



Removing 2,4-Dichlorophenoxyacetic Acid (2,4-D) from Polluted Water using Zinc Ferrite Nanoparticles



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2,4-Dichlorophenoxyacetic acid (2,4-D), is one of the most commonly herbicides used in agricultural farms to control weeds. Accumulation of 2,4-D in natural water stream constitutes a serious issue because of the adverse effects on human and animal health. This study aimed to monitor and treat 2,4-D in different water resources in Egypt. Treatment obtained by zinc ferrite nanoparticles ($ZnFe_2O_4$) which prepared by sol-gel combustion method. The batch experiments were carried out to study the optimum removal conditions such as pH, dose, 2,4-D initial concentration, contact time, ionic strength and temperature. Results recorded tentatively the presence of 2,4-D in the Rosita River Nile and agriculture drainage channels with concentrations ranged from 0.35 to 21.31 $\mu\text{g L}^{-1}$ using LC/MS/MS analyzer. The optimization study showed a maximum percent of removal is 97.84% for adsorption followed by photodegradation using 0.3 g of zinc ferrite nanoparticles for 15 min. at pH 8.0. Adsorption capacity was 0.34 mg/g at initial concentration (C_0) 10 mg/L after 15 min. Pseudo-second order model is well fitted with the experimental data with a correlation coefficient 0.999. Adsorption is proceeded with Freundlich isotherm model with correlation coefficient 0.986. According to the study findings zinc ferrite nanoparticle was considered as a new novel solution for removing that hazard material.

Keywords: 2,4-Dichlorophenoxyacetic acid, Zinc ferrite nanoparticle, Photodegradation, Adsorption isotherm, Thermodynamic, Reaction kinetic

Introduction

Increasing use of pesticides, in agriculture and domestic activities for pest control is polluting our water resources, gradually forming a strong class of water pollutants, which is really a great concern, according to the World Health Organization and United States Environment Protection Agency [1]. Pesticides are defined as chemical compounds that are used to kill pests, including insects, rodents, fungi and unwanted plants (weeds). Pesticides are mainly used for benefits like crops protection, preservation of food materials and prevention of vector borne diseases. They are also used in different field like agriculture, forestry, aquaculture, food industry, processing, transportation and storage of wood and

other biological products. Gross use of pesticides cause damage to public health and ecosystem [2]. Pesticides are chemicals used against weeds, diseases and pest to improve crop yield are called pesticides. Among them, herbicides are used as weed killers in agriculture. However, the accumulation of these chemicals in natural water stream constitutes a serious issue because of their adverse effects on human and animal health [3].

The discovery of the herbicidal activity of 2,4-D (2,4-dichlorophenoxyacetic acid) first synthesized in 1941, triggered the development of modern herbicide technology. 2,4-D proved to be an outstanding herbicide. The commercial success of 2,4-D led to the development of other herbicides such as MCPA, silvex and 2,4,5-T,

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Received 04/08/2019; Accepted 01/09/2019

DOI: 10.21608/ejchem.2019.15633.1948

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phenylurea herbicides such as monuron and linuron. The EPA (Environmental Pollution Agency) of the US has classified pesticides according to toxicity into four categories (I, II, III and IV) [4]. 2,4-D is commonly known as a component of the controversial herbicide Agent Orange, which was extensively used by the U.K. in Malaysia and by the U.S. military during the Vietnam War to defoliate jungle regions [5].

2,4-Dichlorophenoxyacetic acid (2,4-D) is a conventional herbicide that has been widely used in agricultural farms to control the weeds [7, 8]. 2,4-D is well known as a versatile herbicide that has been applied in various processes. Moreover, low cost and good performance have increased the 2,4-D application worldwide. Over 600 commercial types of 2,4-D are produced in market for the control of weeds [9]. The extensive application of is 2,4-dichlorophenoxyacetic acid 2,4-D and its high solubility cause contamination of receiving waters. The presence of this herbicide has been frequently reported in drainage water and groundwater in high concentration. 2,4-D is a toxic chemical that can damage human organs such as the liver and kidney [10]. In addition, it has been reported that 2,4-D can be carcinogenic for mammals. It is also well known as an endocrine disruptor [11]. EPA has concluded that there are some concerns on neurotoxicity, acute toxicity and its endocrine disruptive potential

resulting from exposure to 2,4-D [12]. Li et al, [13] observed the cardio and geno-toxicity of 2,4-D on zebra fish. Also, there is a scientific evidence to suggest that 2,4-D causes oxidative stress and immune suppression [14].

Thus, 2,4-D was classified as “possibly carcinogenic to humans” (Group2B). Therefore, it should be taken into consideration that the chemical and biological stability, the urgent attention requires for developing effective technologies and economical approaches to eliminate 2,4-D [15]. The extensive application of 2,4-D and its high solubility cause contamination of receiving waters. The presence of this herbicide has been frequently reported in drainage water and groundwater in high concentration. 2,4-D is a toxic chemical that can damage human organs such as the liver and kidney [10]. In addition, it has been reported that 2,4-D can be carcinogenic for mammals. It is also well known as an endocrine disruptor [11]. Acute symptoms of exposure include coughing, burning, dizziness, loss of muscle coordination, nausea, diarrhea, and vomiting. Blood, liver, and kidney toxicity have all been observed with 2,4-D exposures [16].

Additionally, 2,4-D is one of the few herbicides to cause nervous system damage Effects to the nervous system include inflamed nerve endings, lack of coordination, stiffness in the arms and legs,

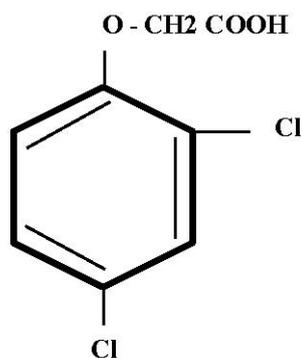


Fig. 1. 2,4-D: 2,4-dichlorophenoxyacetic acid [6].

TABLE 1. Physical properties of 2,4-D [1]

Adsorptive	2,4-D
Molecular weight (g/mole)	221.04
Molecular form	C ₈ H ₆ Cl ₂ O ₃
Water Solubility T=293 K (mg/L)	900

inability to walk, fatigue, stupor, coma, and death. In persons with impaired cardiovascular function, inhalation of 2,4-D may exacerbate preexisting conditions [16]. Researchers from a 2004 study also found that dermal exposure to 2,4-D can lead occasionally to mild gastrointestinal irritation and progressive nerve damage [17]. These researchers also found that some of the neuromuscular effects such as muscle twitching, weakness, and loss of tendon reflexes were permanent in patients [16]. Poor semen quality has also been associated with 2,4-D exposure. A study of men living in the agricultural Midwest reported that men with poor semen quality also had 5 times more 2,4-D levels in their urine compared to men with normal semen samples [18].

Endocrine Disruption 2,4-D has the ability to interfere with the hormonal system. A direct correlation of urinary levels of 2,4-D with elevated levels of the luteinizing hormone (LH) –responsible for stimulating the production of testosterone in males and regulating the menstrual cycle and ovulation in females– suggests a direct effect on hormonal levels by the chlorophenoxy herbicide [19]. 2,4-D is also known to interfere with the thyroid hormone. According to EPA, data “demonstrate effects on the thyroid and gonads following exposure to 2,4-D, [and] there is concern regarding its endocrine disruption potential.” [16] Their results also indicate that exposure to 2,4-D was associated with changes in biomarkers that have been linked to risk factors for acute myocardial infarction and type-2 diabetes [20].

