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Develop an Fe_2O_3/Cu/Ag nanocomposite for removing tetracycline (TC) pollutants from aqueous solutions

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ABSTRACT: *In this study, iron oxide, silver, and copper were used to create a Fe2O3/Cu/Ag nanocomposite with the aim of removing tetracycline (TC) as pollutants from aqueous solutions. Various techniques were employed to analyze the composite structure, including X-ray crystallography (XRD), transmission electron microscopy (TEM), scanning electron microscopy(SEM), energy-dispersive X-ray spectroscopy (EDS), mapping, and Fourier transform infrared (FTIR). The impact of environmental pH, reaction time, temperature, and the maximum amount of TC on removal efficiency was investigated. The findings showed that an optimal pH of 5, 150 mg of Fe2O3/Cu/Ag, and 20-minute reaction time at room temperature resulted in 98.53% removal of tetracycline. In conclusion, Fe2O3/Cu/Ag adsorbents show promise for effectively eliminating tetracycline from aqueous environments.*

KETWORDS: *Adsorption, wastewater, Tetracycline (TC), antibiotic pollutants, Fe_2O_3/Cu/Ag, nanocomposite*

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INTRODUCTION

The high consumption of drugs in humans and animals has caused environmental pollution [1]. Antibiotics, due to their structure and resulting metabolites, account for 15% of this pollution, with tetracycline (TC), owing to its antimicrobial properties and its widespread use in the treatment of infectious diseases [2-3]. The indiscriminate utilize of antibiotics increases the antibiotic resistance of pathogenic bacteria in living organisms [4]. With around hundred tons of thousands of antibiotics are consumed annually, drinking water purification is of utmost importance [5]. Due to the inadequacy of the wastewater treatment system for pollutants such as TC, this antibiotic has been detected in wastewater [6]. Several methods have been introduced to remove tetracycline antibiotics, including electrochemical processes [7], membrane separation [8] photocatalytic degradation [9, 10], and adsorption [11].

In the literature on tetracycline removal, adsorption methods are more well-known and valuable due to their high removal capacity from aqueous media, variety of adsorbents, ease of operation and affordability [12]. In recent years, compounds with a nanostructure, such as silica [13], graphene oxide [14], metal-organic framework [15–19], carbon nanotubes [20], and various iron oxide composites such as MnFe2O4 [21], CoFe2O4 [22], and Fe3O4 [23], have been developed to remove antibiotics from aquatic environments.

Mechanical stability and area specificity of composites have been applied in many fields such as improving pollutant removal efficiency [24]. Furthermore, new properties are created when different metals are combined. Nanostructures consisting of two or more metals have been studied for their ability to create unique properties [25,26]. At the nanoscale, elements placed together create new properties that differ from the properties of the metal alone [27]. For example, a compound with both antibacterial and magnetic properties is synthesized with the presence of silver and iron [28]. However, a composite of iron and silver produces a combination of both anti-bacterial and magnetic properties.

In this study, the Fe2O3/Cu/Ag nanocomposite was synthesized via the co-precipitation method and its effectiveness in removing TC in aqueous environments was assessed. Additionally, the effects of factors such as time and temperature on the removal of tetracycline were examined.

MATERIALS AND METHODS

Raw material and chemicals

We used a 99% pure TC antibiotic, silver nitrate, $Cu(NO_3)_2{\cdot}4H_2O$, $FeCl_3{\cdot}6H_2O$, $FeCl_2{\cdot}4H_2O$, $AgNO_3$, NaOH (0.1 N), HCl (0.1 N), H_2SO_4 and HNO_3 (1.0 N)(Merck C.). All samples used in the study were prepared with a volume of 100 mL and a concentration of 50 ppm TC in double-distilled water.

Characterization methods

The characterization methods for Fe_2O_3/Cu/Ag nanocomposites are described in the Supplementary Information.

