REMOVAL OF AMITROLE FROM AQUEOUS SOLUTIONS BY ACID ACTIVATED CLAY

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In this study, the adsorption behavior of amitrole on acid activated clay (AC) was investigated using a spectrophotometric method to obtain information on the pesticide removal. The adsorption of amitrole from aqueous solutions by AC has been performed using a batch-adsorption technique. The effect of various experimental parameters, such as initial concentration of pesticide, contact time, temperature and pH on the adsorption process, were investigated. Original pH at the beginning was 5. It was observed that the adsorption percentage of amitrole on AC remained practically constant with increasing temperature and contact time of around 3 h was sufficient to reach the equilibrium for all temperature. Temkin and Harkins-Jura adsorption models were applied to describe the equilibrium isotherms and the isotherm constants were calculated. It was found that the data were fitted Temkin adsorption model better than Harkins-Jura adsorption model. The present study showed that the asit activated clay was abundant snd low-cost. Clay can be used as sorbent for the removal of amitrole from aqueous solutions.

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Introduction

Increasing use of pesticides in agriculture and domestic activities for controlling pests is polluting the environment day by day.[1] The contamination of soils, ground water and surface water by pesticide is currently a significant concern throughout the world due to the detrimental effect of them to both human life and environment.[2] Toxicity of present pesticides and their degradation products is making these chemical substances a potential hazard. When these pesticides are introduced into the environment through spraying on crops, the pesticide droplets fall on soil, plant and water. While some part of these chemicals stays in the area where it is applied, major parts are transported to various environmental media. The adsorption/desorption phenomena of pesticides in soil are of great importance from environmental point of view. Pesticide sorption process affects other processes like transport, degradation, volatilization and bioaccumulation, which influence the final fate of these compounds in the soil.[3-5]

In industry, the cost of water not only includes the direct cost but also costs incurred in bringing the water to certain specifications prior to use. Present and future legislation will lead to more stringent controls on industrial effluent pollution.[6] Industries such as food and beverage industry, chemical, petrochemical, pharmaceutical and refining industries, pulp and paper industry and the electronics industry all generate large volumes of waste streams with significant residue content for treatment and recycling.[7] In general, reduction of waste water in any given industry can be achieved by a number of ways including process modification, changes in raw materials used or water consumption reduction programmes leading to significant environmental and economic benefits.[8, 9]

Current technologies for waste stream treatment and recycling include membrane technology encompassing reverse osmasis, micro filtration and ultra filtration.[10-13] Alternatives to membrane systems include oxidation methods based on chemical oxidation an air/oxygen based catalytic (or noncatalytic) oxidation. The first category includes advanced oxidation processes such as the use of ozone, hydrogen peroxide and UV radiation to generate hydroxyl radicals used for oxidation.[14-17] These processes tend to be limited by their intensive costs. The second category includes dry oxidation, wet air oxidation and catalytic wet air oxidation.[18-20]

Adsorption is another example of a physical procedure used in waste water treatment. Adsorption technology has been used for the removal of organics from waste waters, primarily focusing on the use of activated carbon as the adsorbent choice. Regeneration of the spent adsorbent material can be a costly and intensive process.[21] This has led to an interest in developing alternative adsorbents for the removal of organic pollutants from aqueous waste streams.[22,23]

This study aims to remove the undesired pesticide termed amitrole from water using a natural clay material which is sulphuric acid washed and dried. This study is furnissed with some experimental parameters.

