded samples was simply carried out by thermal treatment at 500°C. The adsorption of malathion is maintained untill the third cycle without a significant activity loss. The simplicity of the method along with the low cost and safety of the materials reported here make it promising in the field of pesticides removal from aqueous media.

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