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Research Article

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Removal study of imidacloprid from aqueous solution by adsorption onto polyacrylamide cross-linked

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ABSTRACT

The polymeric hydrogel was used as an adsorbent for removing Imidacloprid from aqueous solution. The adsorption experiments were carried out by using Visible- spectrophotometer. The effect of pH, existing salt, initial pesticide concentration and temperature were studies. The data was found that Freundlich isotherm model fits and the adsorption isotherms are of S-curve type according to Giles classification. The adsorption phenomenon was examined as a function of temperature (10, 15, 20, 25 and 30°C). The extent of adsorption of Imidacloprid on hydrogel was found to decrease with increasing temperature (exothermic process). The basic thermodynamic functions have also been calculated. The amount of dye adsorbed on the hydrogel surface at different pH values showed an increase in the following order: 10 < 8 < 6 < 5 < 4 < 2, the adsorption process is affected by the electrolyte concentration. The results indicated an increase in adsorption of Imidacloprid in the presence of sodium chloride.

Keywords: Imidacloprid, polyacrylamide, adsorption, hydrogel

INTRODUCTION

Pollution of surface and ground waters causes risk to environment and human health because of the potential health hazards of their contents of inorganic and organic compounds Also, the contamination of these waters by pesticides is an arduous task that the scientists have been battling to resolve over the years. Pesticides have some undesirable side effects, such as their toxicity, carcinogenic and mutagenic nature [1].

Several physical, chemical, physico-chemical and biological methods have been developed to remove contaminants from wastewater, such as ozonation [2], chemical oxidation with ozone [3], photocatalytic method [4], combined ozone and UV irradiation [5], , membrane filtration [6], and adsorption [7]. Adsorption has been found one of the most popular physico-chemical treatment methods for removing contaminants with potential applications [8,9].

Polymeric hydrogels play an important role in the treatment of waste water. Over the past several decades, polymeric hydrogels have attracted much scientific interest and have found uses in many fields, such as molecular filters and super absorbents [10-12]. The aim of present work is to explore the feasibility utilizing Polymeric hydrogels as adsorbent for dye. Equilibrium analysis was conducted to investigate the mechanism of dye adsorption and optimization of various parameters in dye recovery.

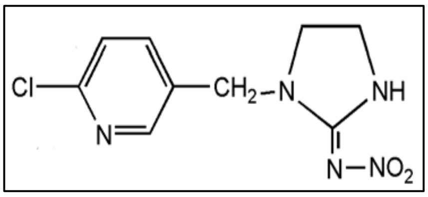
EXPERIMENTAL SECTION

INSTRUMENTS:

1- UV-Visible spectrophotometer, Shimadzu. PC1650, Japan.
2- Shaker water bath, K&K Scientific, Korea.
3- Centrifuge, CL008, Belgium.
4- Electronic Balance, Sartorius Lab., ± 0.0001g, Germany.
5- pH-Meter, HANNA, Electronic Ltd, Romania.
6- Oven, Triup International Corp. Italy.

MATERIALS:

Imidacloprid (Scheme (1)) was supplied by Sigma-Aldrich, sodium hydroxide, hydrochloric acid and sodium chloride were purchased from Fluka.



Scheme (1): The chemical structure of Imidacloprid

METHODOLOGY

PREPARATION OF HYDROGELS

Acrylic amide (5gm) was dissolved in (50ml) de-ionized water and added (1ml) N,N,N',N'-tetramethlene-ethylene-diamine (TEMED) as accelerator , and then the solution was added into triple-necked flask , which was equipped with a stirring apparatus and a reflux condenser. The solution was stirred for 20 min and heated in a water bath of 60°C under nitrogen protection. An amount of (0.1gm) potassium peroxodisulphate (KPS) as initiator dissolved in (10ml) de-ionized water, was slowly added into the flask to initiate the polymerization process after 30min. The reaction was stopped after 2h.The product was precipitated by methanol as white and solid mass. The prepared hydrogel was pourd into a petri dish 90x10 mm and was then dried in the oven of 50°C for 24h. The polymeric hydrogel was ground and sieved to a particle size of 250 μm.

ADSORPTION ISOTHERM

Wavelength of maximum absorbency (λ_{max}) was recorded for Imidacloprid dissolved in aqueous media and found 270 nm (Figure (1)). This value was utilized for estimation of quantity of pesticide adsorbed. Solutions of different concentrations were prepared by serial dilution. Absorbance values of these solutions were measured at 270 nm and plotted against concentration values. The calibration curve in the concentration range that falls in the region of applicability of Beer-Lambert's law was employed.