Experimental studies

Adsorbate

Amitrole is a pesticide used in agriculture that is supplied by Hektaş AŞ. in Turkey. It is used as a herbicide to control grass and weeds growing around fruit trees, bushes, vines and cereal crops. It is also used on weeds along paths,

railways tracks and industrial areas as well as on aquatic weeds in marshes and ditches. Amitrole is toxic to some types of aquatic organisms. It slows down the growth of bacteria and the energy-processing mechanisms in plants. Due to its high solubility in water, amitrole is likely to end up in water resources where it may take up a month or so to break down. It does not accumulate in aquatic organisms. In soils, amitrole is broken down by microbia within 2-4 weeks. It is not considered likely that amitrole pollution has any effect on the global environment.[24] The chemical formula is given in Fig. 1 and its characteristic properties are listed in Table 1.
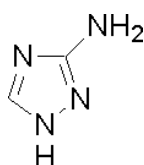
Figure 1. Chemical structure of amitrole

Table 1. The characteristics properties of amitrole

Molecular weight	84.08 g mol^{-1}
Color	Beige
Form	Pullar
Smell	none
Melting point	149-152 ºC
İgnition point	225 ºC
pH (20 ºC)	6.5 (100 g L^{-1})

Adsorbent

The chemical composition of the clay sample was estimated by X-ray fluorescence (XRF) (Philips) Magic PW 2424. X-ray diffraction spectroscopy (XRD) analysis was carried out with PANanytical X-ray diffractomer (Philips) and the results are given in Table 2. The observed chemical composition of clay as given below indicated that silica, alumina and iron(III) oxide are major constituents.

Table 2. Chemical composition of clay

Compound	%
SiO$_2$	60.89
Al$_2$O$_3$	17.35
Fe$_2$O$_3$	8.48
K$_2$O	0.67
CaO	2.156
TiO$_2$	0.86
MgO	4.69
Moisture	4.904

Acid activated clay was prepared from the natural clay by refluxing for 1 h with 36 N sulphuric acid. The resulting activated sample was washed with distilled water to remove all the excess acid and dried in a drier for 2 h at 110 °C until a constant weight was reached. It was then ground in a ball mill and sieved to particular size -75+180 μm for the adsorption study. The BET surface areas of clay were measured with nitrogen as 165 m^2 g^{-1}.

Adsorption studies

The amitrole stock solution was prepared by dissolving 0.01 g amitrole in 100 ml distilled water. A 5 ml solution was diluted to 20 ml with distilled water. The absorbance-calibration data were obtained from this stock solution at the selected wavelength (λ=214 nm).

The experimental solutions were prepared by using 5 ml stock solution diluted to 20 ml with distilled water as 25 μg mL^{-1} concentration. The amount of adsorbent used in the experiments was kept constant as 0.1 gram. The solutions were shaken in a water bath until adsorption equilibrium was attained as was indicated by ATI/UNICAM UV/VIS spectophotometer at λ=200 nm and 214 nm for λ$_{max}$ max absorbance and λ$_{min}$ first derivative, respectively. λ$_{min}$ data were taken into consideration. The adsorption data were measured in half an hour intervals. After the liquid phase was centrifuged at 100 rpm for 5 minutes, 2 ml supernatant was diluted to 10 mL. The experiments were done at 25, 35, 45 and 55 ºC. And they were performed at different pH values to see the effect of pH changes on the adsorption yield.

Effect of pH

The experiments were performed at different pH values such as 1.5, 3, 5, 7, 9, 11. The pH value of the stock solution was monitored using either 0.1 N hydrochloric acid or 0.1 N sodium hydroxide solution. The measurements were performed using WTW Inolab pH meter. The pH value of the initial experimental solution was 5. 0.1 g adsorbent was added to each solution. After 3 hours, the absorbance values at equilibrium were measured by UV spectrophotometer. The experiments were performed at temperature of 25 ºC.

Uptake (φ, %) was determined from the formula given below.

$$\varphi\% = \frac{C_0 - C_e}{C_0} \times 100 \qquad (1)$$

C_o = initial concentration of pesticide, μg mL^{-1}
C_e = equilibrium concentration of pesticide, μg mL^{-1}

Effect of initial concentration

The effect of initial amitrole concentrations in the range of 2-10 μg mL^{-1} on the adsorption mechanism was determined. The samples were continuously agitated with a speed of 300 rpm at the room temperature for 3 hours.

