

PREPARATION OF MAGNETIC Fe₃O₄/ACTIVATED CARBON FIBER AND A STUDY OF THE TETRACYCLINE ADSORPTION IN AQUACULTURE WASTEWATER

PRIPRAVA MAGNETNIH, S Fe₃O₄ AKTIVIRANIH OGLJIKOVIH VLAKEN IN ŠTUDIJA TETRACIKLINSKE ADSORPCIJE V ODPADNIH VODAH ZA GOJENJE VODNIH ORGANIZMOV

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Fe₃O₄/activated carbon fiber (F-ACF) was synthesized by a simple precipitation method and used as an adsorbent for tetracycline (TC) removal in aquaculture wastewater. The structural and chemical properties of the F-ACF were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), energy-dispersive spectrometry (EDS) and Brunauer–Emmett–Teller (BET) analyses. Effects of various parameters such as solution pH (2–10), reaction time (0–24 h) and extra ion on TC adsorption onto F-ACF were investigated. The equilibrium result has shown that the adsorption was fitted well with Langmuir models compared to Freundlich models. The maximum Langmuir adsorption capacity was found to be 58 mg/g. The adsorption behavior of TC on F-ACF was best fitted with the pseudo-second-order kinetics model.

Keywords: activated carbon fiber, Fe₃O₄, composite, adsorption, antibiotic

Avtorji so s Fe₃O₄ aktivirana ogljikova vlakna (F-ACF) sintetizirali z enostavno precipitacijsko metodo in jih uporabili kot adsorbent za odstranitev tetraciklina (TC) v odpadnih vodah za gojenje vodnih organizmov. Strukturne in kemične lastnosti F-ACF so okarakterizirali z vrstičnim elektronskim mikroskopom (SEM), rentgensko difrakcijo (XRD), energijskim disperzijskim spektrometrom (EDS) in analizo po Brunauer–Emmett–Tellerju (BET). Analizirali so vpliv različnih parametrov, kot so pH raztopine (2–10), reakcijski čas (0–24 h) in ekstra ion med TC adsorpcijo na F-ACF. Rezultati v reakcijskem ravnotežju so pokazali, da se je adsorpcija v primerjavi s Freundlichovimi modeli dobro ujemala z Langmuirjevimi modeli. Ugotovili so, da je maksimalna Langmuirjeva adsorpcijska kapaciteta 58 mg/g. Obnašanje adsorpcije TC na F-ACF se je najbolje ujemalo z pseudokinetičnim modelom drugega reda.

Ključne besede: aktivirana ogljikova vlakna, Fe₃O₄, kompozit, adsorpcija, antibiotik

1 INTRODUCTION

With the extensive use of antibiotics in veterinary medicine and aquaculture for disease control and to enhance growth,^{1,2} the global environment concern has focused on the emergent problems it posed. The bacterial resistance to antibiotics has generated, and human and animal health have been threatened due to the misuse of antibiotics.³ In recent years, massive antibiotics, which are widely used in humans, animals and plants for preventing bacterial or fungal infections, are found in surface water and seawater.⁴ Tetracycline (TC) is a kind of important antibiotic used extensively in livestock feed. In recent years, TC has been detected in aquaculture wastewater (seawater) and represents an uptrend. However, there is little research on antibiotic and practical application to remove antibiotics in aquaculture wastewater. Therefore, the effective actions are needed to remove the antibiotics from contaminated water.

The mainstream methods for the degradation of TC including adsorption, Fenton oxidation, electrochemical oxidation and photocatalysis oxidation have been used for the degradation of antibiotics.^{5–8} Overall, (chemical or physical) adsorption has been considered as one of the most effective and facile techniques for TC removal from water.⁹ Up to now, various kinds of adsorbents, such as graphene oxide, natural zeolite and activated carbon have been developed for this purpose.^{10,11} Among these, graphene oxide possesses the most excellent adsorption capacity for antibiotics, but it is very expensive.¹² Therefore, it is necessary to develop other economic and efficient material.