The synthesis of Fe_2O_3/Cu/Ag

To prepare a Fe2O3/Cu/Ag nanocomposite, separate solutions of AgNO3, Cu(NO3)2 and Fe(NO3)3 at a concentration of 0.1 M each were prepared and stirred for 1hour at room temperature to create a homogeneous solution. Next, 0.02M sodium borohydride (NaBH4) was added and the solution was allowed to sit undisturbed for 45 minutes. The solution was then centrifuged at 4000 rpm for 10 minutes to collect the precipitate. Wash the obtained product with distilled water and acetone several times to remove organic and ionic impurities. The precipitate is then dried at 100 °C in an oven and then at 400 °C for 12 hours in a furnace[29].

TC batch adsorption

Important parameters (water pH, time, temperature and TC concentration) were investigated in the removal process. A 100 mg/liter TC solution was prepared, and other necessary solutions were subsequently created by diluting it accordingly.

To assess the impact of pH on TC removal, the pH levels were adjusted and measured from 2 to 10 using HCl and NaOH (0.1M). The Fe2O3/Cu/Ag nanocomposite was then individually added to a 10 ml solution containing a 10-ppm concentration of TC a similar pH level. This mixture was kept at a temperature of 25°C for 20 minutes in a shaker set at a speed of 200 rpm. After the 20-minute period, the remaining TC was measured using a spectrophotometer at a wavelength of 357 nm. The amount of removal was subsequently calculated using equation 1.

$$\% \text{ Removal} = (C_i - C_f)/C_i * 100 \qquad \textbf{Eq 1}$$

RESULTS AND DISCUSSIOS

In this section, the Fe2O3/Cu/Ag nanostructure is first characterized using SEM, EDX, mapping, TEM, XRD and FTIR. After synthesizing the Fe2O3/Cu/Ag structure, it is used as a remover of TC.

Characterized of Fe_2O_3/Ag/Cu

Fig. 1 shows the XRD peak of the Fe2O3/Ag/Zn composition. By comparing this peak with the standard peaks of Fe2O3 (012, 104,110,113,024,116,018, 214), it can be seen that there are several additional peaks, indicating that the structure of Fe2O3 is preserved and peaks related to copper and silver are also present.

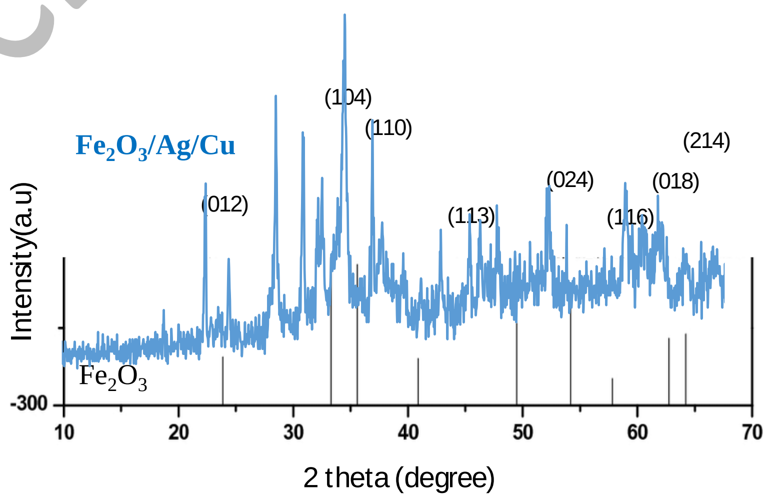

Fig. 1: *XRD patterns of Fe_2O_3/Cu/Ag*

Fig. 2 displays the surface morphology by SEM, which is spherical.