Effect of Temperature

The effect of temperature was searched by performing the experiments at different temperatures like 25, 35, 45 and 55 °C temperatures.

Adsorption isotherm model

Some adsorption isotherm models were applied for describing the relationship between adsorbate and adsorbent patterns. The Temkin equation suggest a linear decrease of sorption energy as the degree of completion of the sorptional centers of an adsorbent is increased . The heat of adsorption and the adsorbent-adsorbate interaction on adsorption isotherms were studied by Temkin and Pzyhev.[25] The Temkin isotherm equation is given as

$$q_e = B_T (\ln A_T + \ln C_e) \tag{2}$$

where $\qquad B_T = \dfrac{RT}{b}$

T is the absolute temperature in K,
R is the universal gas constant, 8.314 J mol^{-1} K^{-1},
A_T is the equilibrium binding constant (L mg^{-1}) and
B_T is related to the heat of adsorption.

The Harkins-Jura adsorption isotherm can be expressed as[26]

$$\frac{1}{q_e^2} = \left(\frac{B}{A}\right) - \left(\frac{1}{A}\right)\log C_e \tag{3}$$

where

B and A are the isotherm constants.

The Harkins-Jura adsorption isotherm accounts to multilayer adsorption and can be explained with the existence of heterogeneous pore distribution.

Adsorption kinetics

The adsorption kinetics are searched using the pseudo first order and pseudo second order equation by Lagergen and Svenska.[27]

The pseudo first order equation is determined by

$$\ln(q_e - q_t) = \ln q_e - k_1 . t \tag{4}$$

where

q_e is the amount of pesticide adsorbed (mg g^{-1}) at equilibrium
q_t is the amount of pesticide adsorbed at time t (mg g^{-1})
k_1 is the rate constant of the adsorption process (h^{-1})

The second order of pseudo kinetic model was implemented to verify the suitability of the experimental data. The pseudo second order kinetic model is given by the following equation

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_t}\right)t \tag{5}$$

where

k_2 is the rate constant of the adsorption process (mg mL^{-1} h^{-1})

Thermodynamic parameters

The thermodynamic parameters like $\Delta G°$, $\Delta H°$ and $\Delta S°$ were calculated to determine the nature of the adsorption. Adsorption standard free energy changes (ΔG^o) are determined using the following equation.[28]

$$\Delta G^0 = -RT \ln K \tag{6}$$

where

R is the gas constant 8.314x10^{-7} kJ K^{-1} mol^{-1}),
T is the temperature (K) and
ΔG^o is the Gibbs free energy of adsorption.

The equilibrium constant was calculated from

$$K = \frac{q_e}{C_e} \tag{7}$$

where

q_e (mgg^{-1}) and C_e (µgmL^{-1}) are the equilibrium concentrations of pesticide on the sorbent and in solution, respectively.

The sorption distribution coefficient can be expressed in terms of enthalpy and entropy changes as a function of temperature

$$\ln K = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \tag{8}$$

The enthalpy change (ΔH^o) and the entropy change (ΔS^o) can be calculated from the plot of ln K versus 1/T. The slope and the intercept represent -$\Delta H°$/R and $\Delta S°$/R, respectively.

Results and discussion

Phase contact time and initial adsorbate concentration

The effect of initial concentration of amitrole was studied . The adsorption became constant after 3 hours. Fig 2 shows the relationships between equilibrium concentration and time at different temperatures. Fig 3 shows the variation of q_e as a function of time and temperature. The amount of adsorption at equilibrium, q_e(mg g^{-1}) was calculated using the following equation:

$$q_e = \frac{(C_0 - C_e)V}{W} \tag{9}$$

Table 3. Isotherm constants

Temperature, °C	Temkin			Harkins-Jura		
	A_T(L mg^{-1})	B_T	R^2	A	B	R^2
25	1.75	0.57	0.99	-9.73	690.83	0.78
35	1.55	0.51	0.91	-4.29	288.1	0.74
45	1.67	0.31	0.99	-1.68	2462.88	0.53
55	1.65	0.31	0.99	-1.01	3115.45	0.35

where,

C_o (µgmL^{-1}) and C_e (µgmL^{-1}) are liquid phase pesticide concentrations at initially and at equilibrium, respectively.