Activated carbon fiber (ACF) is an economic and efficient adsorbent. Compared with the traditional granular activated carbon, ACF has a large specific surface area and rich micropores. It has been widely applied in the chemical industry, environmental protection, catalysis, medicine, the electronics industry, food hygiene and other fields.¹³ Studies have shown that the adsorption capacity of activated carbon for certain heavy metals and organics can be improved by loading a certain amount of

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Table 1: Experimental conditions

| Set | Aim of experiment | TC concentration (mg/L) | Adsorbent dosage (g/L) | Reaction time (min) | pH | Temperature (K) |
|-----|--|-------------------------|------------------------|---------------------|------|-----------------|
| 1 | Effect of pH | 10 | 0.06 | 180 | 2–10 | 298 |
| 2 | Effects of presence of Na ⁺ , NH ₄ ⁺ , NO ₃ ⁻ , and H ₂ PO ₄ ⁻ | 10 | 0.06 | 180 | 8 | 298 |
| 3 | Isotherm | 10–400 | 0.06 | 1440 | 8 | 298 |
| 4 | Kinetics | 10–30 | 0.06 | 10–1440 | 8 | 298 |

iron and its oxide particles on activated carbon through iron salt modification.¹⁴ In this paper, F-ACF was investigated as an adsorbent for TC.

The aim of this study was to evaluate the removal of TC in aquaculture wastewater (seawater) using F-ACF. In the experiment, the effects of several factors were also examined and the adsorption kinetics and isotherm were also studied.

2 EXPERIMENTAL PART

2.1 Materials and instruments

Activated carbon fiber (ST-1300) was provided by Jiangsu Nantong Fiber Industry Co. All the reagents required include tetracycline, NaOH, HCl, FeSO₄, FeCl₃, NaCl, (NH₄)₂SO₄, NaNO₃, KH₂PO₄. A stock solution of TC was configured using seawater for the aquaculture area.

The spectrophotometric measurements were made with a UV-Vis spectrometer (SP-752). Specific surface area analysis and the distribution of the pore size analysis was performed on Quantachromem 3.0. The SEM and EDS analyses were performed using SU 1510. The FTIR analyses were performed using FTIR-650. Furthermore, a shaker (XB SHA-CA), pH meter (STARTER 3100, made in CHINA), electric drill (JJ-1) and magnet were used.

2.2 Pre-treatment and preparation of ACF

Pre-treatment: Prior to the experiments, the activated carbon fiber was sheared into fraction with 5 mm × 5 mm and boiled in pure water at 450 °C for 1 h to remove the organics and soluble salts on the surface.

The preparation of F-ACF: FeCl₃·6H₂O, FeSO₄·7H₂O and ACF, at a ratio (quantity) of 6:3:1, were added to the beaker with a certain amount of ultrapure water and stirred by electric drill at 80 °C. Then, NaOH was slowly added as precipitant to generate precipitation until pH reached 10, stirred for 1 h. Then, the precipitate was placed, sucked out using the magnet, washed and dried at 105 °C.

2.3 Batch experiments

The batch experiments were carried out in a 250-mL flask containing 50 mL of aqueous solution, and the pH was adjusted with H₂SO₄ and NaOH. The aqueous samples were filtrated and the concentrations of TC in

the solution were analyzed after the reaction. The details of the experimental conditions are presented in **Table 1**.

2.4 Adsorption kinetics

The kinetics data were fitted by pseudo-first-order and pseudo-second-order kinetic rate equations for modelling the kinetics of TC adsorption (Equations (1–2)).^{15,16}

$$q_t = q_e (1 - e^{-k_1 t}) \quad (1)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (2)$$

Among the constants, q_e and q_t are the adsorption capacity (mg·g⁻¹) of TC for ACF when it reached adsorption equilibrium and when time reached t , respectively. k_1 and k_2 are the pseudo-first-order and pseudo-second-order constants, respectively.