However, one study reports that a significant increase in the percentage of chromosome aberrations in bone-marrow and spermatocyte cells was observed after oral administration of 2,4-D in mice. Here, 2,4-D also induced a dose-dependent increase in the percentage of sperm head abnormalities [21]. 2,4-phenoxyacetic acid (2,4-D) is a popular herbicide applied against broad leaved weed species in cereals [22]. This synthetic auxin causes uncontrolled growth and eventually death in susceptible plants. 2,4-D presence in plants causes the accumulation of abscisic acid (ABA) and ethylene. Both compounds induce the production of reactive oxygen species (ROS), which are responsible for an increase in oxidative stress [23]. High ROS accumulation makes the cell membrane more permeable, which leads to cell death [24]. One of the most popular crops in Poland and Europe is wheat (*Triticum aestivum*

L.), which is often protected against weeds by using 2,4-D [22]. However, there are some reports of harmful effects of the herbicide on wheat. Some researchers have observed that in the presence of 2,4-D, cytological, hysiological, morphological parameters and overall growth of the wheat plant are disturbed (i.e. reduced plant height, delayed maturation) [25].

As a result of wide spread application and water solubility along with low soil adsorption coefficient, 2,4-D has been found in superficial water resources, air, human food, urine and drinking water in concentrations which is in the range of 1.8 to 4.6 ng/g in soil and 2.2–3.2 µg/L in drinking water [11, 26, 27]. It is recommended that the maximum permissible concentration of 2,4-D in potable water should be 70 µg/L [15]. The reference dose (RfD) for 2,4-D is 0.01 mg/kg/day. The threshold limit value, or TLV, for 2,4-D is 10 mg/m³ for an 8-hour time weighted average exposure. This limit is based on results of animal feeding experiments. This same dose was selected by the Occupational Safety and Health Administration (OSHA) for the permissible exposure limit (PEL) for an 8-hour time weighted average exposure and by the National Institute for Occupational Safety and Health (NIOSH) for the recommended exposure limit (REL) for a 10-hour workday and a 40-hour workweek [28]. LD50 values range from 639 mg/kg to 1646 mg/kg in rats depending on the chemical form of 2,4-D utilized in the study. Researchers found that 2,4-D was more toxic for mice, reporting an LD50 of 138 mg/kg [28].

The development and use of novel nanomaterials for environmental protection and water treatment in particular, has received widespread attention in recent years in view of their larger surface area to volume ratio and smaller particle size [29, 30]. Recent years have witnessed increased interest on the application of nanoparticles as adsorbents in water treatment. Nanotechnology shows great promise as the best feasible way to treat persistent as well as emerging contaminants [31].

Although the pioneering investigations in this field have been carried out using UV-light absorbing photocatalysts [32], the current demand for efficient solar light harvesting systems has directed the interests to visible light-absorbing semiconductors. In this sense, ferrites with the general formula of MFe_2O_4 have been reported to be promising compounds for water splitting

[33, 34] and water treatment [35] due to their low cost, chemical and thermal stability, and narrow bandgap (ca. 1.9 eV [33]). Most ferrites of this stoichiometry crystallize in the spinel structure with oxide anions arranged in a cubic close-packed lattice and M and Fe cations occupying tetrahedral and/or octahedral sites [33]. Zinc ferrite, $ZnFe_2O_4$, one of the most widely studied ferrites for photocatalytic and photoelectrocatalytic applications, has been reported to exhibit a normal spinel structure, with Zn^{2+} and Fe^{3+} cations in tetrahedral and octahedral sites, respectively [36-38]. Zinc ferrite semiconductor photocatalyst has been applied widely to degrade the organic pollutants for the remediation of hazardous wastes, contaminated groundwater and the control of toxic air contaminants [39].

The effect of titanium dioxide photocatalyst with different concentrations (50, 100, 200, 500 and 1000 mg/l) on the simultaneous removal of phenol and heavy metal (chromium) from aqueous solution of the closed system was investigated. In order to determine the optimal concentrations of photocatalyst, all the tests were conducted in pH = 7, using ultraviolet light with 100 watt power. The highest rate of phenol and chromium removal was observed at concentration of 100 mg/ml which was equal to 72.3% and 67.2% respectively. Study of the reaction kinetics showed that the reactions of phenol and chromium removal were zero and first order, respectively [40].

Cellulose Dusts is a low-cost and efficient adsorbent for the removal of methylene blue from aqueous solutions. The optimum conditions for methylene blue removal were methylene blue concentration of 75.50 g L^{-1} , pH 9.84, adsorbent dosage 4.38 g L^{-1} and time 208.13 min, where 98.05% of methylene blue removal could be obtained from the proposed model. The data which was obtained from the equilibrium state was satisfactorily in agreement with Freundlich isotherm equations ($R^2 = 0.99$). It was concluded that the adsorption rate was close agreement with the pseudo-second-order model and had an acceptable correlation coefficient. Our results taken together show that Cellulose Dusts an interesting low-cost adsorbent candidate for the removal of methylene blue from aqueous solutions [41].

Magnetic iron oxide nanoparticles were synthesized by co-precipitation method. The obtained results revealed that, the maximum adsorption capacity for Fe ions was 28.225 mg/g

and the removal percentage reached nearly 85% at adsorbent dosage 0.22g, temp. 600C, time 210min., pH 4 and initial concentration 117.275mg/L. The adsorption capacity was increased with the increase of temperature and decrease of adsorbent dosage. The reaction obeyed both the pseudo second-order model and Langmuir isotherm model (with correlating constant R^2 is 0.98) [42].

The adsorbent is applied for removal of Thiocyanate in water samples using Titanium Dioxide (TiO_2) nanoparticles as effective sorbent. Prediction amount of Thiocyanate removal was investigated with novel algorithms of neural network. For this purpose, six parameters were chosen as training input data of neural network functions including pH, time of stirring, the mass of adsorbent, volume of TiO_2 , volume of Fe (III), and volume of buffer [43].

One of the challenges of water treatment via low cost and high efficiency adsorption process. This paper aims to monitor dangerous hazard material 2,4-Dichlorophenoxyacetic Acid (2,4-D) in different water resources in Egypt using (LC/MS/MS) analyzer and to use zinc ferrite nanoparticles for treatment of 2,4-D. zinc ferrite nanoparticles was not investigated before for treatment of Dichlorophenoxyacetic Acid (2,4-D). The effects of different parameters such as, pH, dose, contact time, initial concentration, temperature and ionic strength on the adsorption efficiency were assessed. The obtained zinc ferrite nanoparticles displayed good activity for removing that hazard material.

Experimental

Materials

2,4-D stock standard solution $1000 \mu\text{g/ml}$ obtained from (Ultra scientific- USA). Potassium phosphate dibasic and potassium phosphate monobasic were purchased from Panreac. Absolute methanol 99.9%, ammonia solution, ferric nitrate, and sodium hydroxide were obtained from Sigma/Aldrich. Thiourea and zinc nitrate obtained from CarloErba. n-Hexane, HCl 37% and H_2SO_4 98% was obtained from Fisher.

Preparation of zinc ferrite nanoparticles

Zinc ferrite powders ($ZnFe_2O_4$) were prepared by sol-gel combustion method. Analytical grades of $Fe(NO_3)_3 \cdot 9H_2O$, $Zn(NO_3)_2 \cdot 4H_2O$ and Thiourea ($CS(NH_2)_2$) were used as raw materials. Appropriate amount of nitrates and thiourea (fuel) was first dissolved into deionized water to form

a mixed solution with molar ratio of nitrates to thiourea 1:2. pH value of the solution was adjusted to about 9.5 using ammonia solution, then, solution poured into a dish and heated at 70-100 °C under constant stirring to transform into a dried gel. Water removal from the dried gel is a major problem in the sol-gel method, dried gel burnt in a self-propagating combustion way to form loose powder, that performed by heating at 350°C in the oven the transparent solution turned to viscous brown gel followed by foaming of the gel, the combustion reaction was completed within a few seconds and loose powder was formed. The powder crushed and ground thoroughly. The puffy, porous brown powders was calcined at the temperature of 750–1000 °C for 4 h with a heating rate of 10 °C/min [44].

Preparation of 2,4-D solutions

100 µl from 2,4-D stock solution (1000 µg/ml) transferred to 10 ml volumetric flask then diluted to the mark using methanol to prepare 10 µg ml⁻¹ working solution. Series of standard solutions were prepared in milli-Q deionized water deionized water for both instrument calibration and batch experiments.