V is the volume of the pesticide solution (mL) and

W is the mass of adsorbent (mg)

As the temperature was increased, the removal percent was decreased that was seen on Fig. 3.

Figure 4. Uptake % versus pH at 25 ºC (Adsorbent dose:0.1 g/25 ml, equilibrium time:3 h)

Effect of initial concentration

The effect of initial amitrole concentration in the range of 2-10 µg mL^{-1} on adsorption mechanism was investigated under the specified conditions. Figure 5 shows the adsorption of amitrole on clay (q_e) vs initial pesticide concentration. Increasing the pesticide concentration led to an increase in the amitrole adsorption by clay. The maximum adsorption capacity found to be 0.105 mg g^{-1}. The acid treatment has the positive effect of the adsorption capacity of clay.

Figure 2. Concentration versus time at different temperatures (*T*: 25 ºC, 35 ºC, 45 ºC, 55 ºC; adsorbent dose: 0.1 g/25 ml)
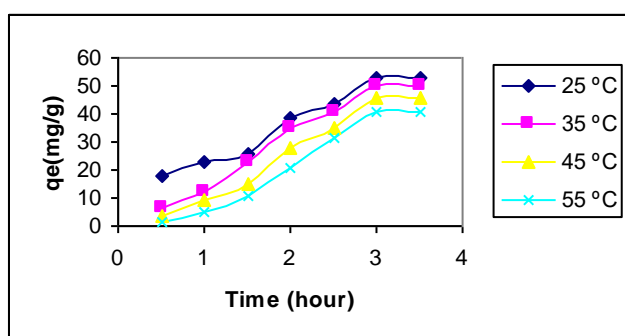

Figure 3. q_e versus time and temperature (*T*:25, 35, 45 and 55 ºC, adsorbent dosage: 0.1 g/25 ml)

Effect of pH

The effect of pH is shown in Figure 4 in terms of uptake % - pH. The uptake percent was reached to approximately 80 % at pH 3. The H$^+$ ions of amine group has the positive effect on the adsorption. Hameed found the highest adsorption of 2,4-6 trichlorophenol onto activated clay at pH=2.[29] The pesticide removal capacity is gradually decreased until the pH value of 8. Later, it is almost stable around the pH value of 12.
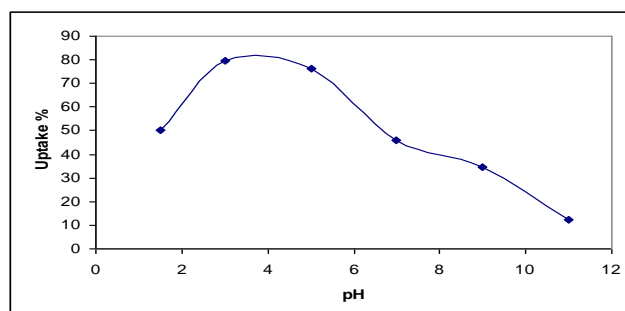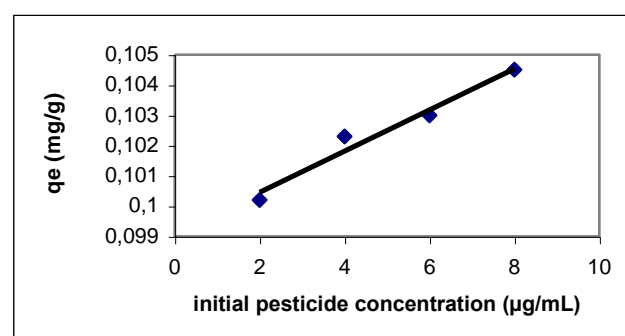