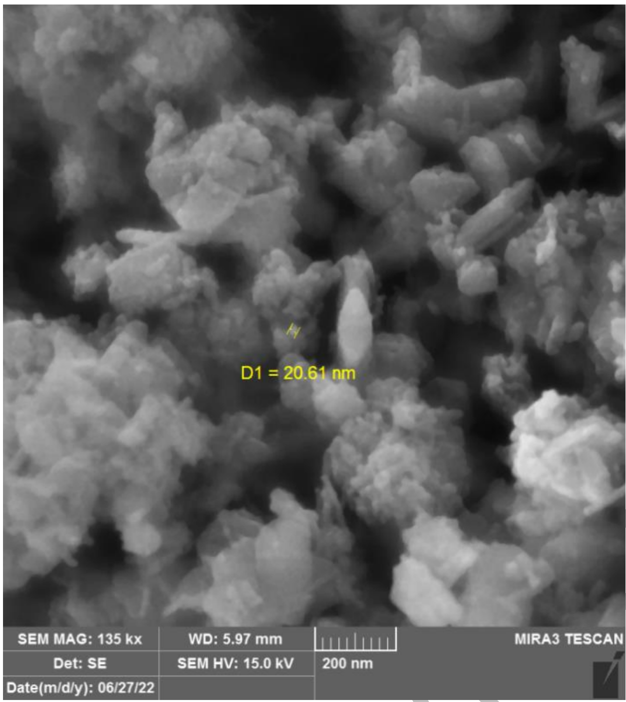

Fig. 2: The SEM images of Fe_2O_3/Cu/Ag

Fig. 3 shows the EDX spectrum and mapping. The mapping image displays three elements: silver, copper, and iron, which are uniformly dispersed on Fe2O3/Cu/Ag in green, white and red, respectively (**Fig. 3A**). The EDX spectrum showed 27.9% silver, 12.2% copper and 59.9% iron in Fe2O3/Cu/Ag (**Fig. 3B**).

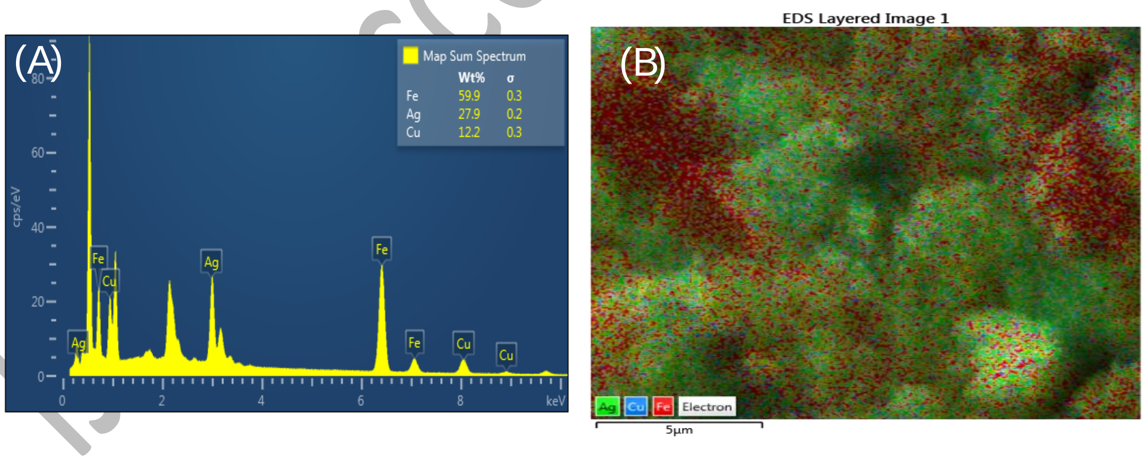

Fig. 3 A) The EDS images of Fe_2O_3/Cu/Ag Fig. 3 B) the mapping images of Fe_2O_3/Cu/Ag

Using linear scanning, the various elements in the structure, including iron, silver and copper, are shown in **Fig. 4**.

