

**STUDIES ON REMOVAL OF FIPRONIL (FP) PESTICIDE FROM ITS
AQUEOUS SOLUTION BY A LOW-COST ADSORBENT**

A

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CERTIFICATE

This is to certify that the thesis entitled “Studies on removal of Fipronil(FP) pesticide from its aqueous solution by a low-cost adsorbent” is an authentic record of my own work carried out as per requirements for the award degree of **M.Sc (Chemistry) at Thapar Institute of Engineering & Technology, Patiala** under the guidance of **Dr. Sanghamitra Barman, Associate Professor, Department of Chemical Engineering and Dr. Anoop Verma, Associate Professor, School of Energy & Environment, Thapar Institute of Engineering and Technology, Patiala**, during January 2019-July 2019.

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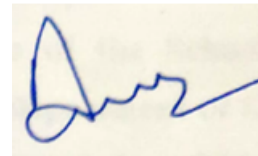
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Abstract

The current investigation was carried out to figure out the performance of Cu-X as an adsorbent for the elimination of FP pesticide from wastewater. 13X zeolite were modified with copper nitrate solution & modified zeolite was used for adsorption studies. To prepare the adsorbent, 13X zeolite was refluxed with ammonium nitrate solution at 90° C for 6 hours, for three times and calcined for 3 hours at 350°C in between to form HX. After final calcinations, it was refluxed with copper nitrate solution at a temperature of 90°C for 72 hours. Adsorption experiments were carried out over copper modified zeolite (Cu-X) as adsorbent varying different parameters such as pH of the solution, stirring speed, dose of adsorbent, initial concentration of the solution. The modified adsorbent Cu-X was used to remove Fipronil pesticides from its aqueous solution. Experimentation was performed at least twice a time and the mean values were reported to assure the accuracy of the results. FP pesticide was removed from its aqueous solution increases with increase in adsorbent dose and contact time, the best % removal of Fipronil was obtained to be 92.3%. At optimum pH 3, 84.2% removal of Fipronil is obtained. The elimination of Fipronil decreases with the increase in initial conc. of pesticide. Effect of temperature on Fipronil elimination was also studied. At 25°C, the maximum percent removal reported being 92%. Also, the maximum removal is 92.3% at an optimum stirring speed of 200rpm. In the data of experimentation, the Freundlich isotherm fitted properly whereas the process of adsorption obeyed second-order kinetic model. Thermodynamics study was also carried out.

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ABBREVIATIONS/SYMBOLS

FP – Fipronil

EDCs – Endocrine Disrupting Compounds

SBU – Secondary Building Units

Cu-X – Copper Modified Zeolite X

K_L – Langmuir Constant ($L \cdot mg^{-1}$)

K_F – Freundlich Constant [$(mg/g) \cdot (L/mg)^{1/n}$]

k_1 – first order rate constant (min^{-1})

k_2 – second order rate constant ($g/mg \cdot min$)

R – Universal gas constant ($J/mol \cdot K$)

R^2 – Correlation coefficient

T – Temperature

T – Time (min)

Water is the mother of the entire world. Life is originated from water and is also sustained by water [1,2]. Environmental issues are the effective protection of the precious freshwater resources of the world. There are so many human-made chemical substances which are present in water as contaminants and thus affect the quality of water. Water bodies in oceans are contaminated by pollution of water. It is necessary to remove these contaminants to protect our water resources to get water of desired quality. Since many years various technologies were used to eliminate the toxic compounds (organic pollutants) by degrading them into non-toxic ones. Amongst these, endocrine disrupting compounds (EDCs) are considered as the most undesirable.

EDCs are the harmful chemical compounds that induce adverse effects on the endocrine system of aquatic life and humans. EDCs are categorized into different classes such as Equol and Formononetin, plasticizers (Bisphenol A, etc), diethyl phthalate and chlorinated organic pesticides (atrazine, fipronil) [3,4]. The endocrine-disrupting compound i.e. Fipronil (FP) is an insecticide which is widely produced in insecticide industry. This EDC is needed to be eliminated from the wastewater effluents of insecticide industries [5]. Fipronil is used against pests or field corns and their deposits are found in agricultural runoff water [6,7] and thus contaminate the drinking water. For killing the futile organisms present on agricultural land, public places various pesticides are used. Therefore, the removal of carcinogenic and mutagenic. EDCs from wastewater is utmost necessary before discharging it into the environment.

The results given by the biological treatment are not fruitful and economic for wastewater treatment processes [8]. The technique named AOP i.e. Advanced Oxidation Process is also popular and is used for wastewater treatment. This technique is costly and utilizes more energy, chemical agents [9]. Besides all these, adsorption is the phenomenon which is the cost-effective, user-friendly and energy-efficient [10-12] process. For wastewater treatment, commonly used adsorbents are activated carbon, metal oxides, agricultural waste, clay, fly ash, zeolite, etc. Among these adsorbents, zeolites are the most user-friendly as it has a long life, stable structure, regenerative and eco-friendly nature. In the present investigation, the copper modified zeolite is used as adsorbent which appeared to be highly adsorptive and helps in elimination of Fipronil Pesticide from its aqueous solution.

Zeolite:

Zeolites are micro-porous, hydrated aluminosilicates having a three-dimensional network of orthosilicate and aluminium hydroxide [13]. The silica and alumina tetrahedra assemble to form the primary building unit as an array of interconnecting channels or a system of cage-like voids as shown in Fig:2[14].

Structure of the Zeolite

Zeolite is considered to be the primary building unit of tetrahedron structure made of silica and alumina. Primary building blocks are rearranged in an array to form a secondary building unit (SBU). The zeolite framework is consisted of polyhedral building blocks forming characteristic cages. Shapes of the SBUs are considered to be polyhedron such as prisms of hexagonal shape. Fig:1 and Fig:2 show structures of zeolite. The chemical formula of zeolite is $M_{x/n}O \cdot [AlO_2 \cdot x SiO_2 \cdot y] \cdot zH_2O$.

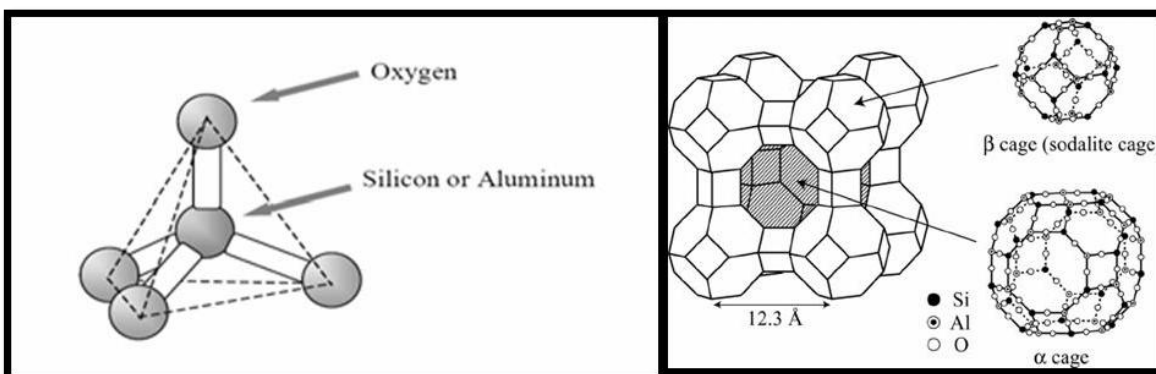


Fig 1: Tetrahedron structure of zeolite

Fig 2: Cage like structure of zeolites

Types of Zeolite

Table:1 Common type of zeolites

Zeolites	Typical oxide formula
Zeolite A	$Na_2O \cdot Al_2O_3 \cdot 2SiO_2 \cdot 4.5H_2O$
Zeolite X	$Na_2O \cdot Al_2O_3 \cdot 2.5SiO_2 \cdot 6H_2O$
Zeolite Y	$Na_2O \cdot Al_2O_3 \cdot 4.8SiO_2 \cdot 8.9H_2O$

Target of the present work.

