Removal of Tebuconazole from Wastewater by Zeolite X: Kinetics and Thermodynamics Studies

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Abstract- **Tebuconazole, a widely used fungicide is toxic to the environment and has been reported as a water contaminant. In this study, the adsorption of aqueous solution tebuconazole onto faujasite X (NaX) was investigated in batch mode. Equilibrium sorption data at 303 K were analyzed using Langmuir, Freundlich, and Temkin isotherm models. The adsorption data was found to be described by the models in the order Langmuir > Freundlich >Temkin model. For the 293 – 323 K temperature range studied, the percent removal of the pesticide decreased with increase in temperature. The sorption process was found to follow the pseudo-second-order kinetic model while Intraparticle diffusion model indicated that the adsorption process was multi-mechanistic and pore diffusion was not the sole rate-controlling step. The calculated thermodynamic parameters ΔG, ΔH and ΔS for the adsorption reaction were obtained as -181 J mol^{-1} (at 303 K), -38.81 kJ mol^{-1}, -54.41 Jmol^{-1}K^{-1} respectively, indicating the adsorption process was spontaneous and exothermic. FT-IR and XRD was consistent with adsorption of tebuconazole onto NaX being an external surface chemisorption process at the single-four-rings (S4R) of the zeolite framework with involvement of the Na$^+$ cations.**

Keywords— Adsorption, Faujasite X, Tebuconazole, Water

I.   INTRODUCTION

Tebuconazole (Fig 1) is a triazole fungicide widely used in agriculture for crop protection. Due to its broad spectrum antifungal activities [1], tebuconazole is widely used in cultivation of numerous crops including maize, vegetable crops, grapevines and cereals [2]. Eventually, like most pesticides, tebuconazole finds its way to water sources either through leaching, uncontrolled dumping of agrochemical refuse, release of untreated industrial effluents, surface run-off, sewer overflows, leaking of faulty equipments and farmyard deposition [3,4] resulting to deterioration of water quality that endangers human health, indigenous ecologies and environmental matrix. Tebuconazole has been detected in wastewater and in lakes at levels exceeding the EU's set allowable limit of 0.1 µgL^{-1} for drinking water [5], with concentrations up to 175-200 µgL^{-1} in surface waters [6,7,8] and up to 19.2 µgL^{-1} in urine samples of agricultural workers [9]. The presence of tebuconazole in stream waters has been shown to be on the rise in recent years [10]. Tebuconazole is classified as group C-possible human carcinogen [11]. In addition, it has been reported to be toxic to aquatic life and may cause long-term diverse effects in aquatic environment [12]. Due to its toxicity, the environmental fate of tebuconazole is of great concern. However, work on remediation of tebuconazole from contaminated waters at environmentally relevant concentrations is scanty and the available literature is insufficient.

Zeolites are of great interest in pesticide remediation due to their high adsorption capacities, catalytic chemical reactivity and the intrinsic capacity to be regenerated while maintaining their initial properties [13,14]. They have the potential to adsorb on both their interior and external surfaces and chemically decompose pesticides through nucleophilic reactions to environmentally less toxic products than the parent molecule [15,16].

Zeolites show selectivity for different adsorbates depending on the polarity, shape and size of the diffusing molecules relative to the zeolites openings; the presence of exchangeable cations and impurities in the zeolite structure and the physical and tunability of the zeolite [14,17].

In this study, the adsorption of tebuconazole on faujasite X (NaX) was studied at concentrations near the environmental levels and the data fitted to Langmuir, Freundlich and Temkin adsorption isotherm models to predict the adsorption processes. Kinetic study was investigated using both pseudo-first order and pseudo-second order models and the effects of concentration, contact time and temperature parameters were also evaluated. The mechanism of adsorption was inferred by the use of intraparticle diffusion model, XRD and FT-IR analysis. The data obtained would be useful in predicting the suitability of zeolite X as an end-of line water treatment adsorbent.
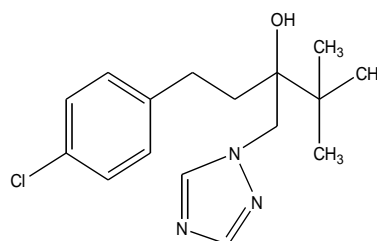