Instrumentation

pH meter model (ThermoScientific, Orion2 star) equipped with reference electrode used to adjust the solutions pH, Analytical balance four digits (Sartorius), Oven (Binder), Muffle furnace (ThermoScientific, Thermolyne), Rotor shaker 15 position model (THERMO, SHKE2000) equipped with timer used to batch experiments, (LC/MS/MS) ultra-performance liquid chromatography (Acquity UPLC) equipped with mass selective detector (Xevo -TQS) used to quantification of 2,4-D in the aqueous phase. Each sample before analysis was centrifuged at 5000 rpm for 15 min to remove fine zinc ferrite particles, then 10 µl aliquot was injected (direct injection) into a reverse phase UPLC column C8 (1.7 µm*2.1*50mm). Separation of the analytes was achieved using gradient eluent conditions with a mixture of (A) water and (B) methanol HPLC grade. Eluent gradient started by 90% (A) in the first 2.5 min, 10% (A) from 2.5 to 7.75 min, 100% (B) from 7.75 to 8.50 min and then backed to 90% (A) from 8.5 to 10 min. The flow rate was 0.45 ml min⁻¹, after elution from the UPLC column, the analytes were detected by MS/MS detector using Electron-Spray-ionization (ESI) in positive mode with the following conditions, 264.1(m/z) parent ion was fragmented into 58(m/z)

daughter ion by 11 volt collision energy, 20 V cone volt, 450 °C desolvation temperature, 800 L/ hr desolvation, 150 L/ hr Cone and 7.0 bar Nebulize (r). Each batch controlled by calibration curve, Lab Control Sample (LCS) and reagent water blanks. Calibration curve consists of five points from 0.1 to 10 µg L⁻¹ to cover water samples concentration and lab control sample (LCS) concentration was 2.0 µg/L to check LC/MS/MS instrument performance. Reagent water blanks to control cross contamination during sample preparation blank concentration should be less than limit of quantification (LOQ) (0.1 µg L⁻¹).

Adsorption batch experiments

The batch experiments were carried out to study the optimum conditions for removal processes such as solution pH, zinc ferrite nanoparticles dose, initial concentration of 2,4-D, contact time, ionic strength and reaction temperature. Batch experiments were carried out at room temperature (22 °C) by adding a known amount of zinc ferrite nanoparticles to 50 ml of 2,4-D solution into number of 100 ml conical flasks sealed with aluminum foil on a rotary shaker at 250 rpm for 15 min. The effect of pH was conducted by adding 0.2 g of zinc ferrite nanoparticles to 50 ml of 1 µg/L 2,4-D solution at different pH values (3.0 to 11.0) which was adjusted by phosphate buffer solution and 0.1 M HCl or 0.1 M NaOH. The effect of adsorbent dosage was conducted by adding desired amounts of zinc ferrite nanoparticles (0.01, 0.05, 0.1, 0.2, 0.3, 0.4 and 0.5 g) to 50 ml of 5 µg/L 2,4-D solutions at the optimum pH value 8.0. To investigate the effect of 2,4-D concentration, experiments were carried out by adding 0.3 g of zinc ferrite nanoparticles to 50 ml of 2,4-D solutions at concentrations (0.001, 0.005, 0.05, 0.01, 0.05, 0.1, 0.5, 5.0, 10.0 and 15.0 mg /L) at optimal pH value. Equilibrium time was conducted by adding 0.3 g of zinc ferrite nanoparticles to 10 mg/L 2,4-D solutions at different time intervals (5, 15, 30, 45, 60, 90 and 120 min). To investigate the effect of thermodynamics the experiments were carried out at optimal pH, concentration and adsorbent dose at equilibrium time. To investigate the effect of ionic strength, experiment carried out at different concentrations of CaCl₂ (0.01, 0.05, 0.1, 0.3, and 0.5 M) at optimum conditions that mentioned previously.

The following Fig. 2 describes the steps of monitoring, analysis and detecting of 2,4-D on LC/MS/MS

Results and Discussion

Monitoring of 2,4-D in different water samples

As recorded in Table (2), the highest concentration of 2,4-D was observed in AR Rahawi and Maryotia agricultural drainage channels, it was 21.31, 17.34 $\mu\text{g}/\text{L}$ respectively, after that the concentration decreased gradually in the next points due to dilution factor of drainage water. The presence of 2,4-D in that drains affect the water quality of Rositta branch so we found a small concentration in different points but it disappeared in the effluent of drinking water plants due to chlorination disinfection. Due to presence of 2,4-

D in different influents of drinking water plants in Egypt, the treatment of 2,4-D is essential, so this study in your hands aims to treat 2,4-D using simple nanoparticles substance suitable for use in drinking water treatment process.

Results that indicated the presence of 2,4-D agreed with a study was conducted to assess the occurrence of pesticide residues, in water at the estuaries of Rosetta and Damietta branches of the Nile river. The results indicated that organochlorine pesticides compounds (OCs) including HCB, lindane, p,p'-DDE, p,p'-DDD, p,p'-DDT, aroclor 1254 and aroclor 1260 were

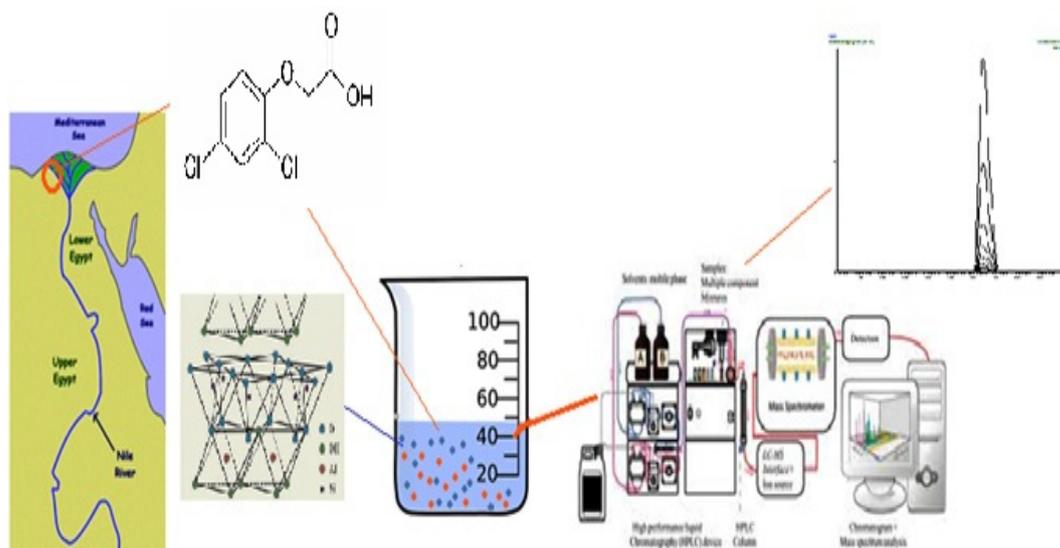


Fig. 2.steps of monitoring and detecting of 2,4-D.

TABLE 2. Results of 2,4-D monitoring in different water samples

NO.	Samples location	Values of 2,4-D($\mu\text{g L}^{-1}$)	NO.	Samples location	Values of 2,4D ($\mu\text{g L}^{-1}$)
1	El Maryotia point (1)	17.34	8	Influents of Fuwwah	1.46
2	El Maryotia point (2)	9.45	9	Effluents of Fuwwah	>LOQ
3	AR Rahawi point (3)	21.31	10	Influents of Mutubas	0.87
4	AR Rahawi point (4)	15.79	11	of Mutubas Effluents	>LOQ
5	AR Rahawi point (5)	10.65	12	El- of Influents Mahmoudya	1.33
6	Rositta branch before mixing with AR.Rahawi point (6)	>LOQ	13	of El- Effluents Mahmoudya	< LOQ
7	Rositta branch after mixing with AR.Rahawi point (7)	35	14	Influents of Menyet El-Saeed	0.35
			15	of Menyet Effluents El-Saeed	>LOQ

present in all the water samples at concentration levels ranging between 0.195–0.240, 0.286–0.352, 0.035–0.067, 0.019–0.033, 0.024–0.031, 0.390–0.70 and 0.166–0.330 $\mu\text{g/l}$, respectively [45].