Target of the current investigations are:

- 1) To develop a suitable adsorbent by modifying zeolite 13X with copper metal.

- 2) Characterizations of the adsorbents by XRD, BET, SEM/EDS.
- 3) To check the adsorption efficiency of copper modified Zeolite to eliminate the Fipronil pesticide from aqueous solution.
- 4) Carrying out experimentation and to study the effects of conc. of initial adsorbate, time of contact & dose of the adsorbent, speed of stirring, pH, and temperature for the process of adsorption of Fipronil over modified zeolite in batch mode.
- 5) Thermodynamic study of adsorption
- 6) To study the adsorption kinetics using the various kinetic model

Applications of Zeolites

- **Molecular Sieves:** These are used as molecular sieves where they can retain molecules where they can fit into their molecular cavities.
- **Ion Exchangers:** Zeolites are used in ion exchanges columns where the zeolite ions can be exchanged with other ions. Also, performed in Hardening of Water.
- **Catalyst:** It is used as a catalyst helps to eliminate harmful pesticides and dye from contaminated water.

Fipronil Pesticide:

Fipronil is considered to be an EDCs. Fipronil refers to the phenylpyrazole family. Fipronil(FP) is broadly applied as pesticides as well as insecticide. It is white powder with mouldy odour.

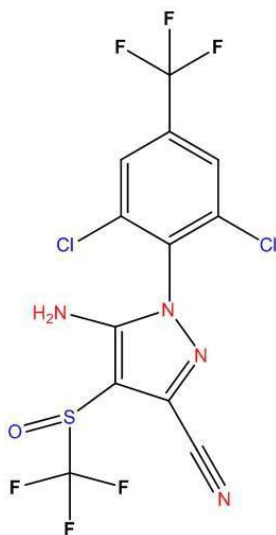


Fig 3. Structure of Fipronil

From the chapter-2, the behaviour of zeolite as adsorbents for the elimination of pesticides & other toxic dyes for wastewater treatment are described.

Literature Survey

Zeolite as an adsorbent for the removal of pesticides

Goyal., et al [16] studied the eliminate of EDCS from its aqueous solutions by synthesized Nanozeolite Y. During the synthesis of nano zeolite, tetramethylammonium hydroxide was added to the mixture to make it more ionic. The percentage removal of Geneistein was 92.8% and that of BPS was 93.1%. Model study, isotherm and thermodynamic studies were carried out.

Rathi., et al.[17] modified zeolite HZSM-5 with cerium by an ion-exchange scheme and tested this adsorbent for elimination of FP from wastewater. Different adsorption parameters were studied. Kinetic study and isotherms were also studied. 90.5% removal of Fipronil was attained.

Barbusinski., et al. [18] studied the removal of pesticide (γ -HCH and inactive isomers α - and β -HCH, DDT, DMDT, fenitrothion and chlorfenvinphos) from industrial water by Fenton's reaction. Pesticides organochlorine related were eliminated with the efficiency about 90%. The best ratio of $[\text{Fe}^{2+}]$ to $[\text{H}_2\text{O}_2]$ was from 1:3 to 1:2 while the best pH was from 3.0 to 3.5.

Li., et al [19] carried out catalytic oxidation of triazophos pesticide from industrial water using Fenton reagent at bench-scale study. Different parameters were varied such as the dosages of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and H_2O_2 , the pH, the stirring speed and removal of COD from the synthesized wastewater were evaluated,

Zhang., et al. [20] reported the elimination of estrone & 17β -estradiol from wastewater by the use of different adsorbent such as granular activated carbon, chitin, chitosan, ion exchange resin and a carbonaceous adsorbent arranged from wastewater. Outcomes explained capacity of adsorption process of activated carbon was decreased with an increase in conc. of adsorbent and by the presence of humic acid and surfactant.

Goyal., et al. [21] carried out the modification of surface of a nanozeolite NaX by tetraethylammonium hydroxide and tested it as an adsorbent for the elimination of BPA from its aqueous solutions. The synthesized zeolite having a surface area i.e. $572 \text{ m}^2/\text{g}$ & small particle size i.e. 35 nm were very active

to remove BPA rapidly and effectively. The adsorption capacities of multilayer and monolayer were calculated to be 122.6 mg per gram & 42.8 mg per gram.

Liu., et al [22] elimination of trace organic pollutants by a connection between adsorbent and photocatalyst on PET filter cloth which was prepared by using a sol-gel & a dip-coating scheme. It removed 93% pollutant such as BPA profitably; by adsorption onto the membrane in a batch of experimentation, About 40% removal was attained in dynamic filtration/adsorption test, which also eliminated. At the same time, around 98% kaolinite suspended solids.

Wang., et al[23] performed solid-phase extraction-LC/MS/MS detection method to study the concentrations and sludge adsorptions of nine estrogenic endocrine disruptors (EEDs) in an up-flow anaerobic sludge blanket & an anaerobic filter, Genistein in AF is removed by more than 80%.

Hartono., et al [24] reported the adsorption by bamboo fibre powders as a capacity; cost efficient sorbent for elimination of harmful compounds of organic in aqueous solution. BPA was removed by the process. The removal efficiency of the bamboo fibre powders reached about at 39 %. After bamboo treatment, with the help of cationic surfactant dosage becomes 4 g L^{-1} . Effect of contact time, sorbent dosage, and particle sizes such as 55, 300, and 1000 micrometers of cationic surfactant-treated bamboo fibre powders towards the BPA elimination were further determined in experimentation.

Removal of Dyes

Setthaya., et al [25] synthesized the TiO_2 -zeolites photocatalysts. The synthesized products were characterized by X-ray Fluorescence spectrometer, X-ray diffraction, scanning electron microscopy, the Fourier transform infrared, ultraviolet-visible, particle size analyzer and measurement of surface area. The adsorption and degradation capacity of the TiO_2 -zeolites photocatalysts obtained from impregnation method is 99.43% which is slightly higher than a solvothermal method of 97.32%. Studies such as desorption conclude the chemisorption process, which might be the foremost mode of adsorption.

Robinson., et al [26] studied the removal of dyes by two cost efficient, available in abundance, renewable biosorbents such as apple paste and wheat straw. Experimentation done at various dye conc. of 10- 200 mg/l were performed with a synthetic effluent consisting of an equal mixture of 5 dyes which is used for textiles. The different parameter of adsorption such as initial dye conc., biosorbent size of particle, the quantity of biosorbent, were studied. One gram apple paste reported

elimination about 81% of dyes at a size of 2 mm×4 mm and 91% at 600 μm. Dyes adsorption by apple pomace occurred at a high rate in comparison to wheat straw.

Tan., et al [27] reported that $MgCl_2$ has been used as a coagulant for the elimination of colouring matters. By visible spectrophotometry, the conc. of dye solutions was calculated. Different parameters such as the coagulant effect & aid of coagulant doses. Also, effects of various coagulants have been studied. Outcomes demonstrate that $MgCl_2$ is able to perform to eliminate (<90%) of the colouring material at pH 11 & a dose of 4 g per litre $MgCl_2$ of dye solution.