2.5 Adsorption isotherm

The equilibrium data were fitted by Langmuir and Freundlich (Equations (3–4)).^{17–19}

$$\frac{c_e}{q_e} = \frac{1}{k_1 q_m} + \frac{c_e}{q_m} \quad (3)$$

$$q_e = k_e c_e^n \quad (4)$$

Among the constants, q_m and c_e are the maximum of the adsorption quantity (mg/g) and the residual solution concentration (mg/L), respectively. The other constants, including k_1 and k_f , were calculated from the intercept and the slope of the plots obtained from Equations (3–4).

2.6 Characterization of ACF and determination of TC

ACF and F-ACF were characterized by SEM, BET and XRD analyses. The concentration of TC was determined by ultraviolet spectrometer at λ_{\max} value of TC (357 nm wavelength) and the amount of TC adsorbed (mg/g) was calculated based on a mass-balance equation as given in Equation (5). The degradation rate of TC was calculated as given in Equation (6):

$$q_e = \frac{(c_0 - c_e)V}{W} \quad (5)$$

$$\text{Degradation rate} = \frac{(c_0 - c_e)}{c_e} \quad (6)$$

q_e is the equilibrium adsorption capacity (mg/g); c_0 is the initial concentration of TC in the solution (mg/L); c_e is the final or equilibrium concentration of TC in the solution (mg/L); V is the volume of the solution (L), and W is the weight of the ACF (g).

3 RESULTS AND DISCUSSION

3.1 Characterization

Morphology analysis

Table 2: Surface properties of ACF and F-ACF

| Samples | S_{BET} (m ² /g) | V_{micro} (cc/g) | $D_{average}$ (nm) |
|---------|-------------------------------|--------------------|--------------------|
| ACF | 848.012 | 0.347 | 3.829 |
| F-ACF | 779.484 | 0.283 | 3.407 |

The surface morphology of ACF and F-ACF obtained by SEM is given in **Figure 1**. The surface feature of the origin ACF was relatively smooth and flat. Fe₃O₄ particles with 10 nm in diameter were evenly distributed on the surface of the F-ACF.

The XRD and EDS patterns of ACF and F-ACF obtained are given in **Figure 2**. One intense peak at 23.5° is observed in both patterns of XRD, which suggests that the Fe₃O₄ particles on ACF do not result in any evident change in the ACF structure. The signature Fe₃O₄ peaks are obviously observed in the XRD pattern of F-ACF at 30.12°, 35.47°, 43.11° and 57.02°, which are assigned to the (220), (311), (400) and (511) plane (JCPDS card no. 26-1136), respectively. The sizes of the Fe₃O₄ crystallites were estimated with XRD peak analysis as 2.5 nm. It can be seen from the EDS pattern that, apart from the signature peak of C and O, the signature peak of Fe in F-ACF clearly appears, whose percent reaches 4.8%. Besides, the signature peak of P in original ACF appears, whose percent reaches 2.7%. The appearance of P is due to the phosphoric acid that was used to activate the ACF during the preparation of ACF, and P disappeared after the pretreatment of ACF.