Removing 2,4-Dichlorophenoxyacetic acid using zinc ferrite nanoparticles

The following Fig. 3 describes the flow chart for using zinc ferrite nanoparticles

Effect of pH

The first reaction condition is keeping the 2,4-D solution containing zinc ferrite nanoparticles in dark to establish adsorption–desorption equilibrium after that the suspensions were exposed to solar light for further photodegradation, Fig.4 depicts the removal of 2,4-D by zinc ferrite nanoparticles in dark and sunlight respectively. The curve noted that the effect of pH on reduction of 1 $\mu\text{g/L}$ 2,4-D using 0.2 g zinc

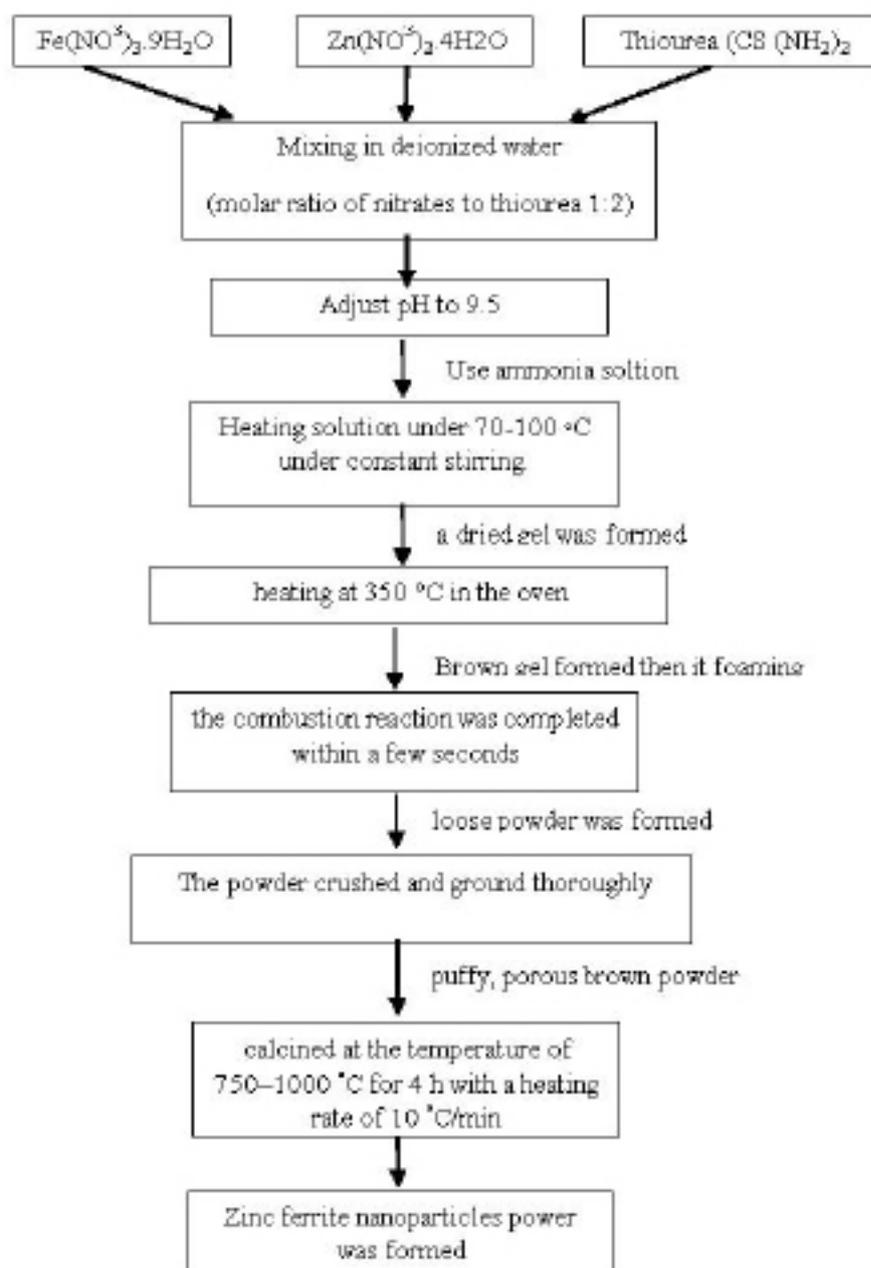


Fig. 3. flow chart flow chart for the agent based modeling (ABM)

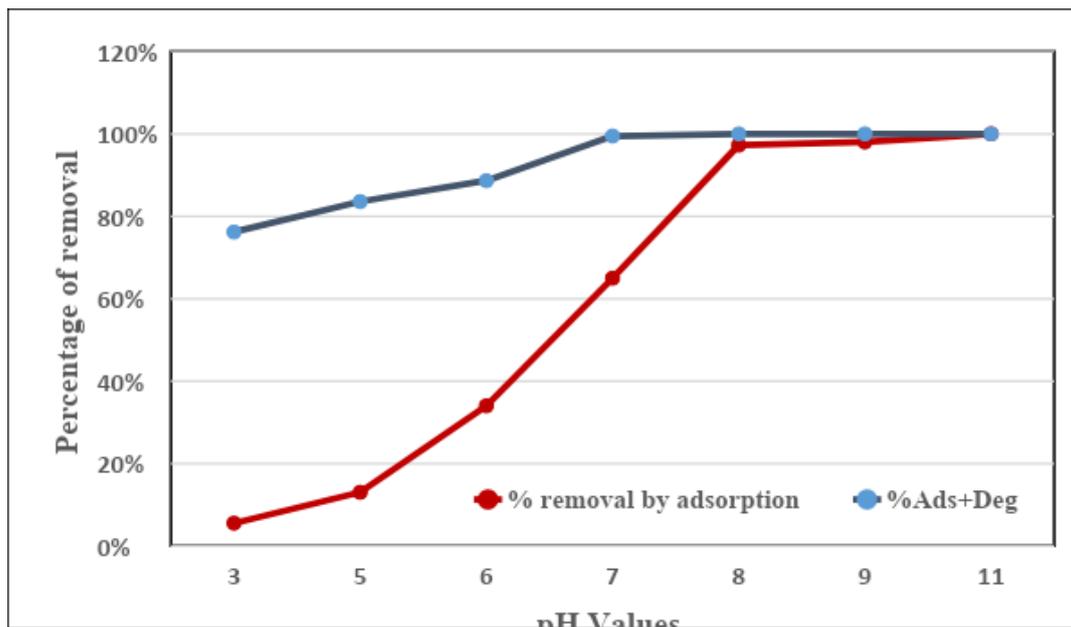


Fig. 4. Effect of pH on the removal %. Initial 2,4-D concentration 1 $\mu\text{g L}^{-1}$, zinc ferrite nanoparticles dosage 0.2 g and contact time 15min.

ferrite nanoparticles at variance initial of pH values 3.0–11.0. The results shown from adsorption in dark indicated that removal percentage improved from 5.56% to 97.28% by rising pH value from 3.0 to 8.0. Then removal slightly improved from 97.28% to 100.00% by rising pH value from 8.0 to 11.0, while, the reduction in case of adsorption then photodegradation by sunlight improved from 76.19% to 99.49% with pH value rising from 3.0 to 7.0. The maximum 2,4-D reduction 100.00% conducted at pH 8.0. The optimal pH value is 8.0, this is due to the increasing of the pH value increase the adsorption capacity due to electrostatic attraction [46].

Effect of amount of zinc ferrite nanoparticles.

Fig. 5 show the effect of catalyst dosage on removal% of 2,4-D by zinc ferrite nanoparticles in dark and sunlight respectively, varying zinc ferrite dose was used on reduction of 5 $\mu\text{g/L}$ 2,4-D, contact time was 15min and pH value was 8.0. Results obtained from adsorption conditions in dark indicated rising the removal percentage from 25.08% to 76.19% by increasing the weight of zinc ferrite nanoparticles from 0.01 to 0.3 g. Then removal percentage slightly increased from 76.19% to 79.11% by increasing the weight from 0.3 to 0.5 g. While, the reduction in case of adsorption then photodegradation by sunlight improved the removal percentage of 2,4-D from 47.90% to 97.84% by increasing the weight of zinc ferrite nanoparticles from 0.01 to 0.3 g.