Figure 5. Effect of initial concentration on amitrole adsorption (*T*=25 ºC)

Adsorption isotherms

A Temkin plot of q_e vs ln C_e at studied temperature is shown in Fig 6. The Temkin isotherm constant, B_T shows that the heat of adsorption increases with increase in temperature, indicating endothermic adsorption. In our study, this value decreases showing the exothermic behavior. Hameed studied the adsorption of 2,4-6 trichlorophenol adsorption onto HCl activated clay. He applied Langmuir, Freundlich and Temkin isotherms to the experimental data.

The R^2 values are good (0.95, 0.90 and 0.89) and B_T constants of isotherms are decreased with increasing temperature as 25.24, 17.45 and 14.73 showing exothermic nature of adsorption.[29]
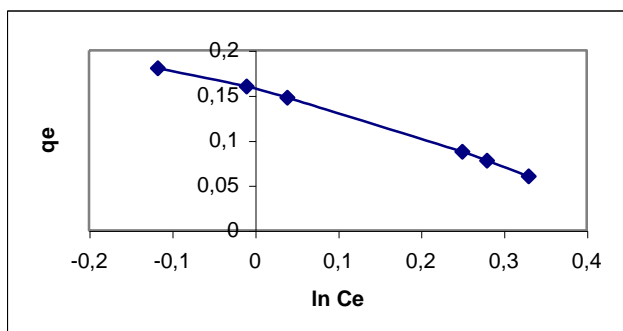

Figure 6. Temkin isotherm at 25 °C

The Harkins Jura plot ($1/q_e^2$ vs log C_e) is given in Fig 7. The low R^2 values indicate that the adsorption of amitrole by clay does not support this isotherm model.
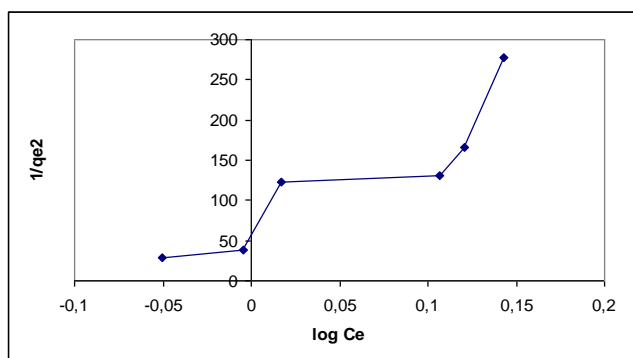

Figure 7. Harkins Jura isotherm at 25 °C

Nevine Kamal Amin studied the removal of direct blue 106 dye from aqueous solution using new activated carbon derived from pomegranate peel. She applied some isotherm models to the adsorption data like Langmuir, Freundlich, Temkin, Dubunin-Raduskevich (D-R) and Harkins-Jura isotherms. The correlation coefficients (R^2) of Harkins-Jura and D-R isotherms are lower than the other models.[30]

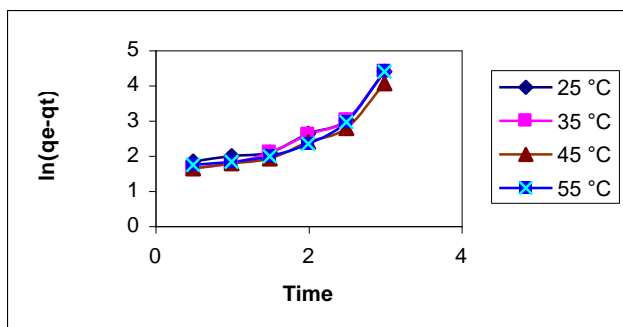The constants and correlation coefficients of the study are summarized in Table 3.