2.2. Gaps in literature

From last few decades, different removal techniques have been used for removal of contaminants or pesticides, but no reported work so far for the removal of FP pesticide even though it is a novel contaminant found in wastewater coming from the pesticide industry. Also, very scarce literature is available on the removal of FP over copper modified zeolite as an adsorbent.

Problems in Research

The problem is to develop a suitable, stable and regenerative adsorbent with a more surface area to remove the toxic pesticides from wastewater. After a detailed study of adsorption kinetics and knowing the thermodynamic conditions, a proper laboratory-scale adsorber can be designed for complete removal of pollutants which can be further scaled up to a lab-scale adsorber in the industries for the desired removal.

Summary

Many works are reported on the removal of pesticides and dyes with different adsorbents. Adsorption was carried out varying parameters such as pH, dose of adsorbent, stirrer speed and so on. Isotherms are ordinarily used. The kinetic model study is also performed to find the different parameters.

Materials

13X zeolite was procured from Allied Products Pvt Ltd. Ammonium Nitrate, Copper nitrate were obtained from Loba Chemie and its Mol.Wt=24.60. FP was procured from Bayer Crop Science Ltd., India.

Adsorbent Preparation

Commercially available 13X zeolite was refluxed with ammonium nitrate solution at 90° C for 6 hours for 3 cycles and thus modified to form HX. Then, the catalyst molecules were centrifuged at 7000 rpm for 5 min & washed with distilled water for 2-3 times, & then oven is used for drying for 12 hours at 80° C. After calcination, HX was refluxed with copper nitrate solution for 72 hours at 375 K to exchange its H⁺ ions with Cu⁺⁺ ions. Then the modified zeolite was centrifuged at 8000 rpm for 7 min followed by washing with distilled water to eliminate the contaminants. Washed zeolite was drying in an oven for 2 days at 60° C [28- 29]. Finally, zeolites are modified with copper. The methodology is presented in **Figure 4**.

Preparation of Pesticide Solution

FP pesticide stock solution having formula C₁₂H₄Cl₂F₆N₄OS was prepared by 5mg/L in one litre of deionized water to form a conc. 50mg/L. Dilutions were made in the form of series of 10, 20, 30, 40 and 50mg/L in accurate proportions. Curve of calibrations for pesticides was arranged by calculating the value of absorbance of the pesticides.

Methods

Batch studies of the adsorption process

Procedure for the batch study for the elimination of Fipronil FP using zeolite consists of the following steps.

- 1) FP stock solution was prepared by dissolving FP in C₂H₅OH, diluted it into different concentrations with distilled water having ratio C₂H₅OH/H₂O ratio=1:20v/v

- 2) At the time of starting, the adsorption studies were performed in different flasks i.e.250ml by adding one gm per litre of copper modified zeolite in 10mg per litre solution of EDC in incubator shaker (Bionics).
- 3) The pH values calibrated to 1- 10 , using 0.2M HCL and 0.2M NaOH solutions, evaluated by value of pH meter, helps to check the importance of pH on the process of adsorption.
- 4) Adsorption process was also carried out at various temperatures i.e.20° - 45° C to explaine the temperature effect. The experiment was carried out at different stirring speed, performed at 100,120,150,180 and 200 respectively.
- 5) Adsorbate conc. effect on adsorption was studied. The samples were collected from the shaker and centrifugation was done at 5000 rotation per minute for 5 mins.
- 6) The supernatants (clear solution) were investigated by UV-Visible spectrophotometer (Hack, Dr.5000) to demonstrate the concentration of Fipronil (FP) pesticide at λ 276nm. The R % is the removal capacity and q_t , mg per litre is adsorption capacity of the copper modified zeolite were calculated using Eqn (1) & (2) respectively.

$$\text{Removal efficiency, } R\% = \left(\frac{C_i - C_f}{C_i} \right) \times 100 \quad (1)$$

$$\text{Adsorption capacity, } q_t = \frac{C_i - C_f}{C_z} \quad (2)$$

Where the initial concentration C_i (mg per Litre), final concentration C_f (mg per litre) of the Fipronil pesticide remaining in the solution after adsorption, adsorbent mass C_z (grams), the amount of Fipronil adsorbed by the adsorbent at time t (min) i.e. q_t (mg per gram) was.