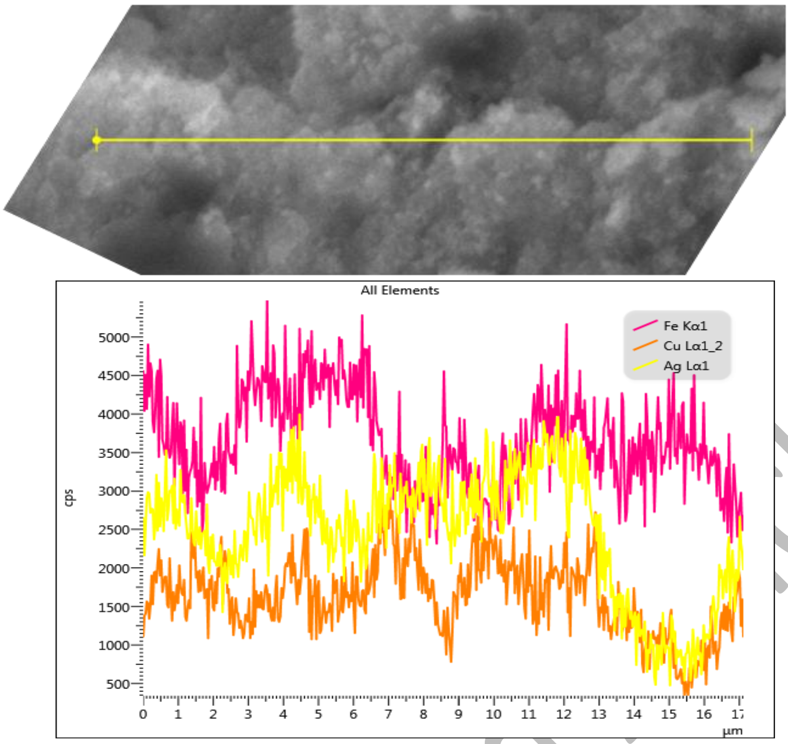

Fig. 4: The EDX line scan analysis for Fe_2O_3/Cu/Ag

The particle size was examined using a TEM, and a spherical structure was observed, indicating that the nanoparticle size is consistent across all surfaces (**Fig. 5A**). The figure related to the histogram of nanoparticles shows that the average size of the particles is 30-50 nm (**Fig. 5B**).

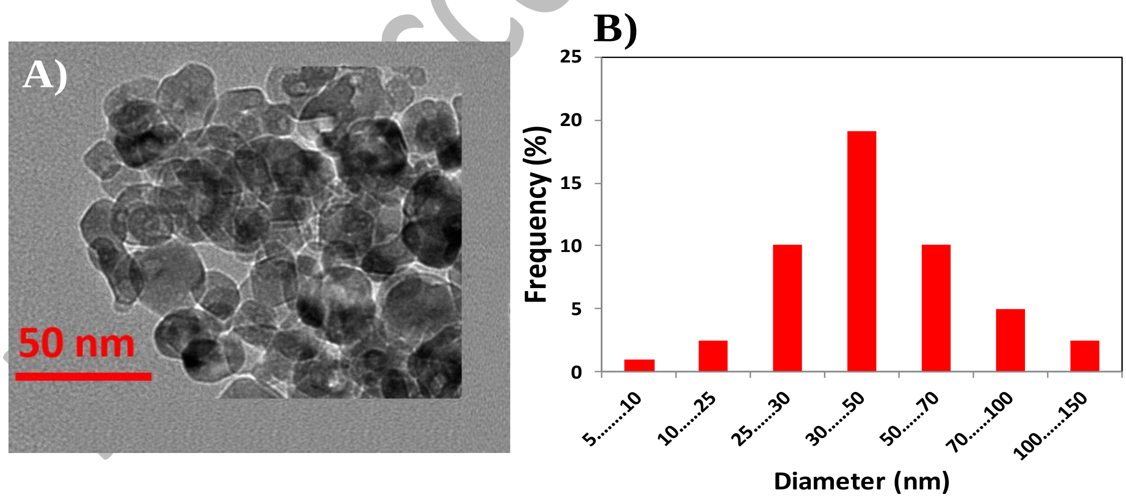

Fig. 5A) The TEM images of Fe_2O_3/Cu/Ag, *Fig. 5B) histogram for TEM of Fe_2O_3/Cu/Ag*

Fig. 6A and 6B show the FT-IR spectra of Fe2O3 and Fe2O3/Cu/Ag. The peak bands at 466.5 cm-1 and 555.5 cm-1 for Fe-O bonds and 3340 cm-1 and 1483 cm-1 in the spectrum can be attributed to the presence of OH in Fe2O3(**Fig. 6A**) and Fe2O3/Cu/Ag(**Fig. 6B**). However, the spectral changes that occur in Fe2O3/Cu/Ag and are observed in the regions of 565.5 cm-1, 550.4cm-1, and 460.8 cm-1 can be attributed to Ag and Cu in Fe2O3.