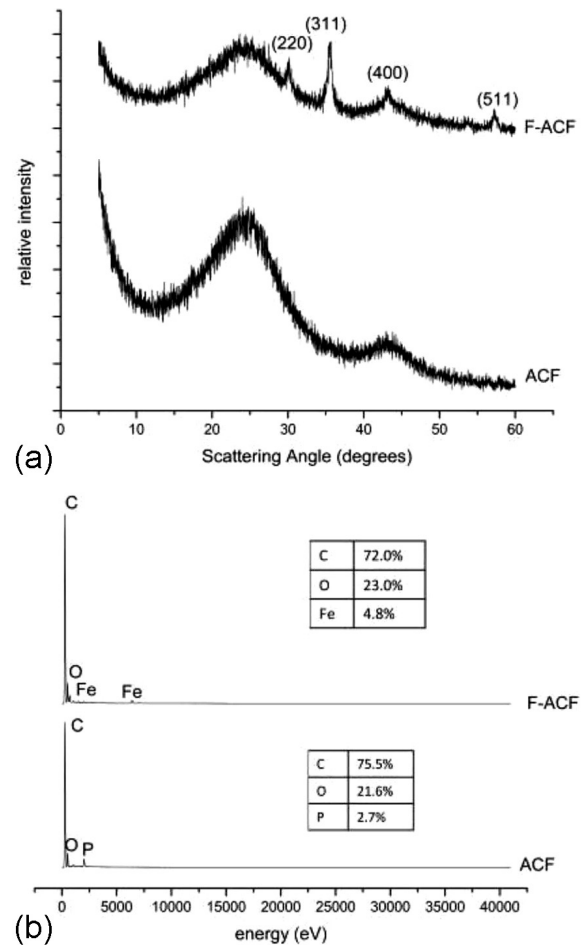


Figure 2: a) XRD and b) EDS patterns of ACF and F-ACF

The BET surface area, micropore volume and average diameter of samples were summarized in **Table 2**. Compared with the origin ACF, the surface area, micropore volume and diameter of F-ACF were reduced. These changes were probably due to the fact that Fe₃O₄ particles were loaded on the surface of activated carbon fiber, contributing to clogged partial pores and a reduced surface area.

Batch experiments

Figure 3a indicates the effect of pH when the pH value was from 2 to 10. As a result, the degradation rate and unit adsorption quantity increased with the increase of pH value, and reached peak, 100% and 16.6 mg/g, when the pH was no more than 4. TC possesses multiple ionizable functional groups, mainly corresponding to three acid dissociation constants ($pK_a = 3.3, 7.7,$ and 9.6), respectively. Therefore, TC exists as a cationic, zwitterionic, and anionic species under various pH values. In addition, many studies indicate the surface of F-ACF may carry a negative charge, which increases with the increase of the pH value. Therefore, the adsorption of TC on F-ACF was driven by electrostatic attraction at low pH value and driven by electrostatic repulsion at high pH value.²⁰ In practice, the removal rate

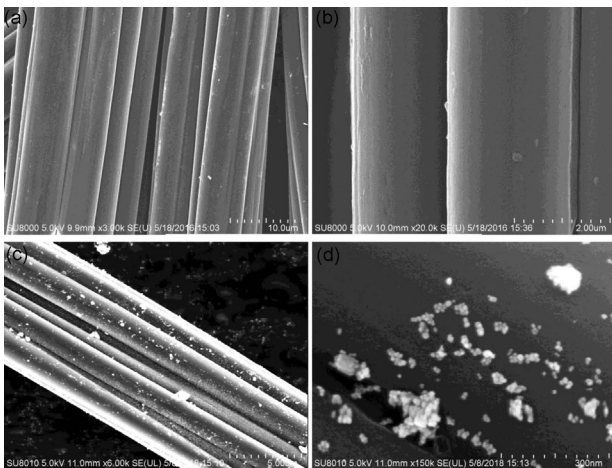
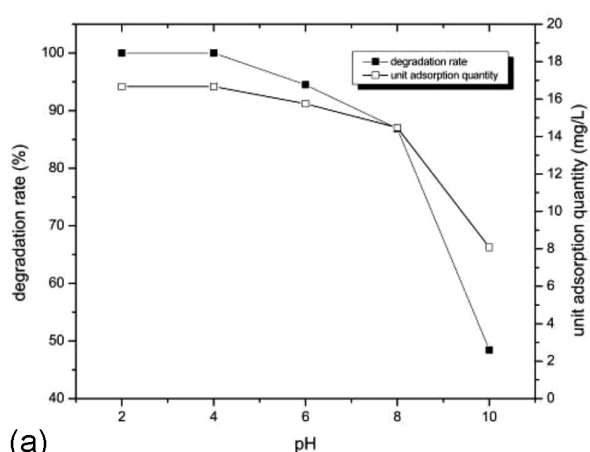
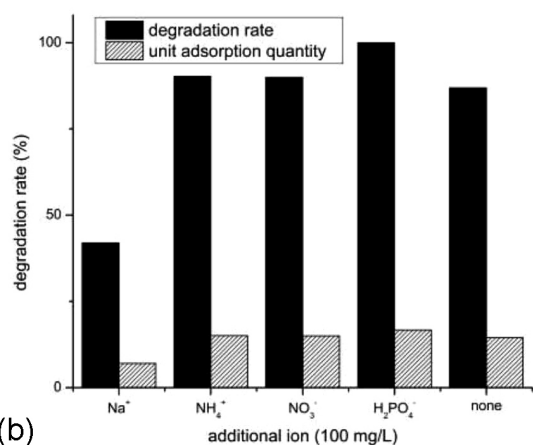