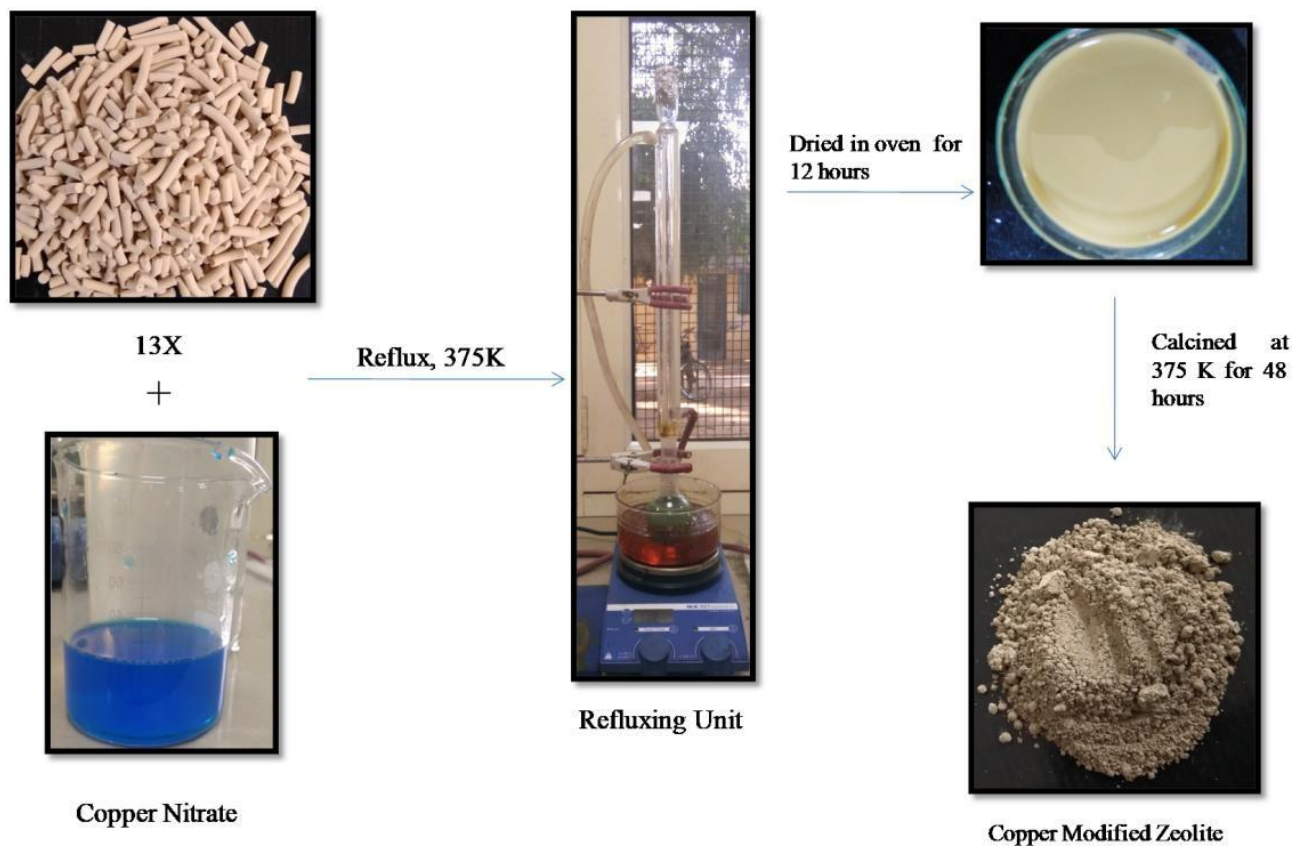


Fig 4: Synthesis of Copper modified zeolite

Adsorbent Characterization Method

BET (Brunauer–Emmett–Teller) and BJH (Barrett–Joyner–Halenda) plot

The surface area of 13X zeolite & Cu-X samples were determined by the isotherms of N₂ adsorption and desorption. The copper modified zeolite and unmodified 13X zeolite possesses type IV isotherm with a hysteresis loop which indicates the presence of mesopore character of zeolite in **Fig:5 (a)**[30]. Plot of BJH **Fig 5(b)**: indicates that distribution of the size of the pore of modified zeolite material (mesoporous) lies in between i.e. 2-50 nm. The BET surface area of copper modified zeolite is 420.7m²/g. The diameter of the mean pore was calculated to be 5.1186 nm. Also, the volume of pore is decreased because of embedded copper, which obstruct the pores of the material. The pore volume of zeolite X was not significantly changed by incorporation of Cu. Although, there is a decrease in the volume of micropore because of Cu loading which is a noticeable point.

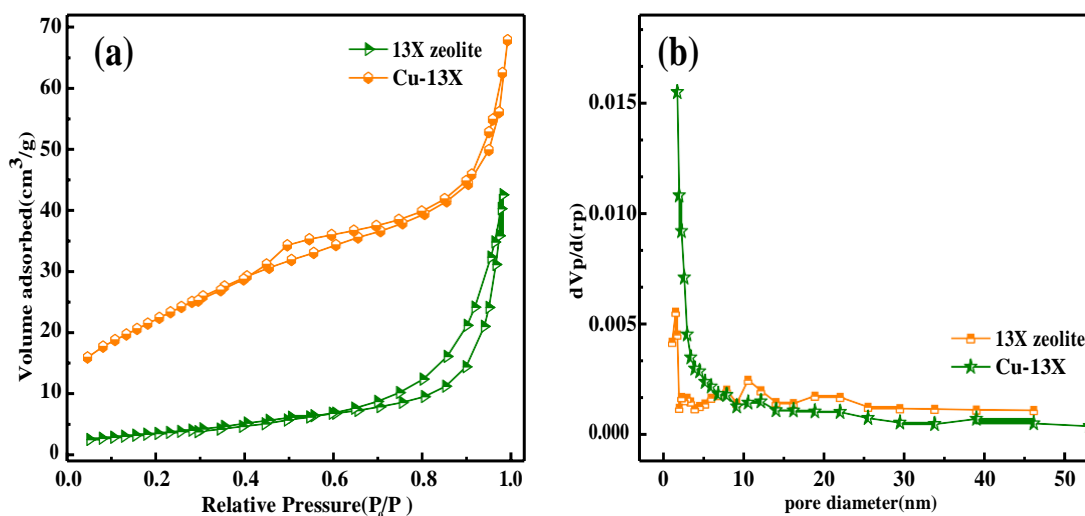


Fig 5: (a) Isotherm of N₂ sorption of zeolite 13X ; copper modified zeolite. (b) BJH plot of the 13X zeolite; copper modified CuX zeolite

Table 2: BET-BJH parameters

Parameters	13X zeolite	Copper modified zeolite
BET Surface area	478.2 m ² /gm	420.7 m ² /gm
Total pore volume	0.212 cm ³ /gm	0.1046 cm ³ /gm
Mean pore diameter	10.8 nm	5.11 nm
Micropore volume	0.200 cm ³ /gm	0.008 cm ³ /gm

XRD Diffraction

XRD of copper modified 13X zeolite was obtained from XPERT -PRO by using Ni -filtered CuK α radiation having specifications such as 45 Kv, 40mA and step size 0.013°. The samples were scanned from 10–50° (2 Θ , where Θ is the angle of diffraction), at a speed of 2°/min. The XRD patterns of Cu-X zeolite, shown in Fig 6, shows a slight shift in the peak positions to lower degree. New emerging peaks have appeared in the CuX. The weak intense peaks were disappeared while the more intense peak becomes broader after incorporation of copper into the zeolite X. Analysis of the Cu-X shows excellent crystalline nature. The overall finding from the XRD pattern suggests the incorporation of copper into the zeolite X framework.

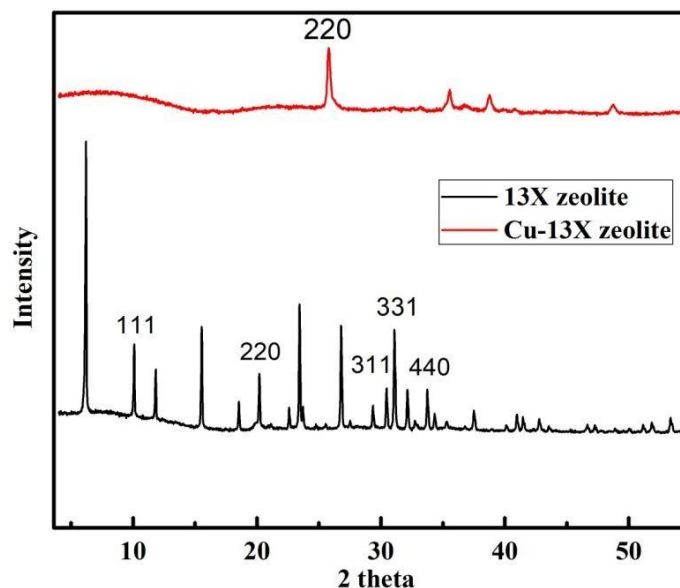


Fig 6. XRD of 13X and CuX

SEM (Scanning Electron Microscopy) / EDS (Energy Dispersive X-ray Spectroscopy)

Morphological analysis of zeolite at 1000x magnification is shown in **Fig.7**. SEM micrographs in **Fig. 7 (a)** depicts that copper particles are of tetrahedral structure [29-30]. The scanned surface of copper modified zeolite confirms the absence of hexagonal oxide particles which gets converted to copper particles in **Fig. 7(b)** [36-37] . Also, the arrangement of commercial 13X is shown in Fig:7 (d) and Fig 7(c). Elemental composition of copper modified zeolite X is shown in **Fig:8**. The results of elemental mapping in **Fig. 9 (a) and Fig. 9 (b)** suggest that there is a homogeneous distribution of oxygen and copper respectively.