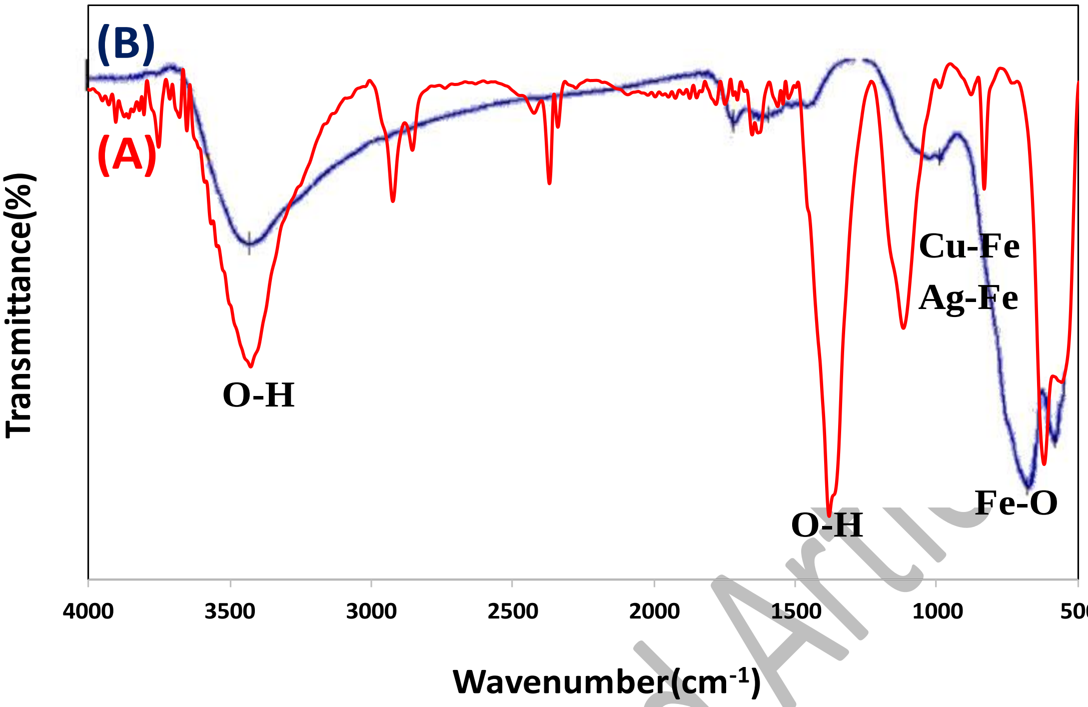

Fig.6A) The FTIR spectrum of the Fe_2O_3, *Fig.6 B) The FTIR spectrum of the Fe_2O_3/Cu/Ag*

The effect of pH

During the investigation of TC detoxification from aqueous solutions and the surface charge of the adsorbent in the pH range of 3 to 10, it was observed that the pH of the environment has a significant impact on the removal of tetracycline (**Fig. 7A**). Specifically, 50% of the detoxification occurs at pH 2 to 3 (below the pKa1 of 3.3 for TC), which is attributed to the positive amine or hydroxyl side groups of TC in acidic pH conditions [29].

Since the point of zero charge(pHPZC) for the adsorbent is between 5-6, the surface charge of Fe2O3/Cu/Ag will be positive at a pH below this value. This results in an electrostatic repulsion force between Fe2O3/Cu/Ag and TC, leading to a decrease in the detoxification rate of TC. However, TC carries a negative charge at a pH below 3.3, which significantly enhances the interaction between Fe2O3/Cu/Ag and TC.

Since the adsorbent surface is negatively charged at a pH above 7,the TC charge is also negative, leading to a decrease in the removal rate[30]. However, a pH of 5 was found to be the optimal condition for TC removal from an aqueous circumstance, with the most effective detoxification of TC achieved by the Fe2O3/Cu/Ag adsorbent reaching 98.53%.

Encapsulation efficiency (EE)

The entrapment or encapsulation efficiency (EE) of Fe2O3/Cu/Ag was measured by first determining the amount of drug through optical absorption at a wavelength of 357nm using a spectrophotometer. EE was then calculated according to formula (2).

$$EE(\%)=((C0-C1))/C0\times100 \qquad (2)$$

In Formula 2, C0 and C1 represent the concentrations of tetracycline before and after the loading study (mg mL-1), respectively.