Figure 1: SEM of a), b) ACF and c), d) F-ACF



(a)



(b)

Figure 3: The effects of: a) pH, b) extra ions on the adsorption of TC

of TC could still reach about 90 % under the condition of weak alkalinity and neutral, which is common pH value in aquaculture wastewater (seawater).

Figure 3b indicates the effect of interfering ions under the existence of extra Na⁺, NH₄⁺, NO₃⁻, H₂PO₄⁻ ions (100 mg/L) that are common in aquaculture wastewater. As a result, these interfering ions generally had little effect on adsorption apart from Na⁺. The metal ions maybe have a certain competition with the adsorption of TC on F-ACF. In addition, TC may form complexion with metal ions, which might cause the decreased adsorption. In practice, the solution of TC was configured by the seawater in which many extra ions exist; therefore, the overall the effects of interfering ions is neglected.

Adsorption kinetics

The adsorption kinetic analysis was studied to analyse the adsorption mechanism, including the adsorption rate and possible rate-limiting steps of the reaction process. **Figure 4** shows the pseudo-first-order a) and pseudo-second-order b) plots. **Table 3** provides the evaluated parameters of two kinetics models. The experimental data fitted well with the pseudo-second-order model.

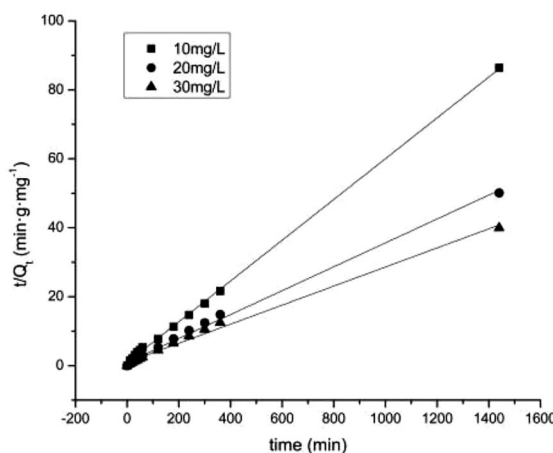
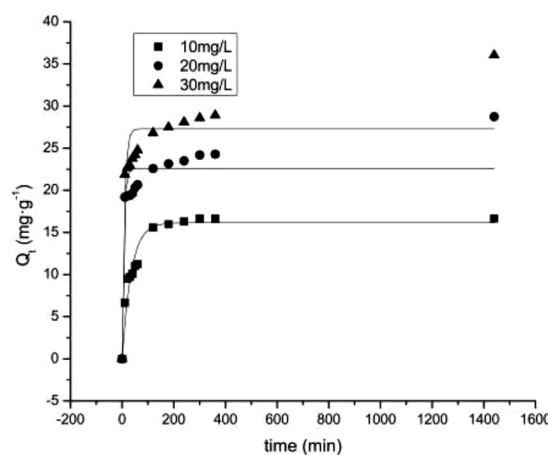


Figure 4: a) Pseudo-first-order and b) pseudo-second-order equation plots for TC (10, 20, 30 mg/L) adsorption onto F-ACF