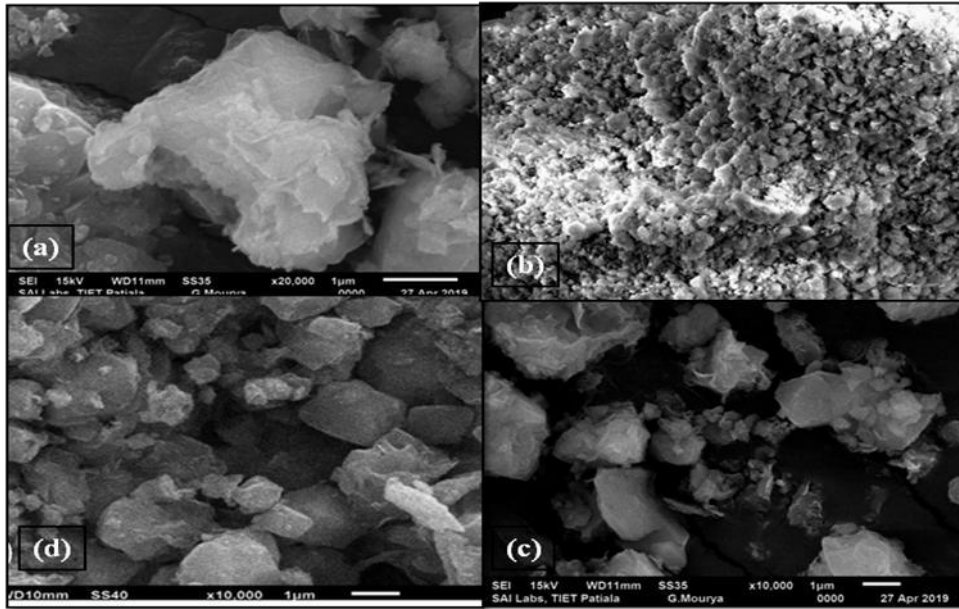


Fig 7: SEM of (a) copper oxide particle (b)copper particles(c) commercial 13X (d) CuX

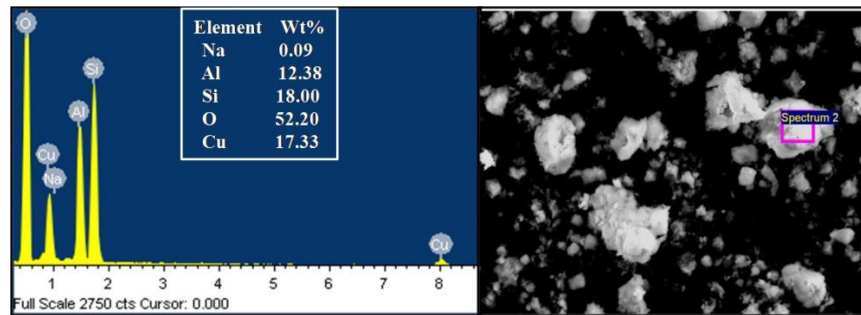


Fig 8: Elemental Composition of Modified Zeolite

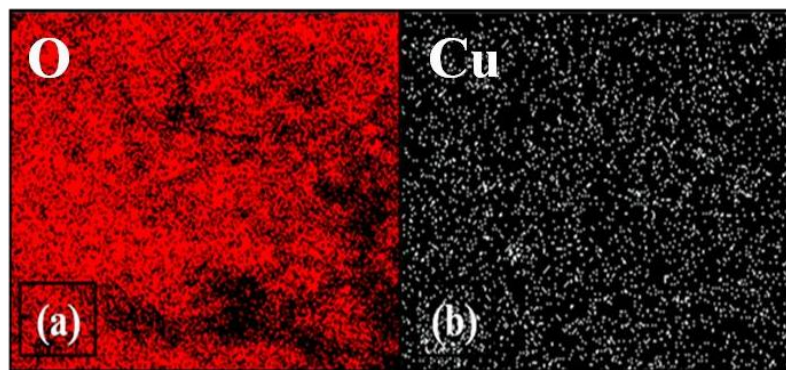


Fig 9: EDS mapping of Oxygen and Copper

Chapter-4 explained about the outcomes of adsorption is described, adsorption isotherms and kinetics models are studied.

Calibration Curve

The value of absorbance were estimated at different given conc. of the FP solution to get a curve of calibration. As shown in **Figure 10(a)**, the data showed the linear fit i.e. absorbance versus dye conc. and gets a straight line with a slope of 0.00127. After adsorption, to determine the unknown sample conc. in the solution can be done by using this calibration curve.

Batch Experimentation:

Batch study of the process was carried out to determine the efficacy of synthesized adsorbents towards Fipronil (FP). The pesticide removal efficiency and adsorption capacity were estimated following the formula given below.

$$\text{Removal efficiency, } R = \left(\frac{C_i - C_f}{C_i} \right) \times 100 \quad (4.1)$$

$$\text{Adsorption capacity, } q_t = \frac{C_i - C_f}{C_z} \quad (4.2)$$

Here C_i = concentration of initial pesticide (mg per Litre), C_f = after adsorption pesticide concentration in the solution (mg/L), C_z = dose of modified zeolite (g/L), q_t = amount of pesticide adsorbed per unit weight of modified zeolite (mg per g).

Effect of adsorbent dose and contact time on the removal of Fipronil

In a series, to increase the dose of Cu-X for the elimination of FP, batch of experimentation were performed and shown in **Fig10(b)**. It was seen that FP removal capacity was increased from 38.49% to 69.9% with the increase in dose of adsorbent and contact time. Initially, with the increase in the dose of adsorbent and contact time adsorption increases rapidly because of higher availability of surface area and active sites[5]. After sometime, removal becomes almost constant due to the shortage of adsorbate in the solution. Removal becomes constant at 120 min onwards.

Effect of initial pesticide concentration on the removal of FP

To analyse the conc. effect of initial FP on the adsorption efficiency, experimentation were carried out at particular FP conc. between 500mg/L to 1000 mg/L and shown in Fig10(c). Outcomes explained that the % removal of FP decreases with the conc. of initial pesticide increase, maximum removal (53.1%) efficiency was attained at the initial concentration of 500mg/L. This point out that the process of adsorption is highly efficient at lower concentrations of FP solution. Further, the adsorption rate continuously decreases because of the rise in driving forces felt by the adsorbate[16]. All the adsorption sites are saturated on increasing the initial concentrations.

Effect of pH on the removal of FP

pH is the most significant parameter in this whole experiment which controls the overall process of adsorption. As a result it can control the charge of the adsorbent surface area. To check pH effect, a series of experiments were carried out at pH 1 to pH 10 at 25° C for 140 min. The best percent removal (84.23%) occurs at pH 3 and shown in **Fig. 10(d)**. It can be concluded that the presence of hydrogen ions leads to electrostatic attraction with negatively charged FP[5]. With an increase in pH after 3, the pesticide removal is decreased because deprotonation occurs in the solution, which weakens the electrostatic forces of attraction as well as adsorption capacity between the FP and Cu-X.

Effect of Temperature on the removal of FP

The effect of this parameter on FP onto Cu-X. Different temperatures were carried out throughout the experiment i.e. 20° C - 45° C and shown in **Fig 10 (e)**. With increase in temp, the adsorption of FP decreases. The best percent removal (92%) at temperature 20° as the FP particles achieved sufficient energy at lower temperature to combine with the sites which are active in nature and present on the surface of adsorbent. Increase in temperature increases solubility of FP in the solution imparting lower tendency to get adsorbed in the CuX surface[40]. Interactions such as electrostatic takes place b/w the FP and the active sites unstable at higher temperature, which shifts the equilibrium of adsorption process towards desorption phenomenon.

Effect of stirring speed on the removal of FP

In adsorption phenomena stirring acts as significant parameter which controls the distribution of the solute & the formation of the external boundary film. The rotation effect on the adsorption of FP over Cu-X was investigated at 20°C for 140min. It is seen in the **Fig.10(f)** shows rapidly increase in the

percent elimination with increase in speed of stirring from 50-300rpm. The best percentage comes to be (92.3%) occurred at 200 rpm. Increased stirring speed promotes FP particle to overcome the film diffusion resistance[16-17]. Degree of agitation reduces the layer resistance of boundary and increases adsorption of FP on CuX. In the present study, the optimum stirring speed obtained is 200 rpm, afterward, all the experiment undergoes saturation.