Fig. 1: Structure of tebuconazole

2. METHODOLOGY

2.1 Reagents and Chemicals

Faujasite X (Si/Al = 1.5) of 0.2 µm particle size was obtained from Sigma-Aldrich Chemical company, (St Louis, MO, USA). HPLC grade methanol was supplied by Mallinckrodt,

(NJ, USA), Phosphoric acid (85%) was supplied by Merck, (Brazil) and tebuconazole standard (purity 98%) was supplied by Dr. Ehrenstorfer, (Germany). For instrumentation, water purifier Milli-Q system UV3 Direct (18.2 MΩ cm resistivity) from millipore (Bedford, MA, USA), Ultrasound bath Bandelin Sonorex RK 510 (Walldorf, Germany), Vacuum Pump Tecnal TE-058 (Piracicaba, SP, Brazil), Liquid Chromatograph Varian (Palo Alto, CA, USA), equipped with pump model 210, diode array detector (DAD) Pro Star 335, data acquisition system Star Workstation 6.0, analytical column Gemini 5 µ C_{18} (250 × 4.6 mm id; 5 µm) and guard column (20 × 1 mm) of the same material, both containing octadecylsilane-modified silica (Phenomenex, Torrance, CA, USA), X-ray diffractometer D8 Advance from Brucker (Germany) with copper radiation (K_α=1.5406), and Perkin Elmer (400 FT-IR spectrometer) with ATR (attenuated total reflection) attached were used.

2.2 Procedure

2.2.1 Preparation of adsorbent

The zeolite was activated under 200 mmHg vacuum. 50 g of zeolite was weighed in a flask that was then evacuated for 30 min. The contents were then heated at 343 K and continuous heating was done by raising the temperature by 30 K every 30 min up to 403 K. Finally, the temperature was then raised to 423 K and heating maintained for 105 min. The flask was allowed to cool at room temperature and the contents transferred to a sealed glass bottle for later use.

2.2.2 Adsorption isotherm experiments

Adsorption of the pesticides was determined in a batch adsorption experiment. Here, 0.1 g of activated zeolite X was dispersed into each Erlenmeyer flask containing 50 mL of various separate concentrations of tebuconazole (100, 250, 500, 700 and 1000 µgL^{-1}). The flasks were magnetically stirred at 300 rpm and 303 K. The pH values of all the solutions were found to be in the range of 8.0-9.0 for all tests unless otherwise indicated. After equilibration for 1 h, the solutions were decanted and the supernatant filtered through 0.2 µm filters. Volumes of 1.0 mL aliquots were withdrawn and transferred into sealed glass vials for residual pesticide analysis. A control experiment was set-up to confirm whether any tebuconazole was adsorbed on the glass container. The concentration of the pesticide adsorbed on the zeolite was calculated as the difference between the spiked amount and the residual concentration after equilibration. The percent adsorption is obtained by:

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

2.2.3 Thermodynamic studies

For the effect of temperature on adsorption study, the method by [18] was adopted. Exactly 0.1 g of activated zeolite X was dispersed into 50 mL of 500 µgL^{-1} of tebuconazole and stirred at 300 rpm and 303 K. After equilibration for 1 h, 1.0 mL aliquots were withdrawn from the flask and transferred into sealed glass vials for residual

pesticide analysis. Similar separate treatments were performed at different temperatures.

2.2.4 Kinetic studies and effect of contact time

To study the effect of contact time, the adsorption kinetic experiment was performed by batch technique [19]. A mass of 0.1 g of activated zeolite X was dispersed into 50 mL of 500 µg L^{-1} of tebuconazole at 303 K and stirred at 300 rpm. At intervals (0, 0.5, 1.5, 2.5, 3.5, 5.5 and 6.5 h) 0.5 mL aliquots was withdrawn from the flask and transferred into sealed glass vials for residual pesticide analysis, making a total of 6% of the total volume.

Tebuconazole was detected by HPLC-DAD at 220 nm. The mobile phase was a mixture of acetonitrile and water (70:30 v/v) adjusted to pH 3 using phosphoric acid (1:1 v/v), with a flow rate of 1 mL min^{-1}. The injection volume was 20 µL [20].