The data under optimal conditions (pH = 5, amount of Fe2O3/Cu/Ag = 150 mg, time = 20 min at room temperature) shows the efficiency of tetracycline entrapment on the nanocomposite. The results indicate that the highest percentage of encapsulation is 98.53%.

Optimize the condition (the amount of Fe_2O_3/Cu/Ag, time, temperature, and TC concentrations)

To study the amount of Fe2O3/Cu/Ag in the removal of TC, varying amounts ranging from 50 to 300 mg of Fe2O3/Cu/Ag to 10 ml of TC solution(10 ppm, at room temperature and pH 5) were added(**Fig. 7A**). The removal efficiency was determined within 20 min by Eq (1) .The maximum amount of removal was observed. Lower amounts of Fe_2O_3/Cu/Ag resulted in low removal(%) and higher amounts had no effect on the amount of removal **(Fig. 7B**).

Fig.7C shows the effect of time on removal, which was studied from 1 minutes to 60 minutes, and as can be inferred from the figure, the amount of TC removal increases with time and reaches its maximum value in 20 min at room temperature and pH 5, with a removal percentage of 98.35%. After 20 minutes due to complete removal, the amount of removal can be ignored. **Fig.7D** illustrates the impact of temperature on the adsorption of TC, with 150 mg of Fe2O3/Cu/Ag achieving the highest removal in 20 min at 25 °C. Fig. 7E indicates the impact of the primary concentrations of TC by Fe2O3/Cu/Ag under optimal condition (i.e., time of 20 min, 150 mg of Fe2O3/Ag and pH= 5). As can be seen in **Fig.7E**, increasing the concentration of TC initially results in a decrease in the amount of TC removed. This can be attribute to the saturation of the catalyst surface and the reduction of active sites.

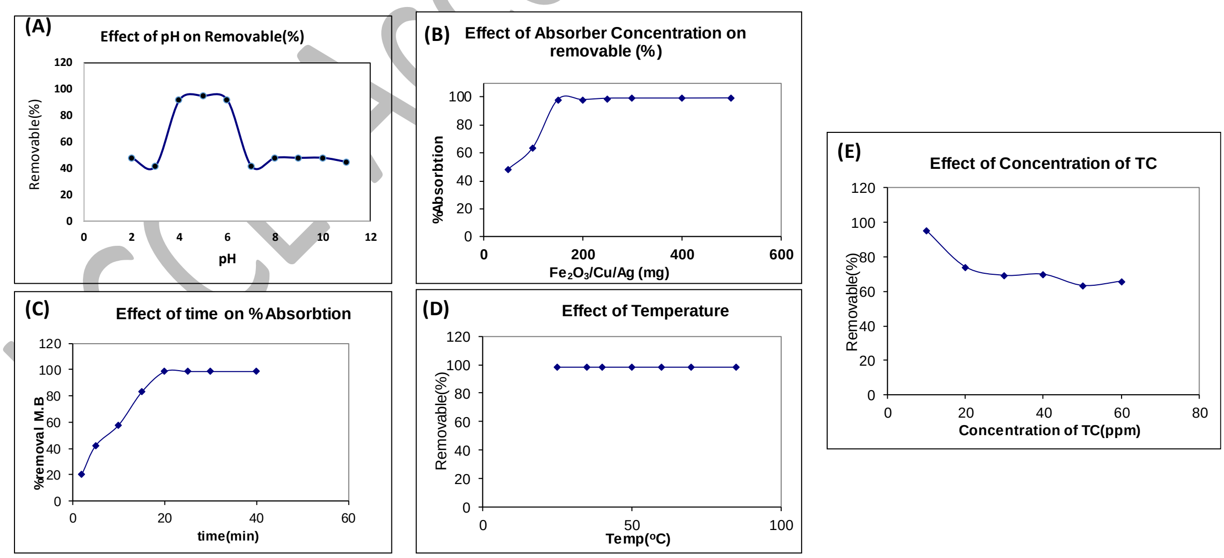

Fig. 7A) The Effect of initial pH on the removable of TC, Fe_2O_3/Cu/Ag. 7B) The effect of the amount of Fe_2O_3/Cu/Ag. 7C) The Effect of time on the removable of TC. 7D) The Effect of temperature on the removable of TC. 7E) The Effect of TC concentrations