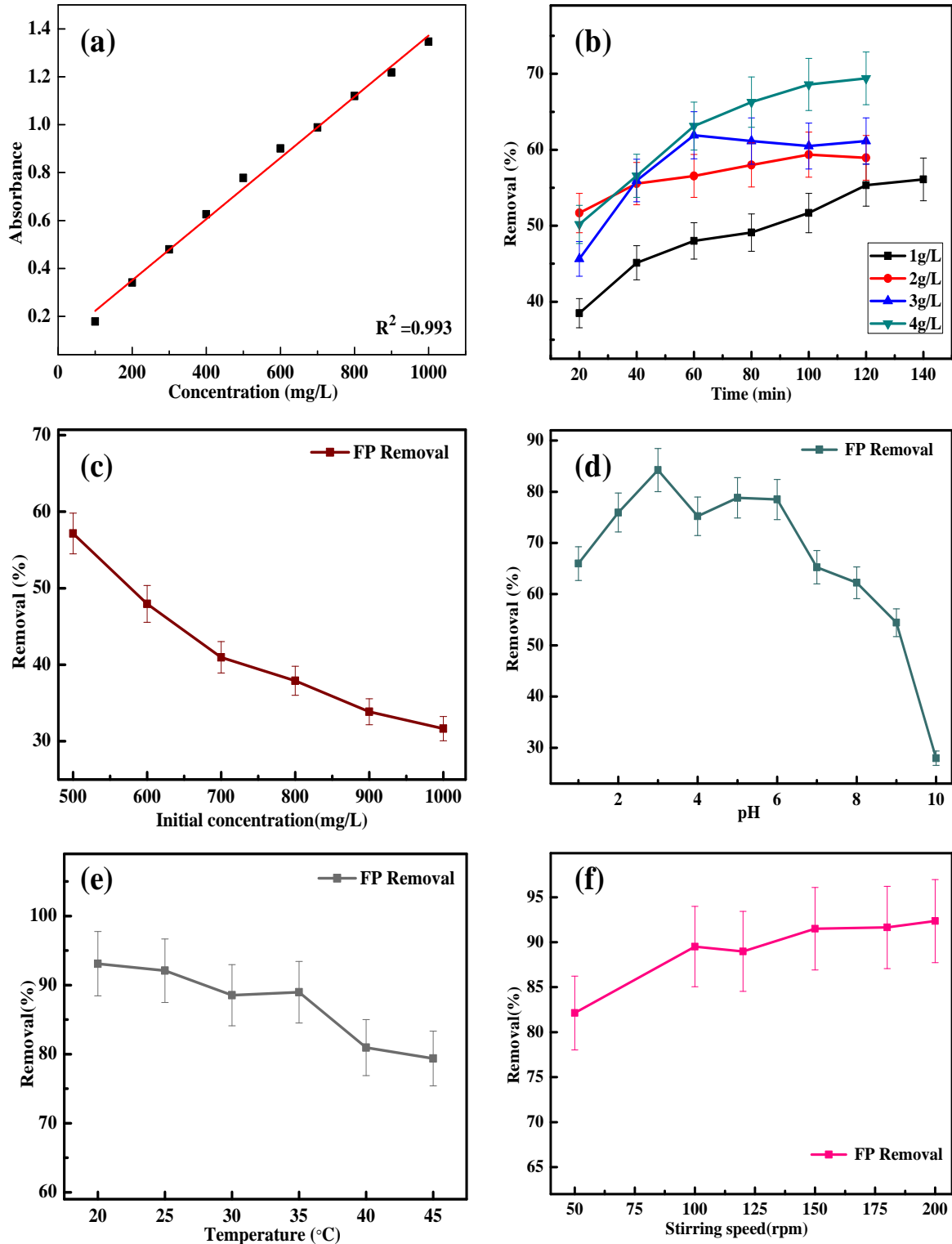


Fig10: (a) Calibration curve (b) Effect of adsorbent dose and contact time on the removal of FP [solution pH-3,temperature 25°C, stirring speed 150r.p.m] (c)Effect of initial concentration of adsorbate[solution pH 3,contact time 140 min, temperature 25°C, stirring speed 150r.p.m] (d) Effect of pH on removal of FP[temperature 25°C, stirring speed 150r.p.m,adsorbate concentration 500mg/L] (e) Effect of temperature on removal of FP [solution pH 3, stirring speed 150r.p.m] (f) Effect of stirring speed [solution pH 3,temperature 25°C, adsorbate concentration 500mg/L]

Adsorption Isotherm Studies

Langmuir Isotherm

The study is situated on the hypothesis of the monolayer formation over the adsorbent particle. It is also considered that no interaction takes place between particles adsorbed on neighbouring sites. The isotherm is expressed in the following equation[41]:

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{q_{max}b} \quad (4.1)$$

Where q_e is the amount of adsorbate adsorbed per unit mass of adsorbent (mg per g) in an equilibrium state, C_e is the adsorbate concentration in solution present in an equilibrium state (mg per Litre), q_{max} is the adsorption efficiency of adsorbent (mg/g), b is a constant. The Langmuir isotherm is shown in **Fig-11 (a)**. In the linear plot R^2 value was found to be 0.988.

4.6.2 Freundlich Isotherm

Freundlich study is situated on the multilayer and heterogeneous adsorption [32]. The isotherm is expressed in the form of eqn:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (4.2)$$

Where Freundlich equilibrium constant K_F is measured in L/g and $\frac{1}{n}$ is an empirical constant linked with the capacity of the adsorption; lower the $1/n$ value, more favourable is the adsorption. Freundlich isotherms for adsorption of Fipronil(FP) onto copper modified zeolite is shown in **Fig-11(b)**. In Freundlich isotherm, the R^2 value is found to be 0.999 for copper modified zeolite. The value $\frac{1}{n}$ was found to be less than 1, indicates unfavourable adsorption.

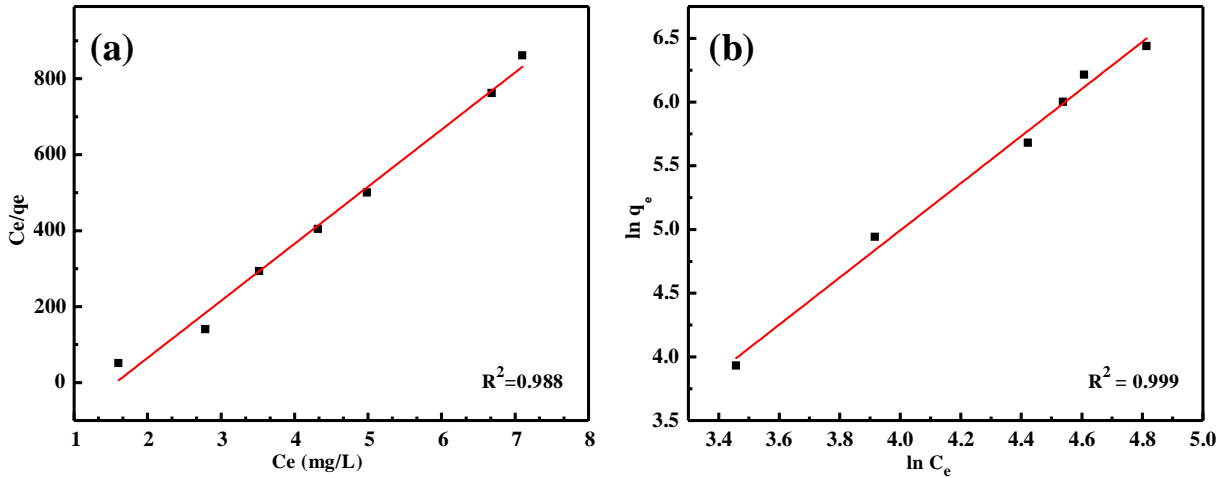


Fig 11. (a) & (b) Isotherms of Langmuir and Freundlich

Table 3: Equilibrium parameters for adsorption isotherms

S. No.	Name of the isotherm	Eqn	Parameters	FP Values
1)	Langmuir	Eqn.(4.1)	Q_m (mg/g) K_L (L/mg) R^2	6.6544×10^{-3} -2.8258×10^{-3} 0.988
2)	Freundlich	Eqn.(4.3)	$K_F[(mg \cdot g^{-1} \cdot (L \cdot mg^{-1}))^{1/n}]$ $\frac{1}{n}$ R^2	0.08984 1.8507 0.999