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Then reduction slightly increased from 97.84% to 100.0% by increase the weight from 0.3 to 0.5 g. Therefore, the optimum weight was 0.3 g for removing 2,4-D using zinc ferrite nanoparticles under the above conditions. That due to the greater availability of the active sites or surface area at higher adsorbent doses [47]. Therefore, the results of increasing the percentage of removal by increasing the zinc ferrite nanoparticles dose agrees with Ali *et al.* concluded that the increase in the bio-sorption dose from 0.25 g to 0.5 g could increase the adsorption capacity [48].

Effect of 2,4-D initial concentration

Fig. 6 show the effect of varying 2,4-D initial concentrations on the reduction percentage at constant weight of zinc ferrite nanoparticles, 0.3 g and pH value was 8.0. Removal percentage under adsorption conditions decreased from 95.10% to 13.25% by increasing concentration of 2,4-D from 1 $\mu\text{g/l}$ to 15000 $\mu\text{g/l}$. The result in Fig. 6. indicated that when increasing the initial concentration of 2,4-D the adsorption capacity was increased until to reach the maximum adsorption capacity for zinc ferrite nanoparticles 0.34 mg g^{-1} at initial concentration (C_0) 10 mg L^{-1} . This results in agreement with [49] reported that removal of penicillin G and phenol.

Effect of contact time

The effect of varying contact time upon 2,4-D reduction in solution with 2,4-D concentration

10 mg L⁻¹ and a constant zinc ferrite nanoparticles weight of 0.3 g at pH 8.0 was studied. There are two reaction conditions, equilibrium adsorption in dark then followed by photocatalysis in sun light. The results as shown in Fig. 7. indicated that removal percentage of 2,4-D rises from 16.74 to 23.89% as the contact time rises from 5 to 120 minutes. This result in agreement with Çalışkan

and Göktürk indicated that as time increased, the adsorption capacity increased [47]. Shikuku et al. concluded that the rapid initial adsorption rate is due to availability of completely vacant active adsorption sites followed by the slow equilibrium phase attributed to saturation of the energetically favorable surfaces [50, 51]

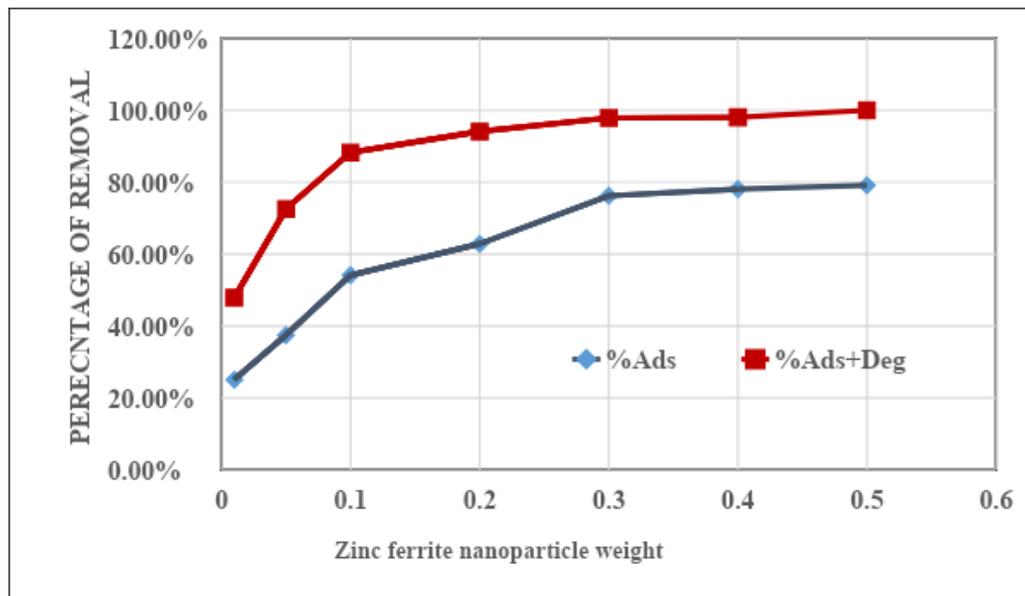


Fig. 5. Effect of zinc ferrite nanoparticles weight on the removal %. 2,4-D initial concentration 5 $\mu\text{g L}^{-1}$ and contact time 15 min.

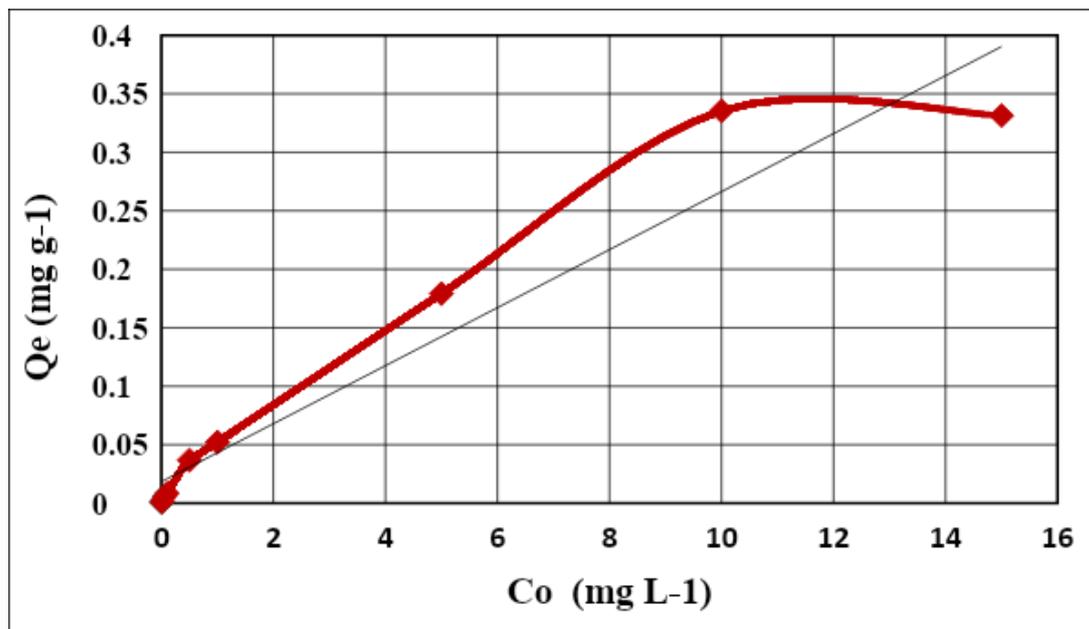


Fig. 6. Effect of adsorption capacity of Zinc ferrite nanoparticles against initial concentration of 2,4-D at Zinc ferrite nanoparticles dosage 0.3g/50ml