2.2.5 Identification of site of adsorption

The used zeolites were then characterized using XRD and FT-IR techniques in order to elucidate the mechanism and identify site of adsorption of tebuconazole onto NaX. The XRD instrument settings were 40 kV, 30 mA, step size of 0.02^o (2θ) and a scan rate of 2θ min^{-1} for 5° ≤ (2θ) ≤ 45° while FT-IR spectra was obtained in the range 400-4000 cm^{-1}.

3. RESULTS AND DISCUSSION

The control analysis indicated that negligible amounts of the pesticide were adsorbed on the glass container walls while the pH changes following the treatment with zeolite were in the range 8-9 for all samples and hence were considered of negligible effect as a variable in the adsorption process.

3.1 Effect of pesticide concentration on adsorption

The adsorption extent was found to vary significantly (p<0.05) with the initial concentration of the pesticide (Fig. 2).
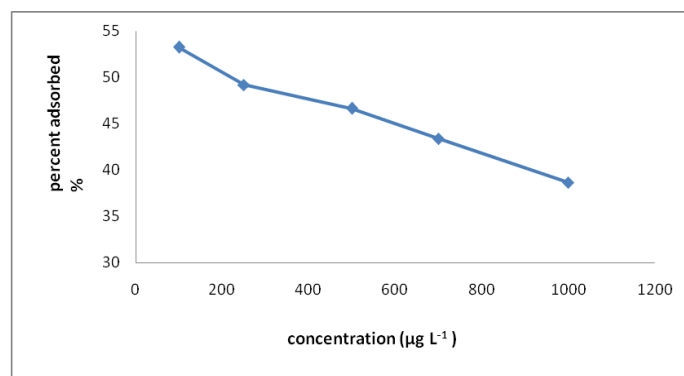

Fig. 2: Percent removal of tebuconazole as function of initial concentration

The percent adsorbed (1) decreased with increase in concentration from ca. 53 to ca. 38%, when the initial concentration is increased from 100 to 1000 µg L^{-1} for adsorbent dosage of 0.1 g/50 mL at 303 K. This decrease in concentration is partly explained that at high initial concentration, tebuconazole molecules do not easily access

the active adsorption sites probably due to sterric hindrance resulting in the low percentage removal.

The progressive adsorption may be explained by the analysis of distribution coefficient (K_d) of the pesticide within the media (2). The distribution coefficient, K_d, was also observed to linearly ($R^2 = 0.986$) decrease with increase in tebuconazole concentration (Fig. 3), an indication that less energetically favored sites become involved in the adsorption process as adsorbate concentration increases. Jamil *et al.* [21] had earlier reported similar observations for atrazine removal using zeolite X prepared from Egyptian kaolin.
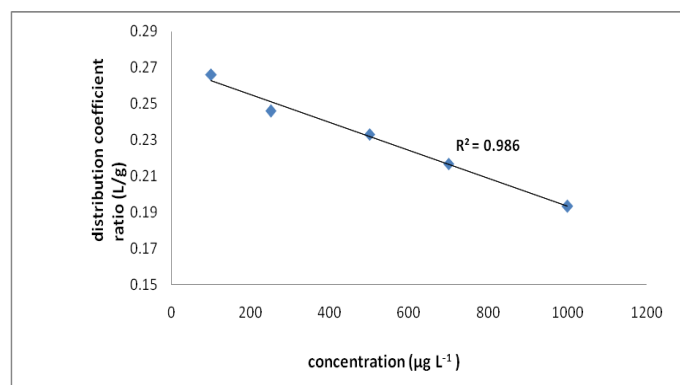

Fig. 3: Variation of tebuconazole distribution coefficient (K_d), as function of initial concentration

The distribution coefficient, (K_d), was obtained using the relations below;

$$K_d = \frac{Amount\ of\ tebuconazole\ in\ adsorbent}{amount\ of\ tebuconazole\ in\ solution} \times \frac{V}{m}$$

(2)

Where V is the volume (L) of solution and m is the mass (g) of adsorbent.