Kinetic model studies:

Pseudo first-order kinetics

Model of Pseudo first order kinetics [33] is expressed as:

$$\log (q_e - q) = \log q_e - \frac{K_1}{2.303} t \quad (4.3)$$

Where q_e mass solute adsorbed at equilibrium in $\text{mg} \cdot \text{g}^{-1}$, q is the mass of solute adsorbed at the time t in mg/g , K_1 is the rate constant of this kinetics (min^{-1}). First order kinetics plot is shown in **Figure 12(a)**. The calculated values of R^2 for this model is given below. Outcomes explained that the kinetics of the first order model, **Fig12(a)** fits well for the process of adsorption of Fipronil pesticide on copper modified zeolite. The coefficient value, ($R^2 = 0.965$) for copper modified zeolite was found to be respectively.

Pseudo second-order kinetics

The model kinetics was developed by Ho and McKay, presumed the absorption efficiency is directly related to the number of active sites occupied the sorbent presented as [38] :

$$\frac{t}{q_e} = K_{2ad} \frac{1}{q_e^2} + \frac{t}{q_e} \quad (4.4)$$

Where rate constant is K_{2ad} ($\text{g}/\text{mg} \cdot \text{min}$). The rate constant K_{2ad} & q_e can be estimated from the intercept and slope, respectively of the plot of t/q_e **against** t . It pointed out that the kinetics fits well with the data of copper modified zeolite ($R^2 = 0.998$) and shown in **Fig: 12(b)**.

Elovich Model

This elovich study is more suitable for demonstrating the surface of adsorbent (energetic) with heterogeneous nature. Model can be explained in the form of equation is given:

$$q_t = \frac{1}{B} \ln(ab) + \frac{1}{B} \ln(t) \quad (4.5)$$

Where a is the initial adsorption $\text{mg} \cdot \text{g}^{-1} \cdot \text{min}$, B is the constant, extent for coverage area. Presence of activation energy for chemisorption mg/g . The graph occurs between q_t vs. $\ln t$ provides a linear trace with a slope of $(1/B)$ and an intercept of $1/B \ln(ab)$. The outcomes of this model for the adsorption of modified zeolite on the elimination of FP pesticide[17] i.e. **Fig-12(c)**.

Intra-particle Diffusion model

Diffusion of Film, diffusion of pore, and transportation of IPD are the three main steps involved during the adsorption process. Rate controlling step will be the slowest one. Kalavathy et al.[42]

found that IPD is the controlling step for most of the time in the batch adsorption process. This diffusion model is given below [35].

$$q_t = K_{id} t^{\frac{1}{2}} + I \quad (4.6)$$

Where k_{id} is the rate constant of IPD ($\text{mg g}^{-1} \text{min}^{-0.5}$), Plot of this model q_t vs. t satisfies the relationship of linearity with the data of experimentation shown in **Fig 12(d)**. This can be expected that the external resistance to mass transfer around the particles is symbolic only in the initial period of adsorption. It can be expressed by the sharper portion. The second linear portion shows the continuous absorption with IPD dominating [36].

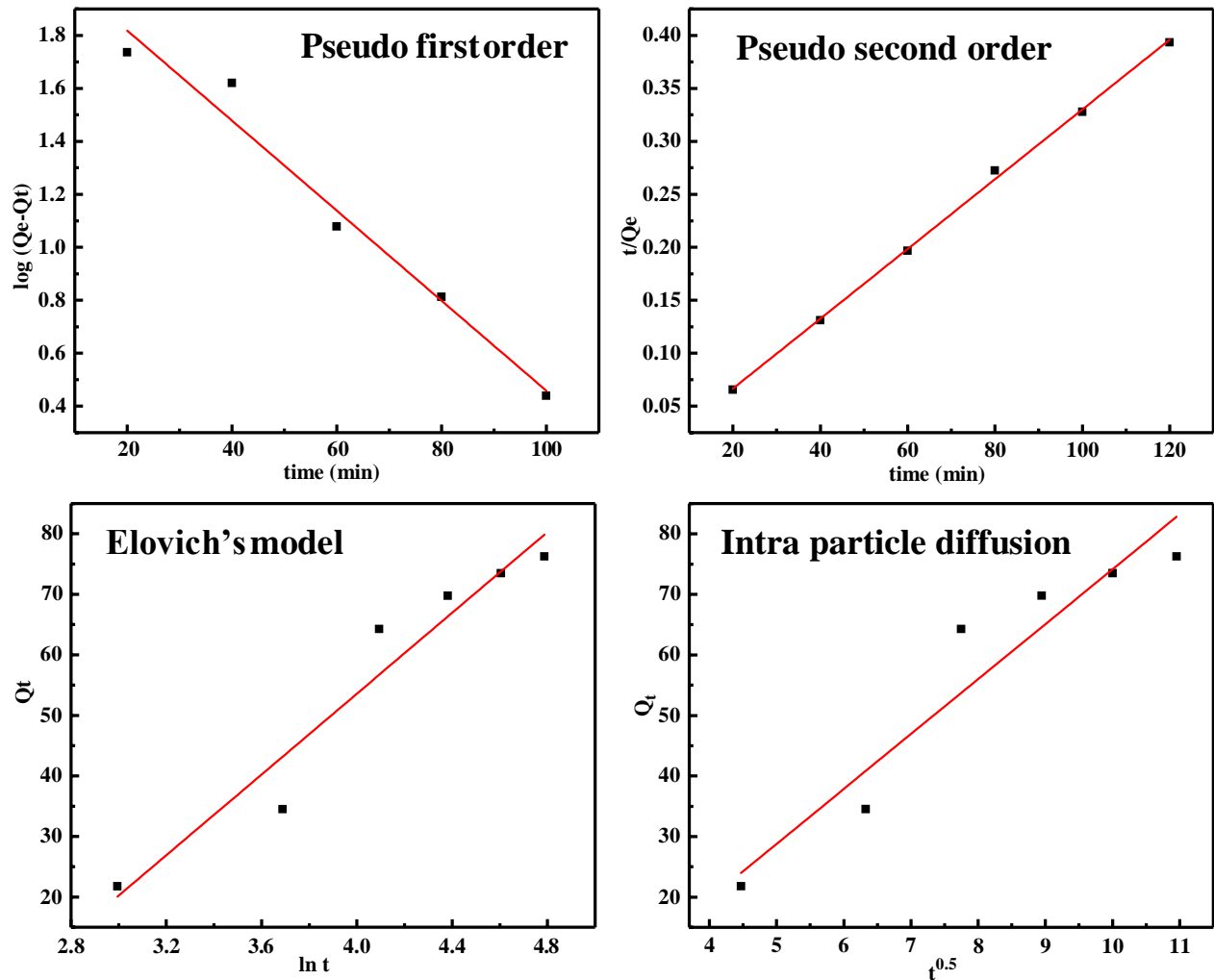


Fig 12: (a) Adsorption of first order kinetics of FP on Cu X (b) Pseudo second order adsorption kinetics(c)Elovich adsorption kinetics for adsorption of Fipronil (d) diffusion model