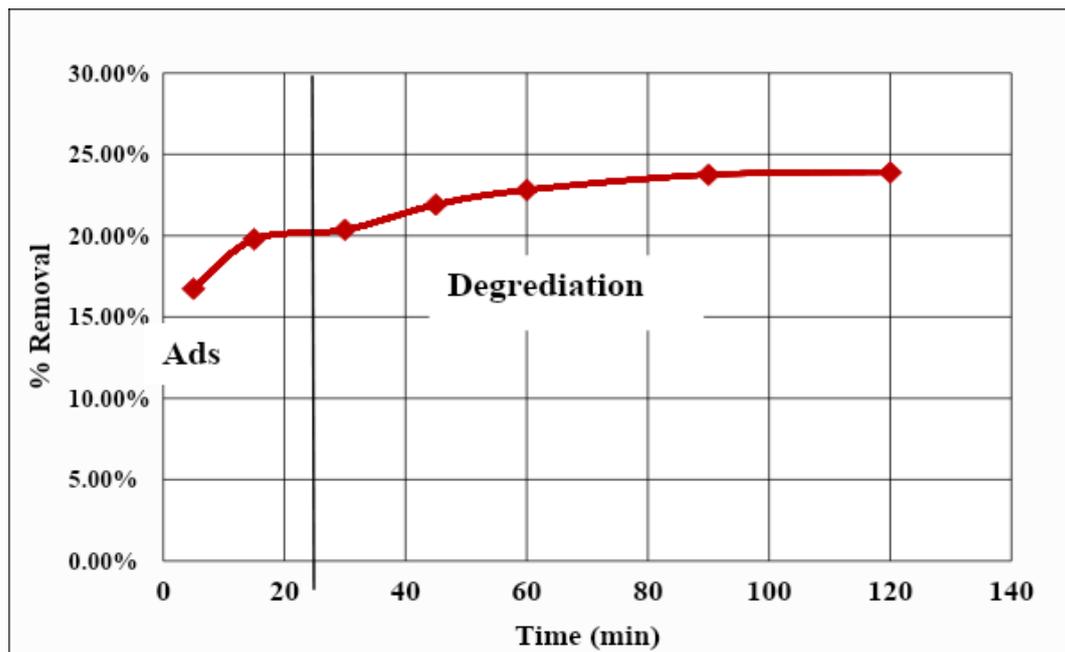


Fig. 7. Effect of contact time. Zinc ferrite nanoparticles dose 0.3g/50ml and 2,4-D initial concentration 10mg L-1

Photodegradation kinetics

For realizing more data about the photodegradation mechanism, different kinetic models are applied; pseudo-first- or pseudo-second-order reaction (Eqs 1, 2)

Pseudo first order:

$$\ln(q_e - qt) = \ln q_e - k_1 t \quad (1)$$

Pseudo – second – order:

$$t/qt^2 = k_2/q_e^2 + k_2/q_e t \quad (2)$$

Where (t) is the degradation time, q_e and q_t , (mg g^{-1}) are the adsorbed amount of 2,4-D at equilibrium and time t and k_1 , and k_2 are the rate constants of pseudo-first order and pseudo-second order, respectively.

Photodegradation kinetics of 2,4-D on zinc ferrite nanoparticles was studied. Photodegradation rate constants for the 2,4-D was calculated by using pseudo-first-order and pseudo-second-order kinetic models which were used to describe the mechanism of the degradation. The conformity between the experimental data and the model-predicted values was expressed by the correlation coefficients (R^2). A relatively high R^2 values indicate that the model successfully described the kinetics of 2,4-D degradation. Fig. 8. presents the pseudo second- order graphics for the degradation kinetics of studied organic pollutant. The data showed good compliance with

the second-order kinetic model in terms of higher correlation coefficients 0.999 for zinc ferrite nanoparticles.

As shown in Table (3) regression coefficient (R^2) for second-order model is higher than first-order one, as well the calculated equilibrium adsorption capacity (q_e calc.) that extracted from second order is 10000 mg g^{-1} that is close to experimentally determined (q_e exp.) 7963 mg g^{-1} rather than the calculated equilibrium adsorption capacity (q_e calc.) that extracted from first order is 3524 mg g^{-1} which is far from the experimental value. This indicated that the degradation of 2,4-D using zinc ferrite nanoparticles is highly fitted with kinetic model of pseudo-second order. The results confirmed by a study stated that the removal of 2,4-Dichlorophenolxyacetic acid (2,4-D) herbicide in the aqueous phase using modified granular activated carbon was best fitted to second order kinetics with $R^2 > 0.99$ [52].

Effect of ionic strength

In this part of the study, the photocatalytic degradation efficiency is considerably found decreasing upon the addition of inert salts like calcium chloride. The effect of varying ionic strength of 2,4-D solution on the reduction percentage by using a dose of 0.3 g zinc ferrite nanoparticles at pH 8.0 and a constant concentration of 2,4-D of $10000 \mu\text{g L}^{-1}$. It was noticed that removal percentage of 2,4-D

TABLE 3. Kinetics parameters of 2,4-D photocatalytic degradation on zinc ferrite nanoparticles

Adsorbent	Parameters	Pseudo – first – order	Pseudo – second – order
Zinc Ferrite Nanoparticle	R^2	0.948	0.999
	$q_{e\text{ calc}}$	3524	10000
	$q_{e\text{ exp}}$		7963

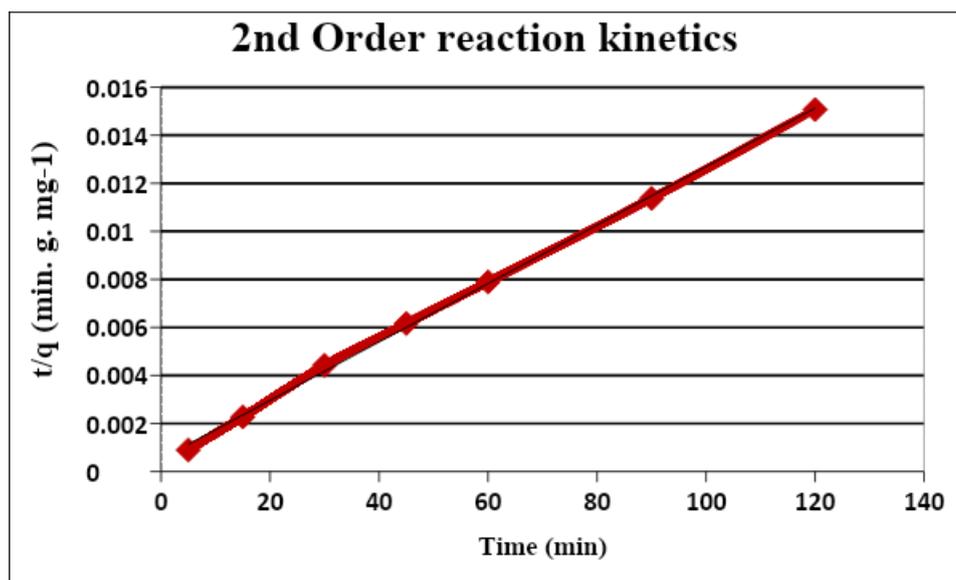


Fig. 8. Kinetic plots of pseudo second order for photocatalytic degradation of zinc ferrite nanoparticles.

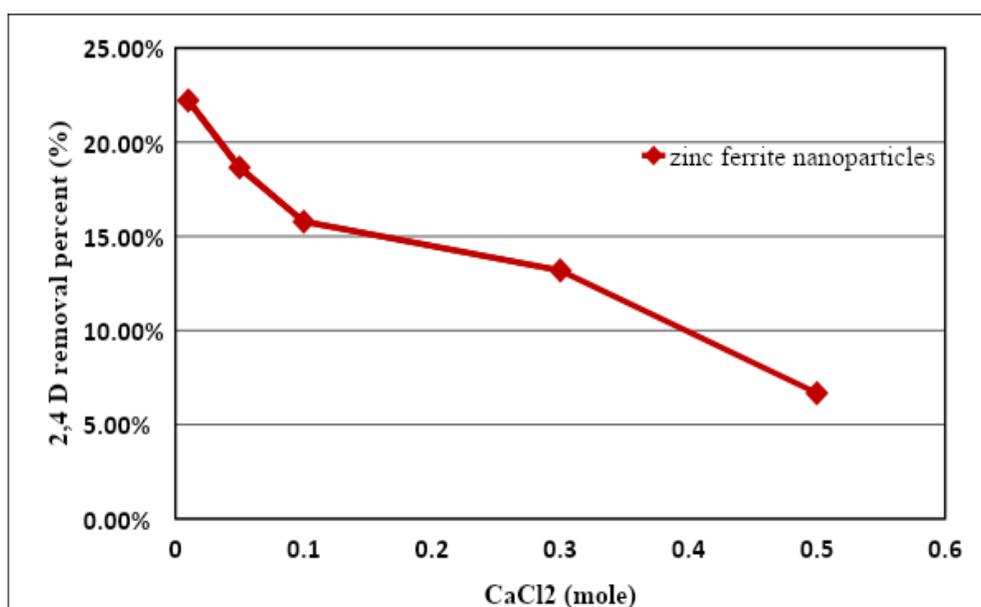


Fig. 9. Effect of ions strength on zinc ferrite nanoparticles photocatalytic degradation. Using a dose of 0.3g/50ml and initial 2,4-D concentration 10mg L-1

decreased from 22.22% to 6.67% by rising the conductivity value of the solution from 2625 to 70800 $\mu\text{S cm}^{-1}$ when varying the concentration of calcium chloride from 0.01 to 0.5 mole.