3.2 Adsorption Isotherm modeling

The adsorption capacity was investigated by fitting the data to three adsorption isotherms; the Langmuir, Freundlich and Temkin isotherms. The calculated isotherm parameters and regression coefficients are listed in Table 1. Fitting of the data into linearised Langmuir equation resulted in $R^2 = 0.999$ indicating that the Langmuir isotherm model best fitted the experimental sorption data within the concentration range applied. The experimental sorption data corresponded to the adsorption isotherm models in the order Langmuir > Freundlich > Temkin.

Table 1: Adsorption isotherm equations and experimentally obtained parameters

Isotherm Model	Ref	Calculated Parameters
		(this study)
Langmuir	[39]	$Q_m(\mu g\ g^{-1}) = 500$ $K_L(L\ g^{-1}) = 0.0012$ $R_L = 0.4545$ $R^2 = 0.999$
Freundlich	[40]	$K_f, = 1.3459$ $n = 1.2739$ $R^2 = 0.994$
Temkin	[41]	$B = 64.88$ $A_T = 0.026$ $R^2 = 0.96$

The Langmuir monolayer maximum capacity parameter (Q_m=500 μg g^{-1}) suggest that tebuconazole may have reached the saturation point of the active sites and any further adsorptions could only take place on new surfaces. Both the Langmuir separation constant (R_L=0.4545) and Freundlich constant (n=1.2739) indicate that the sorption process is favorable [22,23]. The value of 1/n is between 0 and 1 an indication that the surface of the adsorbent is heterogeneous. Such heterogeneity has been reported by Omri *et al.* [24] on the adsorption study of bentazon on activated carbon [24]. The depicted heterogeneity is consistent with the multi-active (I, II, & III) sites, channels and cages in zeolite X [25]. In comparison to others, the data does not fit well the Temkin isotherm model.

3.3 Thermodynamics of adsorption

The effect of temperature was studied in the range 293 to 323 K to determine the thermodynamic feasibility of the adsorption process at 500 μg L^{-1} pesticide concentrations. This concentration was adopted as the level for real environmental samples since no published document so far obtained has reported tebuconazole concentrations in water sources exceeding 500 μg L^{-1} [6]. As the temperature varied from 293 K to 323 K, the percent removal of tebuconazole decreased from 60.3 to 43.9% an indication of an exothermic process. The decrease in adsorption is attributable to the weakening of adsorptive forces between the adsorbent and adsorbate molecules [26] as a result of increased agitation energy. The decrease in adsorption can also be explained on the basis of solubility; where the increase in temperature possibly afforded the pesticides more solubility in the water and lowered their affinity for the adsorbent surface [27,28].

The thermodynamic parameters (Table 2), namely; Gibb's free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) were estimated using the following equations [29]:

$$\Delta G = -RT \ln K_c$$

(3)

$$K_c = \frac{C_{ad}}{C_e}$$

(4)

Where K_c is the equilibrium constant, C_e is the equilibrium concentration in the solution (μg L^{-1}) and C_{ad} is the equilibrium solid phase concentration (μg L^{-1}). Enthalpy and entropy were obtained from slope and intercept of the Van't Hoff plot, respectively.

$$\ln K_c = \frac{\Delta S}{R} - \frac{\Delta H}{2.303R} \frac{1}{T}$$

(5)

Table 2: Thermodynamic parameters and percent adsorbed for removal of tebuconazole by NaX.

Temperature (K)	ΔG (J mol^{-1})	ΔH (kJ mol^{-1})	ΔS (Jmol^{-1} K^{-1})
293	-1059.0	n.d	n.d
303	-180.69	-38.77	-54.36
313	179.45	n.d	n.d
323	653.63	n.d	n.d

Note. n.d = not determined.

The negative ΔG (at 293 and 303 K) and ΔH values confirmed that the adsorption process is spontaneous and exothermic in nature, respectively. Similar results were reported for adsorption of phenol on synthetic NaY zeolite [29]. When the temperature was increased above 303 K, the reaction transitioned to non-spontaneity. This transition from spontaneity to non-spontaneity depicts the temperature dependence of the adsorption reactions which are more spontaneous at low temperatures. Such phenomenon has been observed for pesticides adsorption on various adsorbents [30]. The increase in ΔG with rise in temperature is consistent with the reaction being less feasible with increased temperature. Generally, the magnitude of the ΔH value lies in the range of 40–120 kJ mol^{-1} for chemisorption mechanisms [31]. In the present study, the ΔH value (38 kJ mol^{-1}) suggests a chemisorption mechanism. Additionally, the negative value of ΔS implies less randomness at the solid/solution interfaces during the adsorption process.