Table 4. Parameters of kinetic study

S. No.	Name of the Model	Eqn	Parameters	FP Values
(1)	Pseudo first order	Eqn	k_1 (min^{-1})	0.039151
			q_e (mg/g)	143.946
			R^2	0.965
(2)	Pseudo second order	Eqn	k_2 (g/mg*min)	4.9848
			q_e (mg/g)	303.951
			R^2	0.9986
(3)	Elovich Model	Eqn	a ($\text{mg}\cdot\text{g}^{-1}\cdot\text{min}$)	3.04443
			b (g/mg)	0.02996
			R^2	0.985
(4)	IPD	Eqn	k_i ($\text{mg}\cdot\text{g}^{-1}\cdot\text{min}^{0.5}$)	9.0735
			C_i ($\text{mg}\cdot\text{g}^{-1}$)	-16.588
			R^2	0.891

4.7. Thermodynamic studies:

This studies were investigated in the temperature range of 298 – 313K temperature by keeping other parameters constant mentioned above leads to a maximum % removal of FP pesticide. For adsorption process, the thermodynamic parameters ΔG° , ΔS° and ΔH° that changes in Gibbs energy, entropy change and enthalpy change respectively were estimated by the following equations [43]:

$$\ln \frac{q_e}{C_e} = \ln K_c \quad (4.8)$$

$$\ln K_c = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (4.9)$$

$$\Delta G^\circ = -RT \ln K_c \quad (4.10)$$

Where K_c is the equilibrium constant, T is temperature (K), R is gas constant (8.314 J/mol/K) [44]. The graph is plotted between $\ln K_c$ versus $1/T$ gives straight line shown in **Fig.13** and the thermodynamic parameters such as enthalpy and entropy were obtained from the slope and intercept respectively. Values of entropy were calculated from the above equations at various temperatures. The (-) values of ΔG° pointed out that process was spontaneous & it decreases when temperature goes higher, signifies that the adsorption is exothermic [43]. The (-) value of ΔS° for FP removal verified that the randomness decreases and FP molecules got disordered at the solid-liquid interface [44-46]. ΔG° , ΔH° and ΔS° values were listed in Table 5.

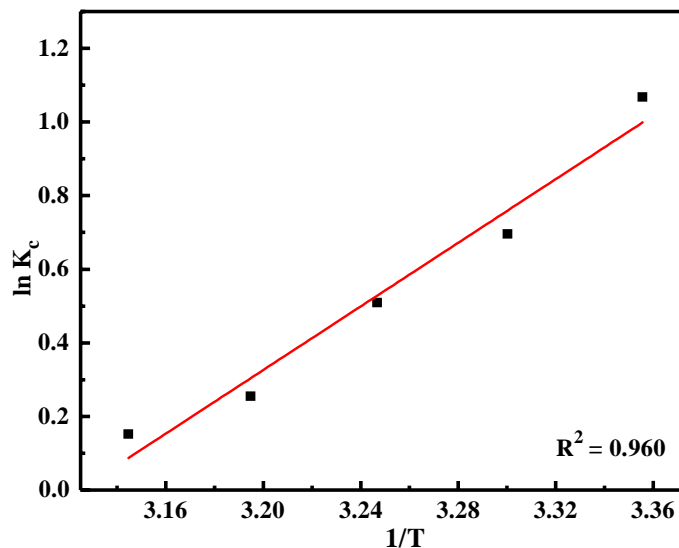


Fig 13:Plot for finding $\Delta^\circ G$

Table 5: Thermodynamic parameters

Temp (K)	ΔG° (kJ/mol)	ΔH° (J/mol)	ΔS° (J/mol K)	R^2
298 K	-6.23444	-35.9149	-112.2118	0.960

Comparison of zeolite performance with a commercial adsorbent

The performance of % removal of copper modified zeolite (CuX) is compared with a commercially available adsorbent (13X). It can be seen from Fig. 19 ; copper modified zeolite performs much better than the commercial adsorbent i.e.13X. The maximum pesticide % removal achieved for the synthesized zeolite is 60% and the % removal for the commercial adsorbent is only 7%.

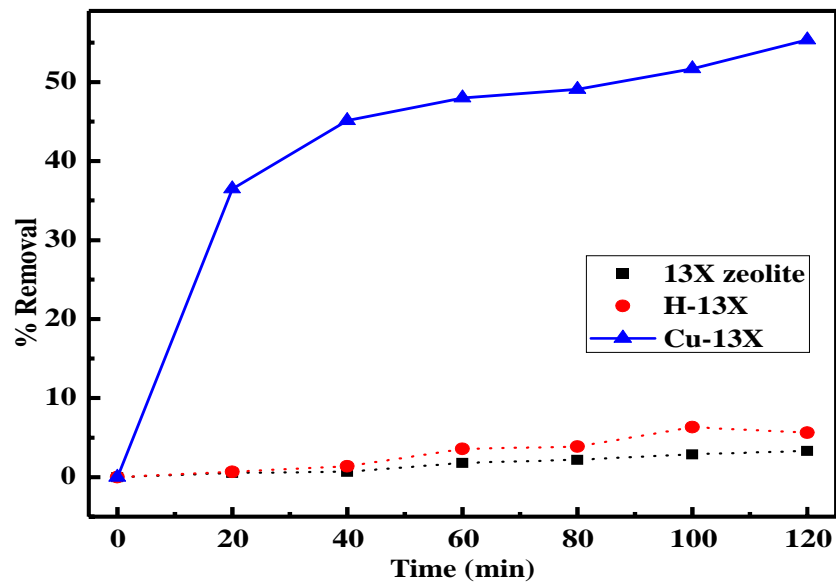


Fig 14: Comparison between modified and unmodified zeolite on the basis of adsorption

The following conclusions have been derived from the experimental analysis carried out so far.

- Cu-X zeolite was synthesized from 13X and Copper nitrate solution using Refluxing treatment method.
- The modified zeolite was characterized by using, SEM/EDS and XRD. Outcomes were found to be in agreement with those reported by other investigators.
- The modified adsorbent i.e. zeolites were checked for their efficacy to adsorb Fipronil from its aqueous solution. Adsorption study of Fipronil pesticide was found to be dependent on operational parameters viz. pH, dose of adsorbent, contact time and initial pesticide concentration.
- Maximum percentage removal was obtained at pH 3. However, in the present study pH, 3 of the solution is considered for all the experiments. The % of elimination decreases with an increase in pH and initial pesticide conc. It increased as dose of adsorbent and time of contact was increased.
- Outcomes of the experiments showed that the zeolite adsorbents explained high adsorption efficiency towards Fipronil pesticide solution. The optimum cond. were found to be at pH=3, initial pesticide conc. = 10 mg/L, adsorbent dose = 40mg & contact time= 140 min. Under these conditions, the % removal of pesticide was found to be 92.3%.
- Experimental data of removal of pesticide from its solution fitted well to the Freundlich than the Langmuir indicated that the removal of the organic pollutant was favourable.
- The adsorption kinetics of copper modified zeolite was studied with the help of pseudo second-order kinetics. Also, second-order kinetic study explained the experimental adsorption data very well.

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