This mean that degradation was most affected by ionic strength as shown in Fig. 9. The increase of ionic strength resulted in a decrease in the reduction of 2,4-D. Anirudhan and Ramachandran indicates that ions that form outer-sphere surface complexes show decreasing adsorption with increasing ionic strength [47]. Ions that form inner-sphere surface complexes show little ionic strength dependence or show increasing adsorption with increasing ionic strength. These results indicate that 2,4-D forms an outer-sphere surface type complex on zinc ferrite nanoparticles.

Effect of temperature on photocatalytic degradation

Photocatalytic degradation of 2,4-D on zinc ferrite nanoparticles were carried out at different temperatures, the initial concentration was 10 mg L^{-1} . The free energy of photocatalytic degradation (ΔG°) was calculated from the following equation

$$\Delta G = -RT \ln K \quad (3)$$

where K is the equilibrium constant and T is the solution temperature, R is gas constant (8.314 $\text{J K}^{-1} \text{mol}^{-1}$). The enthalpy (ΔH°) and entropy (ΔS°) were calculated using the Van't Hoff Eq. (4).

$$K = \frac{\Delta S^\circ - \Delta H^\circ / T}{R} \quad (4)$$

Values of ΔH° and ΔS° were computed from the slopes and intercepts respectively of linear variations of $\ln K$ with the reciprocal of temperature Fig. 10 These thermodynamic parameters are being given in Table (4). As showed in Table

TABLE 4. Thermodynamic parameters for 2,4-D photocatalytic degradation on zinc ferrite nanoparticles under different temperatures

Zinc Ferrite Nanoparticles				
T	Ka	$^\circ\text{G}\Delta$	Slope (ΔS°) $\text{KJ k}^{-1}\text{mol}^{-1}$	intercept(ΔH°) KJ mol^{-1}
313	0.37	2.59	0.08	27.26
318	0.44	2.19		
323	0.49	1.93		
333	0.69	1.04		

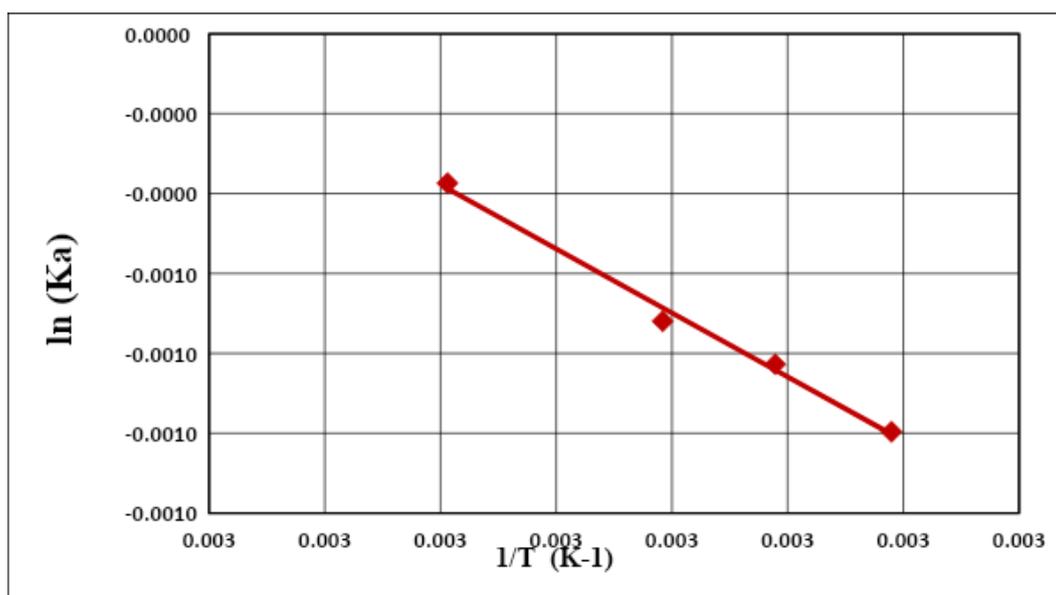


Fig. 10. Van't Hoff Plots of 2,4-D photocatalytic degradation on Zinc ferrite nanoparticles, 2,4-D initial concentration 10mg L^{-1}

(4) ΔG° values were positive in the studied temperature range of 313–333 K for zinc ferrite nanoparticles. Photocatalytic degradation on zinc ferrite nanoparticles indicated that process led to a increase in Gibbs free energy, positive ΔG° indicated that reaction not spontaneous and the positive values of ΔH° indicated that process is endothermic. The positive values of ΔS° suggested that the increased randomness at the solid–solution interface during degradation of 2,4-D in aqueous solution on zinc ferrite nanoparticles. The results in agreement with a study stated that,

thermodynamic parameters of 2,4-D adsorption on activated carbon were evaluated and showed a positive values of ΔH° and ΔS° indicated the endothermic nature and increase in disorder of 2, 4-D adsorption, respectively [48].

Adsorption Equilibria

An adsorption isotherm is a curve show the relation between the equilibrium of an adsorbate on the surface of an adsorbent (q_e), to the concentration of the adsorbate in the liquid (C_e). Langmuir and Freundlich isotherm equations were used to analyze the equilibrium data in

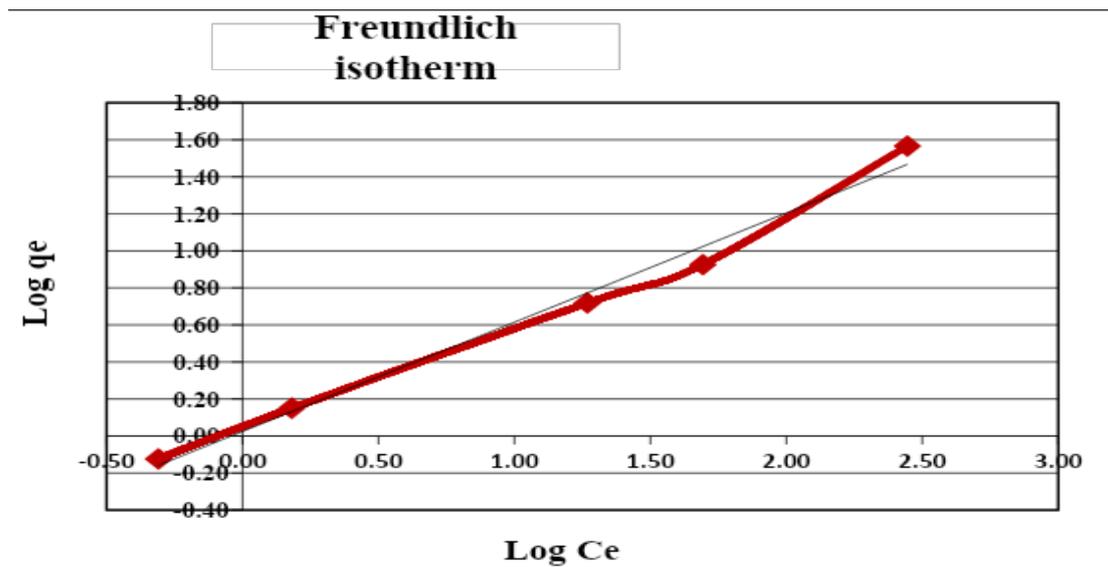


Fig. 11. Freundlich adsorption isotherm of 2,4-D on Zinc ferrite nanoparticles.