3.4 Effect of contact time and kinetics

The equilibrium sorption data was studied using pseudo-first order and pseudo-second order in order kinetic models to predict the adsorption rate which controls the equilibrium time. The low R^2 value for (Table 3) reveals a very poor fitting of pseudo-first order model with the experimental data.

Table 4: Kinetic models for removal of tebuconazole by NaX

Kinetic model Equation	Ref	R^2
$\log(q_e - q_t) = \log q_e - \dfrac{k_1}{2.30}$	[42]	0.01
$\dfrac{t}{q_t} = \dfrac{1}{k_2 q_e^2} + \dfrac{t}{q_e}$	[43]	0.998

However, the high correlation coefficient of R^2=0.998 indicates that the experimental data is best described by the pseudo-second order model. The pseudo-second order model has been proven to be consistent with a chemisorption mechanism [24]. Also the initial sorption rate (S_{rate}) and adsorption half-life was determined using eqn. 6 and 7, respectively [23]. The initial sorption rate (S_{rate}) and adsorption half-life ($t_{0.5}$) was 41 µg g min^{-1} and 0.0634 h respectively.

$$S_{rate} = k_2 q_e^2 \qquad (6)$$

$$t_{\frac{1}{2}} = \frac{1}{k_2 q_e} \qquad (7)$$

A sharp decrease in concentration was observed in the first 30 minutes (Fig. 4), then leveled off and was assumed to have attained pseudo-equilibrium after 60 minutes. Sorption studies show considerable variation of the time required to attain equilibrium [32].
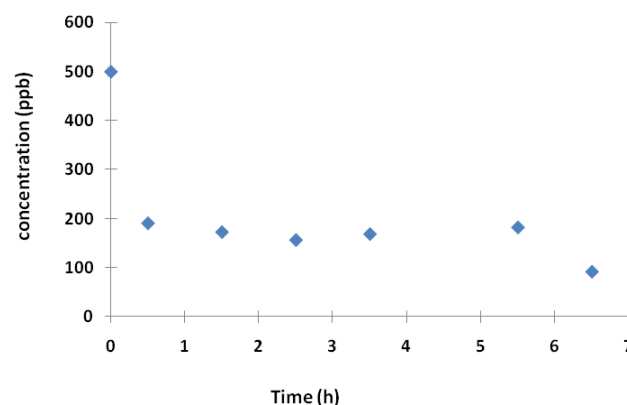

Fig. 5: Variation of tebuconazole concentration with contact time.

Therefore, to obtain a compromise between overall removal efficiency and the time needed for complete analysis, 1 h was chosen as the equilibrium time for obtaining the adsorption isotherms. This conformed to previous results by Yonli *et al*. [17] for removal of α-endosulfan from water by synthetic HY zeolites where equilibrium was established in less than 1 h. The initial decrease in concentration could be attributed to the large number of active sites available at the beginning. Afterwards, the adsorption process is decreased as indicated by the near plateau/pseudo-equilibrium conditions after ca. 60 min. The plateau phenomenon may be due to the difficulty of tebuconazole molecules to reach the less accessible inner active zeolitic sites, probably because of repulsion between the adsorbed molecules, those in bulk solution or simply because of steric hindrance.