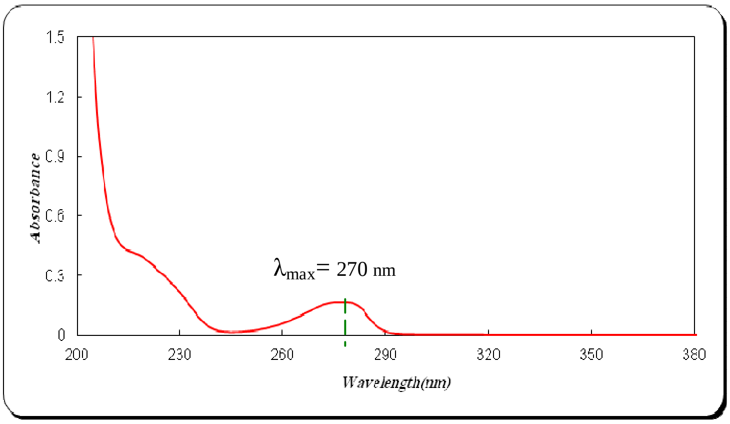


Figure (1): UV-Visible Spectrum of Imidacloprid

The adsorption isotherms were determined by shaking 0.05 g of hydrogel into 10 ml pesticide solutions, having concentrations ranging from 0-50 ppm. After 180 min. of shaking, the suspensions were centrifuged at 3000 rpm for 10 min. The pesticide concentration was determined spectrophotometrically.

The quantity of Imidacloprid adsorbed was calculated according to the following equation[13]:-

$$Q_e \text{ or } \frac{x}{m} = \frac{V\,(C_o - C_e)}{m} \qquad (1)$$

Where:
x : the quantity adsorbed (mg).
m : weight of adsorbent (g).
C_o : initial concentration (mg/L).
C_e: equilibrium concentration (mg/ L).
V : volume of solution (L).

EFFECT OF TEMPERATURE
Adsorption experiment was repeated in the same manner at temperatures of 10, 15, 20, 25 and 30°C to estimate the basic thermodynamic functions.

EFFECT OF PH
Adsorption experiment was carried out as mentioned previously as a function of pH using a fixed concentration of Imidacloprid. Sodium hydroxide and hydrochloric acid were used to adjust the pH. The pH of the suspensions at the commencement of the adsorption was measured as well as at the end of experiment using pH-meter.

EFFECT OF IONIC STRENGTH
The effect of (0.001- 0.300 gm) sodium chloride solutions containing fixed concentration of Imidacloprid were added to flasks containing 0.2 gm of hydrogel. The procedure described for the adsorption experiment was followed.

RESULTS AND DISCUSSION

The adsorption of Imidacloprid from aqueous solution onto hydrogel has been studies at different temperature (10-30°C). The adsorption isotherm of pesticide is given in Figure (2).

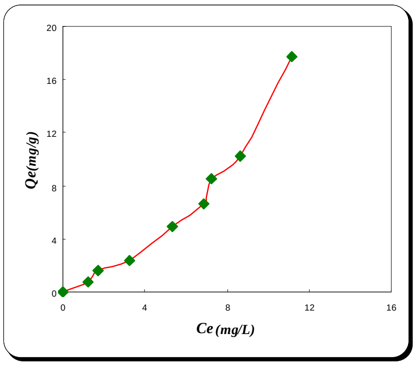


Figure (2): Adsorption isotherm of Imidacloprid onto hydrogel at 20°C

The adsorption efficiency and effectiveness of hydrogel surface increase with increasing initial pesticide concentration [14]. The capacity of adsorption depends on several parameters such as the specific surface area, the expansible character [15]. The shape of Imidacloprid isotherm can be considered as S-type according to Giles classification [16]. The S-type isotherm depends upon the Freundlich assumption about the heterogeneity of the surface. The presence of various planes leads to heterogeneous adsorption behaviour. Heterogeneity is a usual and a general feature of surface properties due to different unsaturated adsorption sites of different energetic behaviour [17].

The equilibrium removal of pesticide can be mathematically expressed in terms of adsorption isotherm. The Langmuir and Freundlich models are the most frequently employed models to describe the experimental data of adsorption isotherms. The Freundlich equation was developed mainly to allow for an empirical account of the variation in adsorption heat with concentration of an adsorbate (vapor or solute) on an energetically heterogeneous surface[18]. It has the general form:

$$Q_e \text{ or } \frac{x}{m} = kC_e^{1/n} \qquad (2)$$

Where Q_e is the amount adsorbed per unit mass of the solid (adsorbent), C_e is the vapor or solute concentration at equilibrium, k is the Freundlich constant, equal to adsorption capacity at $C_e = 1$; and n is an exponent related to the intrinsic heat of solute adsorption.