The pKa of TC varies with different pH values

The proposed mechanism for the process of TC removal is influenced by parameters such as electrostatic interactions, surface interactions, hydrogen bonding and surface pores [31]. Considering that the parameters affecting the process of TC removal are electrostatic interactions, the changes in positive charges on the surface of the adsorbent lead to attractive and repulsive forces between the adsorbent and TC. The performance of the adsorbent is affected by the strength of these forces. As a result, the pH_{zpc} value for Fe_2O_3/Ag/ Cu was determined to be in the range of 5-6. At pHs lower than pH_{zpc}, the surface of the adsorbent has a positive charge, and at higher pHs, it has a negative surface charge. Since TC has a positive charge at a pH of less than 3.3, electrostatic repulsion occurs on the surface in this range, thus resulting in a low removal rate. For pH 7.5 and above, the surface charge is negative and the charge of TC is also negative, causing electrostatic repulsion to occur and thus leading to a decrease in the amount of removal. The best case is related to the range of pH 5-7, as the molecule of TC partially negatively charges and creates an attractive force between the surface and TC. Therefore, a mechanism for the elimination of tetracycline can be proposed based on physical and chemical interactions **(Fig. 8).**

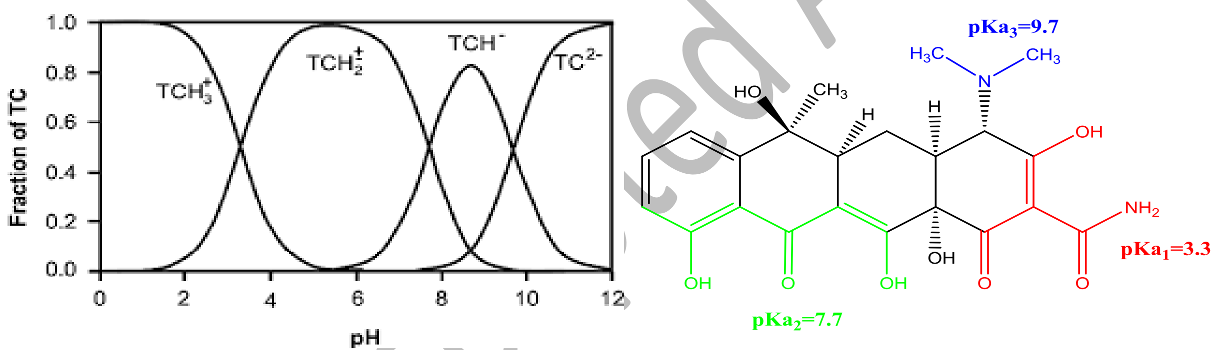

Fig. 8. The pKa of TC varies with different pH values

Freundlich-Lankmuir adsorption isotherms

The data obtained from the studies related to the absorption equations in **Fig. 9A and B** show that the Langmuir model has a better fit for describing the equilibrium absorption of tetracycline due to its higher correlation coefficient than the Freundlich model.