3.5 The mechanism and sites of adsorption

The sorption kinetic data were fitted to intraparticle diffusion model in order to investigate the adsorption mechanism and to identify the rate controlling step in the adsorption process [33]. The model is represented by the expression:

$$q_t = k_p t^{0.5} + C \qquad (8)$$

Where q_t is the amount of tebuconazole adsorbed at equilibrium (µg g^{-1}) at time t, k_p is the intraparticle diffusion rate constant (g µg^{-1} h^{-1}) and C is the intercept to the vertical axis. From the model, when the regression of q_t as a function of $t^{0.5}$ is linear then intraparticle diffusion occurs and when the line passes through the origin, then intraparticle diffusion is the only rate-limiting step. Otherwise, a different mechanism concomitantly occurs with intraparticle diffusion. The plot in Fig. 5 indicates that tebuconazole was adsorbed in a three-phased (labeled I-III) process.
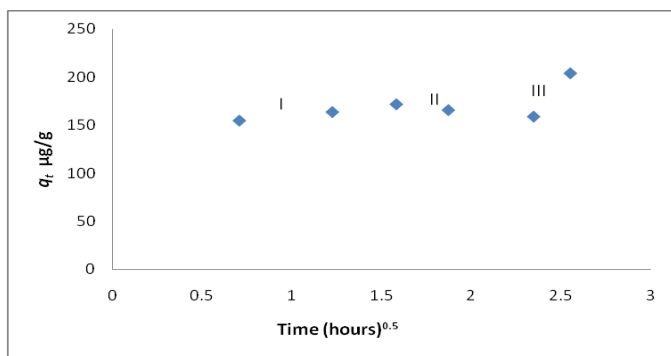
Fig. 6: Intraparticle diffusion model for tebuconazole adsorption onto NaX.

Fig. 7: The XRD spectra for zeolite X in tebuconazole where Fau NoP= zeolite X with no tebuconazole, Fau teba= zeolite X with tebuconazole

The first is a linear phase (I) representing initial rapid adsorption which is characteristic of surface adsorption or boundary layer adsorption [34]. During the second phase, a decrease in adsorption was observed with a near plateau region (II) corresponding to an equilibrium situation. This second phase could be attributed to the heterogeneity of the NaX surfaces and the attempts by the pesticide molecules to reptate through the smaller zeolitic channels and pores. The final phase (III), was attributed to adsorption-desorption processes simultaneously taking place indicating that a dynamic equilibrium had been established. Notably, the plot did not pass through the origin. This indicates that though pore diffusion/reptation may be involved in the adsorption process of tebuconazole onto NaX, it was not the rate-controlling step. Such multi-mechanistic sequences have been experienced before by Yousef *et al*. [35] during the removal of phenol from aqueous solution using a natural zeolite. In the current study, the XRD analysis was performed to monitor cationic migrations from the zeolite framework. Such migrations would imply participation of the Na^+ ions in the adsorption or catalytic breakdown process making the cations to act as point charges that attract the chlorine atoms in tebuconazole molecule. This mechanism of adsorption was postulated by Jamil *et al*. [21] for adsorption of atrazine onto NaX prepared from Egyptian kaolin. Cationic migrations in sodium-type faujasite X are characterized by intensity changes for 9.9^o (2θ) and 11.6^o (2θ) diffractograms [36]. XRD analysis of NaX exposed to tebuconazole (Fig. 6) indicated significant decrease on the relative intensities of the diffractograms at 9.9^o (2θ) and 11.6^o (2θ). These changes indicate that the cations participate in the adsorption process as postulated by Jamil *et al*. [21] consistent with chemisorption mechanism.
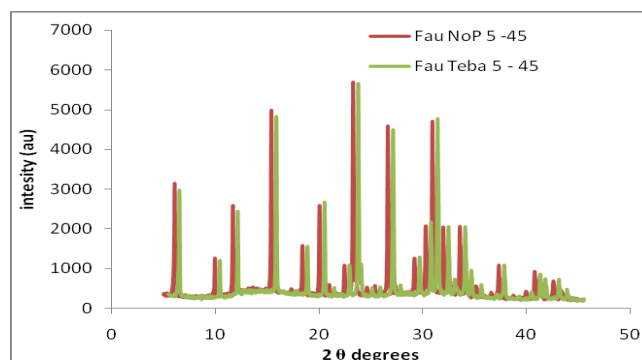
Again, the FT-IR analysis was done to investigate the adsorption mechanism and also identify the site of adsorption of the pesticides on the zeolite framework. In the spectrum of free faujasite X samples, particularly worth considering were the band around 760 ± 2 cm^{-1} resulting from the NaX single-four ring (S4R) vibrations [36]. In the present investigation, the NaX exposed to tebuconazole showed a red shift of the S4R from ca. 756 cm^{-1} to ca. 742 cm^{-1} (Fig. 7) confirming that tebuconazole molecules were adsorbed at the single-four-rings of the zeolite framework.
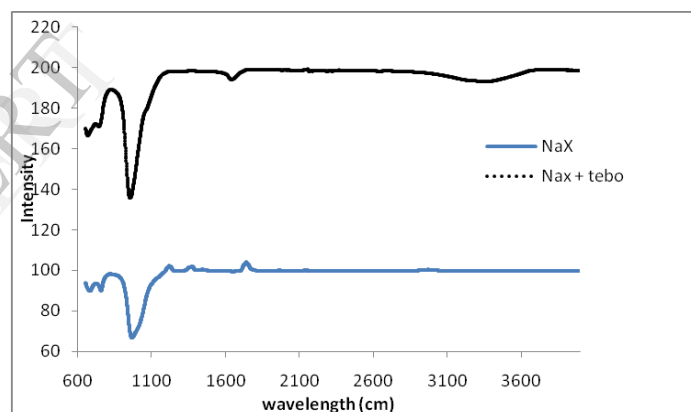