Figure 8. Pseudo first order kinetic of amitrole by AC

Table 4. Kinetic parameters

Temp °C	k_1	R^2	k_2	R^2
25	0.93	0.84	0.92	0.66
35	1.03	0.88	0.32	0.54
45	0.89	0.85	1.31	0.88
55	0.97	0.81	5.50	0.88

Adsorption kinetics

The adsorption kinetic behavior was shown in Fig. 8 and 9 for pseudo first and pseudo second order kinetics, respectively. The kinetic parameters were given in the Table 4. At low temperatures (25, 35 °C) the reaction progressed as pseudo first order but at high temperature (45, 55 °C) both models support the adsorption mechanism.
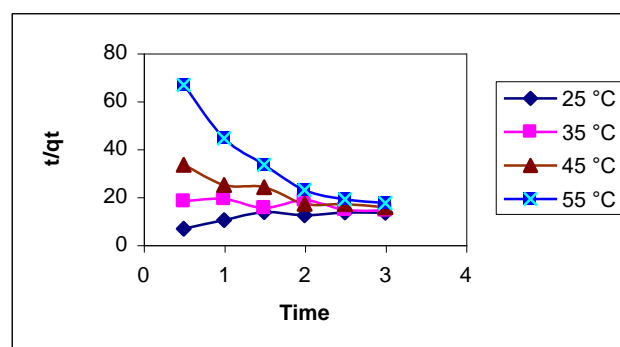

Figure 9. Pseudo second order kinetic of amitrole by AC

Thermodynamic approach

The thermodynamic parameters are calculated from the plot and were shown in Figure 10 and Table 5. The negative value obtained for $\Delta H°$ confirms the exothermic nature of the sorption processes. The negative $\Delta S°$ value reflects the fact no significant change occurs in the internal structure of clay during the pesticide adsorption. The negative $\Delta G°$ values indicate the feasibility and spontaneous nature of amitrole adsorption on acid treated clay.
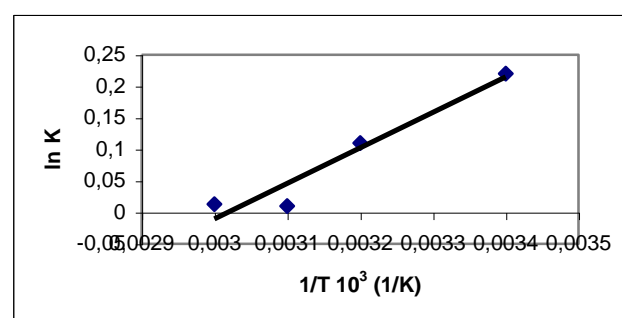

Figure 10. ln K versus 1/T plot for thermodynamic parameters

Bakouri et al. studied the acid activated olive stones for removal of pesticides like aldrin, dieldrin and endrin. They found the exothermic and spontaneous behavior of the process at the studied temperatures (10, 15, 20, 25, 30, 35, 40 °C).[31]

Table 5. Thermodynamic parameters

Temperature °C	$\Delta H°$ (J g^{-1})	$\Delta S°$ (J g^{-1} K^{-1})	$\Delta G°$ (J g^{-1})
25(298 K)	-4680.8	-14.1	-509
35(308 K)			-369
45(318 K)			-229
55(328 K)			-89

Conclusion

In this study, adsorption of amitrole from aqueous solutions on acid activated clay (AC) was investigated under different experimental conditions in batch model. The removal of pesticide was found to be depending on phases contact time, initial concentration of pesticide, pH and temperature. Maximum pesticide was sequestered from the solution within 3 h after the adsorption experiment beginning for all temperatures. The equilibrium adsorption data were very best represented by Temkin isotherm. The reaction is well represented with pseudo first order kinetic model at 25 °C.

Given the facts that clay necessitates no pretreatment, it is ecofriendly and low-cost, and that it has a satisfying adsorption capacity. Present clay especially asit activated clay can well be used in different types of removal activities like textile dyes, phenolic compounds and pesticides.

Acknowledgement

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