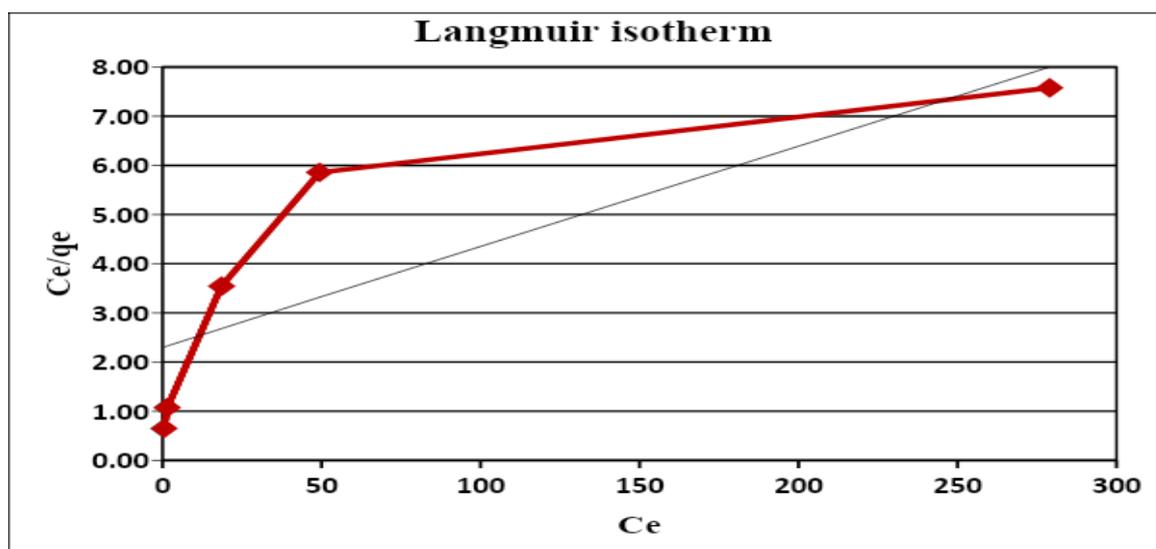


Fig. 12. Langmuir adsorption isotherm of 2,4-D on Zinc ferrite nanoparticles

TABLE 5. Adsorption isotherm parameters of 2,4-D on zinc ferrite nanoparticles.

Zinc Ferrite Nanoparticle		
Langmuir isotherm		
$(\text{mg g}^{-1})q_m$	$(\text{Lmg}^{-1})K$	R ²
48.30	0.01	0.672
Freundlich isotherm		
K _f	n	R ²
1.06	1.69	0.986

order to disclose the adsorption behavior of 2,4-D to zinc ferrite nanoparticles. Linear forms of Langmuir and Freundlich isotherm equations are given in equations (5 and 6). Related constants were calculated and given in Table 5.

$$Ceq_e = Ceq_m + kqm(5)$$

$$\log q_e = \log K_f + n \log C_e(6)$$

Where q_m is the maximum adsorption at monolayer coverage in mg g^{-1} , K is the adsorption equilibrium constant related to the energy of adsorption, K_f and n are Freundlich constants representing the adsorption capacity and intensity respectively.

As seen in Table (5), the Freundlich model gave a better fit than the Langmuir model based on correlation coefficients values (R^2). Fig. 10 described that the correlation coefficients of the removal of 2,4-D using zinc ferrite nanoparticles using Langmuir model was 0.672. While, Fig. 11 described that the correlation coefficients of the removal of 2,4-D using zinc ferrite nanoparticles using Freundlich model was 0.986. Also, the regression equation in fig. 10 and fig. 11 showed that Freundlich constant adsorption intensity (n) were 0.01 and 1.69, respectively. So, Freundlich model gave $1/n$ less than unity referring capability of explaining uptake of 2,4-D by heterogeneous zinc ferrite nanoparticles. This result confirmed by Akcay et al concluded that adsorption of 2,4-D over organophilic sepiolite obey to Freundlich model [55]. Equilibrium data of 2,4-D adsorption onto granular activated carbon were fitted very well to Freundlich equilibrium model [56]. In addition, results in agreement with a study stated that, Adsorption/desorption characteristics of the herbicide 2,4-D on various types of soils were investigated. Batch equilibrium techniques

were used in the laboratory experiments. Data were fitted to the linear and Freundlich sorption equations [57]. It can be concluded that the applicability of the Freundlich isotherm suggests the multilayer coverage of 2,4-D on the surface of zinc ferrite nanoparticles, Freundlich model suggested that the surface of zinc ferrite nanoparticles is heterogeneity and the exponential distribution of sites and their energies.

Conclusion

The proposed study has recorded the presence of 2,4-D in AR Rahawy and Maryotia agriculture drains as a result of that, it contaminates Rosita branch water and some water plants influent. Moreover, the study has considered a new technique to remove 2,4-D using zinc ferrite nanoparticles. The optimization study for 2,4-D reduction showed a maximum percent of removal of 97.84% for adsorption followed by photodegradation using 0.3 g of zinc ferrite nanoparticles for 15 min. at pH 8.0. While, reduction was 76.19% for adsorption conditions. Adsorption capacity of 2,4-D over zinc ferrite nanoparticles was 0.34 mg g^{-1} at initial concentration (C_0) 10 mg L^{-1} after 15 min. 2,4-D photodegradation has been fulfilled pseudo-second-order kinetic model rather than pseudo-first-order. The $q_e(\text{cal})$ has been presented and compared with the $q_e(\text{exp})$. It has been observed excellent agreement between calculation and experimental data which clarify the effectiveness of the utilized model. Other than that, the adsorption of 2,4-D based on zinc ferrite nanoparticles was well fitted by Freundlich isotherms rather than the other studied isotherm model with correlation coefficient 0.986. Furthermore, Thermodynamic calculation has revealed that the photodegradation of 2,4-D over zinc ferrite nanoparticles is not spontaneous and the process is endothermic. To

conclude, the zinc ferrite nanoparticles could be considered as an excellent candidate to be used as sorbent for the removal of 2,4-D from polluted water.

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إزالة ٢ و ٤ داي كلورو فينوكسي أسيتك أسيد من المياه الملوثة بواسطة فريت الزنك النانومتري

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يعد ٢ و ٤ داي كلورو فينوكسي أسيتك أسيد من المبيدات شائعة الاستخدام في الأراضي الزراعية للتحكم في نمو الأعشاب و الحشائش. و تم رصد هذا الملوث في مصادر مختلفة من المياه في مصر مثل بعض المصارف الزراعية و كذلك في فرع رشيد حيث تم إجراء إزالة له بواسطة مادة نانومترية و هي فريت الزنك النانومتري. و قد أظهرت الدراسة لإستخدام فريت الزنك النانومتري عند طريق الامتزاز و بالتحليل الضوئي أن الجرعة المثلى كانت ٠,٣ جرام عند زمن تلامس ١٥ دقيقة و درجة أس هيدروجيني ٨ و قد وصلت نسبة الإزالة ٩٧,٨٤٪. و قد بلغت قدرة الامتزاز لمركب ٢ و ٤ داي كلورو فينوكسي أسيتك أسيد على مركب فريت الزنك النانومتري ٠,٣٤ مليجرام/جرام عند استخدام تركيز ١٠ مليجرام/لتر و زمن تلامس ١٥ دقيقة. و قد تم إجراء التجارب الحركية و الحرارية حيث أظهرت أنه التفاعل ينطبق على نموذج الترتيب الثاني حيث كان معامل الارتباط ٠,٩٩٩, كذلك وجد أن الامتزاز لمركب ٢ و ٤ داي كلورو فينوكسي أسيتك أسيد على مركب فريت الزنك النانومتري يتطابق مع نموذج فريندلش حيث كان معامل الارتباط ٠,٩٨٦, و من النتائج تلاحظ أن مركب ٢ و ٤ داي كلورو فينوكسي أسيتك أسيد يتم تكسيره عند طريق كلا من الامتزاز و التحليل الضوئي باستخدام مركب فريت الزنك النانومتري.