Fig. 8: IR specrum of NaX with and without pesticide

The absence of blue shifted bands also confirmed that there was no loss of cations from the sites. This observation is contrary to results by Ogunah *et al*. [37] for adsorption of malathion onto synthetic NaY zeolite where cation loss was reported. This can be explained by the stabilizing factor of Na^+ present in the supercage site III in NaX zeolite as noted by Kanyi *et al*. [38]. These results coupled with the fact that pore diffusion was not a rate controlling step strongly suggest that tebuconazole molecules were not adsorbed in the internal surfaces of the zeolite matrix.

4.0 CONCLUSION

This work reported that synthetic NaX can be used as an adsorbent for the removal of tebuconazole from water especially at low pesticide concentrations. The equilibrium sorption data was best fitted by Langmuir and Freundlich models at 303 K with theoretical Langmuir maximum adsorption capacity of 500 µg g^{-1}. Both the Langmuir separation constant (R_L=0.4545) and Freundlich constant (n=1.2739) indicate that the sorption process is favorable. The kinetics data of the adsorption process followed the pseudo-second- order model and is not controlled by pore diffusion. Thermodynamic functions were calculated to determine the feasibility of the adsorption process. The negative ΔG (-1024 J mol^{-1} and -180.7 J mol^{-1} at 293 K and 303 K respectively) and ΔH -38.81 kJ mol^{-1} values confirmed that the adsorption process are spontaneous and exothermic in nature, respectively. Binding of tebuconazole molecules takes place at the single-four rings (S4R) of the zeolite framework with electrostatic interactions with the zeolitic cations.

In summary, the change in adsorption enthalpy ΔH values, a pseudo-second order kinetic adsorption reaction, participation of the cations, binding at the S4R zeolitic active site and the fact that pore diffusion is not the rate controlling step are evidences that makes it conceivable that adsorption of tebuconazole onto NaX is an external surface chemisorption process.

ACKNOWLEDGEMENTS

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INDEX

K_L Langmuir isotherm constants (μg g^{-1})

A   Temkin isotherm constant (L g^{-1})

B   Temkin isotherm constant (J mol^{-1})

Ce Equilibrium tebuconazole concentration (μg L^{-1})

C_0 Initial tebuconazole concentration (μg L^{-1})

K_F Freundlich constants (μg g^{-1})

q_e Amount of tebuconazole adsorbed at equilibrium (μg g^{-1})

q_t Amount of tebuconazole adsorbed at time t (μg g^{-1})

Q_m Maximum adsorption capacity of the adsorbent (μg g^{-1})

m   Mass of the adsorbent (NaX) (g)

n Freundlich isotherm exponent

k_1 First order rate constant (h^{-1})

k_2 Second order rate constant (g μg^{-1} h^{-1})

t Time (h)

T   Temperature (K)

R   Universal gas constant J mol^{-1}K^{-1}

k_p Intraparticle diffusion rate constant (g μg^{-1} h^{-1})