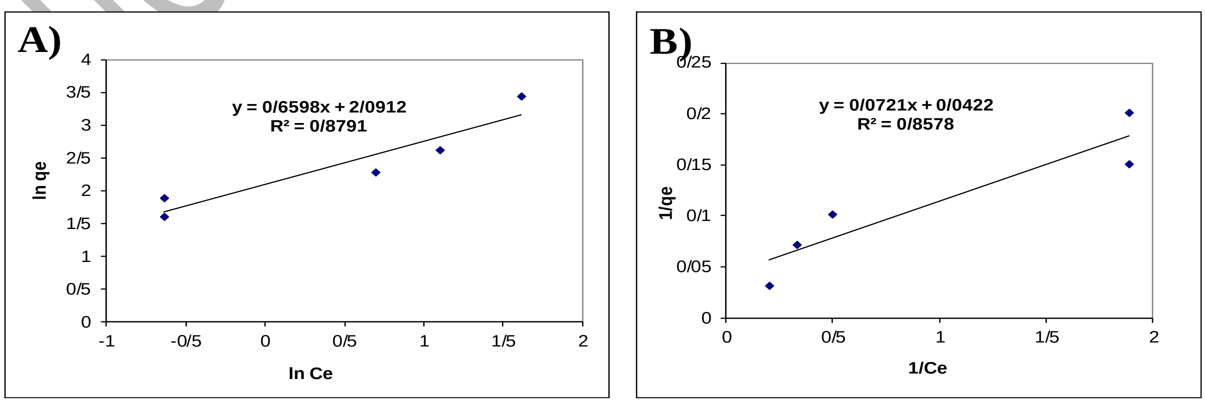

Fig. 9. Freundlich and Langmuir isotherm for tetracycline adsorption on adsorbent at room temperature

Absorption Kinetics

For kinetic adsorption, first and second order simulation models were utilized to examine the invitro kinetic facts. **Fig. 10** displays the data fitting results. It is evident that the second order pseudo model better fits the data compared to the first-order model. Therefore, it is concluded that the rate-controlling step is of the chemical adsorption type, where covalent forces are generated through the sharing or exchange of electrons between the adsorbent and the adsorbate.

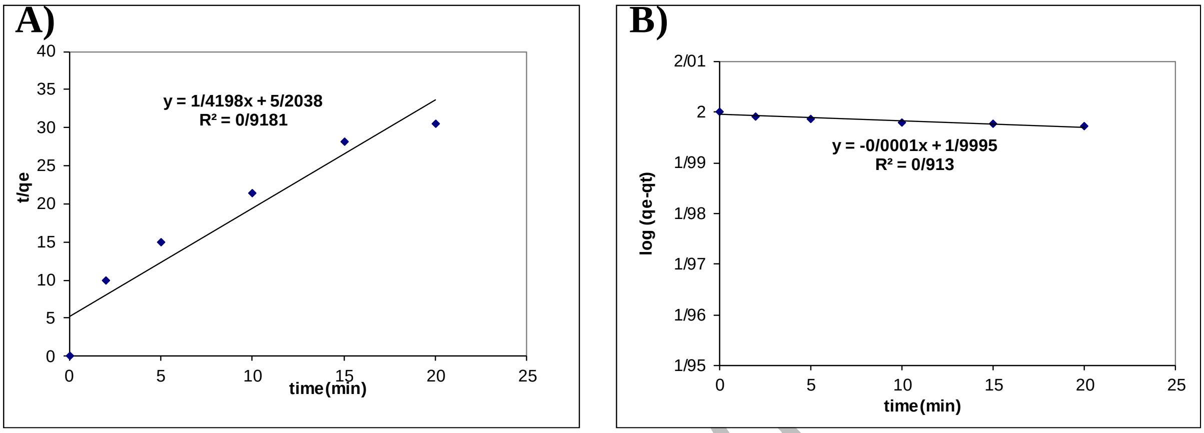

Fig.10. Adsorption kinetic models for tetracycline adsorption on adsorbent at room temperature

CONCLUSIONS

In the present study, a compound with a new structure, Fe_2O_3/Cu/Ag, was used as an adsorbent to remove tetracycline as a pollutant from aqueous solutions. After characterizing Fe_2O_3/Cu/Ag by XRD, SEM, mapping, EDS, TEM, and FTIR, it was used as a TC remover and its various parameters were investigated. The best conditions were found to be 20 min at room temperature and 150 mg of Fe_2O_3/Cu/Ag. In Table 1, a comparison has been made between this research and previous studies. It is evident that the results are satisfactory in terms of removal and reaction time [32–36].

Table 1: A comparison between this research and previous studies on the removal of TCs

S. No	Catalyst	Pollutant conc. (mg/l)	Time (min)	Removal efficiency (%)	Ref.
1	P-S-g-C3N4	10	60	85	32
4	ZnO coated hybrid biochar	10	120	95	33
5	pumice stone	10	120	98	34
6	MnFe2O4	10	120	95	38
7	Magnetic biochar	10	100	96	36

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Data availability

The authors confirm the data of this study are available within the article.

Conflict of interest

The authors declare that there is no conflict of interest.

Research involving Human Participants and/or Animals

The authors declare that there is no Research involving Human Participants and/or Animal

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