The pesticide sorption isotherm followed the linearized Freundlich model as shown in Figure (3).

$$\log Q_e = \log k + \frac{1}{n} \log C_e \qquad (3)$$

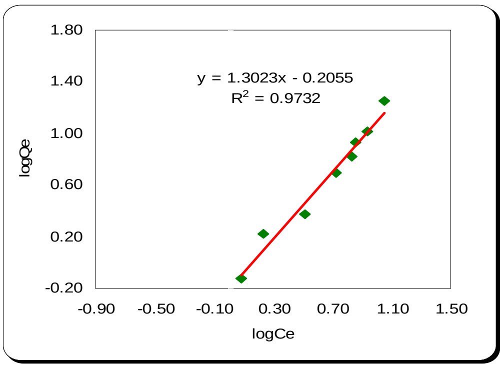


Figure (3) linear form of Freundlich isotherm of Imidacloprid on Hydrogel

Figure (3) shows the linear relationship of $\mathbf{logQ_e}$ versus $\mathbf{logC_e}$. The values of Freundlich constants as well as the correlation coefficient are presented in Table (1). The isotherm data fit the Freundlich model well as indicated from the value of correlation coefficient.

Table (1): Freundlich constants for the adsorption of Imidacloprid on hydrogel

n	K_f	r
0.76	0.67	0.9732

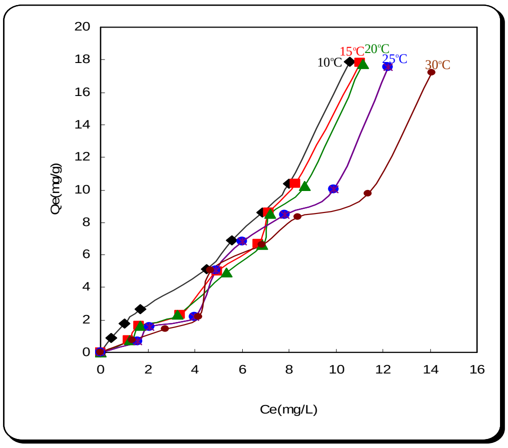


Figure (4): Adsorption isotherms of Imidacloprid on hydrogel at different temperatures

Figure (4) shows the effect of temperature on the adsorption of Imidacloprid, in the range of (10-30°C).

The adsorption capacity of the hydrogel increased with increasing of the temperature from 10 to 30°C. It is found that the higher temperature is to the advantage of adsorption and that the adsorption is an endothermic reaction.

The thermodynamic parameters, namely the enthalpy of adsorption (ΔH), the Gibbs free energy of adsorption (ΔG) and the entropy of adsorption (ΔS) were calculates as shown in equations (4-6).

$$\ln X_m = \frac{-\Delta H}{RT} + \text{Constant} \qquad (4)$$

$$\Delta G = -RT \ln K \qquad (5)$$

$$\Delta = \frac{\Delta H - \Delta G}{T} \qquad (6)$$

Table (2) and Figure (5) demonstrate these calculations. Table (3) shows the calculated values of the thermodynamic parameters for the Imidacloprid adsorption onto hydrogel.

Table (2): Effect of temperature on the maximum adsorbed quantity for adsorption of R.B. on hydrogel

T(k)	10^3/**T**(k^{-1})	**X$_m$**(mg/g)	**ln**$_{(}$**X**$_{m)}$
		Ce = 8	
283	3.53	10.40	2.34
288	3.47	9.700	2.27
293	3.41	9.300	2.23
298	3.35	8.600	2.15
303	3.30	7.900	2.06

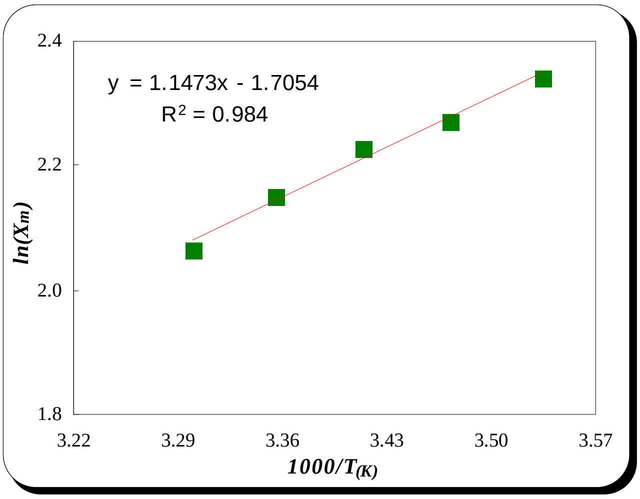


Figure (5): Plot of ln X_m against reciprocal absolute temperature for adsorption of Imidacloprid onto hydrogel

The value of ΔH indicates endothermic adsorption process. One possible explanation of the endothermicity of heats of adsorption is that pesticides and the surface are both solvated in water. In order for the pesticides to be adsorbed, they have to lose part of their hydration shell. The dehydration processes of the pesticides and the adsorbent surface require energy [19]. So, the dehydration processes supersede the exothermicity of the adsorption processes. The negative ΔS values, as well as the very small negative ΔG values have also been considered as the consequence of the diffusion of the pesticide into the chemical structure of the adsorbent.

Table (3): Values of thermodynamic functions of adsorption process of Imidacloprid on Hydrogel

T(°C)	**K**	**ΔS** (J.mol^{-1}.k^{-1})	**ΔG** (kJ.mol^{-1})	**ΔH** (J.mol^{-1})
20	24.25	-6.39	-7.66	-9.53

The effect of the initial pH of the Imidacloprid solution on the amount of pesticide adsorbed was studied by varying the initial pH (2-10) at constant process parameters. An increase in initial pH increase the amount of pesticide adsorbed as indicated form results in Figure (6).

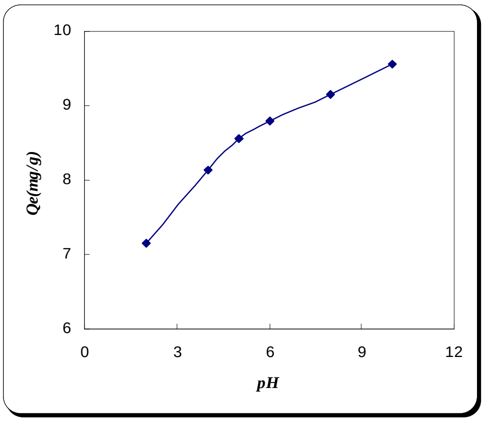


Figure (6): Effect of pH in adsorption uptake of Imidacloprid on hydrogel at 20°C

The nature of the solid surface as well as that of the solute and solvent, may be altered by change in pH. The solution pH affects the surface charge of the adsorbent and, therefore, the adsorption process through dissociation of functional groups, viz, surface oxygen complexes of basic character (such as carbonyl and phenolic groups) or of basic character on the active sites of the adsorbent [20].

The effect of ionic strength on adsorption uptake of Imidacloprid onto hydrogel was studied at variable concentrations of sodium chloride. Figure (7) shows the effect of ionic strength on the adsorption uptake of pesticide on surface. When the concentration of sodium chloride increased, the uptake of Imidacloprid pesticide was increased.

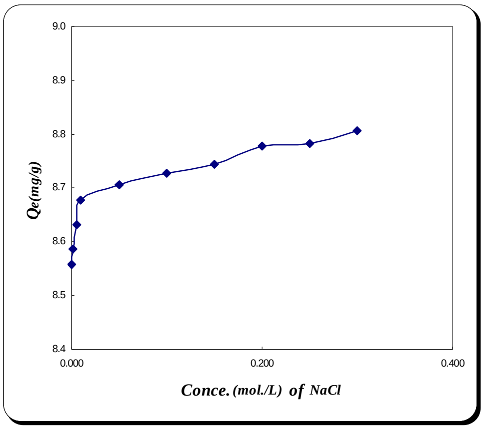


Figure (7): Effect of different concentrations of sodium chloride on the adsorption of pesticides onto hydrogel

The addition of NaCl causes a partial neutralization of the positive charge on the surface and a consequent compression of the electrical double layer by the negative ion[21].

CONCLUSION

On the basis of the experimental results of this investigation, the following conclusions can be drawn:
1- Hydrogel can be used as an adsorbent for the removal of Imidacloprid pesticide from solution.
2- Freundlich isotherm model adequately described the adsorption of Imidacloprid.
3-Thermodynamic studies confirmed that adsorption process of Imidacloprid onto hydrogel was exothermic. The thermodynamic value of ΔG is negative for system, indicating a spontaneous process.
4- The percentage removal of pesticide was dependent on pH solution and ionic strength of solution.

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