Table 3: Kinetic model parameters for TC adsorption onto F-ACF

| Kinetic parameters | 10mg/L | 20mg/L | 30mg/L |
|----------------------------|---------------------|---------------------|-------------------|
| Pseudo-first-order | | | |
| k_1 (min ⁻¹) | 0.029 | 0.15 | 0.11 |
| q_m (mg/g) | 16.15 | 22.58 | 27.28 |
| R^2 | 0.9260 | 0.8440 | 0.8206 |
| Pseudo-second-order | | | |
| q_e (mg/g) | 16.90 | 28.83 | 36.14 |
| k_2 (g/mg/min) | $3.9 \cdot 10^{-3}$ | $1.2 \cdot 10^{-3}$ | $8 \cdot 10^{-4}$ |
| R^2 | 0.9993 | 0.9963 | 0.9934 |

As shown in **Table 3**, the fitting correlation coefficients R^2 were between 0.82 and 0.92, which indicated that the Lagergren first-order kinetic equation is not suitable for describing the F-ACF adsorption characteristics of TC.²¹

Figure 4b shows the pseudo-second-order kinetic fitting line of the adsorption of TC by F-ACF. The experimental data was consistent with the fitting line. The correlation coefficients R^2 of the pseudo-second-order fitting were all greater than 0.993, as shown in **Table 3**. Moreover, the theoretical equilibrium adsorption capacity q_e obtained by the equation fitting was very close to the actual measured equilibrium adsorption

capacity, which was basically consistent with the kinetic adsorption mechanism of other adsorbents on antibiotics.¹⁰

Isotherms

Table 4: Isotherms constants for the adsorption of F-ACF.

| Equilibrium parameters | | | |
|------------------------|--------|--------------|--------|
| Freundlich | | Langmuir | |
| k_f | 21.68 | k_L (L/mg) | 0.074 |
| n | 0.16 | q_m (mg/g) | 58.58 |
| R^2 | 0.8214 | R^2 | 0.9923 |

The adsorption isotherm showed the relationship between the adsorbate concentration and the degree of accumulation on the adsorbent surface. **Figure 5** shows the equilibrium isotherm equation plots for the adsorption of TC onto F-ACF. The adsorption isotherm parameters obtained from all the models were given in **Table 4**. The experimental data fitted well with the Langmuir model.

The fitting correlation coefficients (R^2) of the Freundlich model was no more than 0.90. It could not be employed to describe well the adsorption behaviour of TC by F-ACF. The Langmuir model assumes that each adsorption site can only adsorb a solute molecule, and

the adsorbed solute molecules form a monolayer on the surface of the adsorbent. When all the adsorption sites have adsorbed solute molecules, it will reach saturation. **Figure 5 a** shows the fitting line of the Langmuir equation of F-ACF to TC. In **Table 4**, the coefficient k_L in the Langmuir model was less than 1, which indicated that the adsorption of TC by F-ACF belongs to favourable adsorption. Besides, the theoretical equilibrium adsorption capacity q_e , 58.5 mg/g, obtained by the equation fitting was very close to the actual measured equilibrium adsorption capacity.

Comparison with other adsorbents

A comparison presented in **Table 5** has been employed for the adsorption capacities of different adsorbents for TC. **Table 5** shows the q_m obtained F-ACF was not very high compared with graphene oxide adsorbents. This is due to the configured solution of TC in this paper that was derived directly from aquaculture wastewater, in which many interfering ions exist and the pH value was close to 8. From the former conclusions, the pH value and certain interference ions have a very negative effect on the adsorption of TC. Therefore, under the same conditions as in reference 10, an independent experiment was carried out using F-ACF as adsorbent and the maximum adsorption capacity q_m , 192.1 mg/g was obtained. The adsorption capacity was closed to pure graphene oxide. In addition, graphene oxide possesses higher surface area (>1500 m²/g) than F-ACF, resulting in a higher adsorption capacity. However, the price of graphene oxide is dozens of times more expensive than ACF. So, in terms of cost and efficiency, F-ACF is a promising and economic adsorbent for TC removal from aquaculture wastewater.

Table 5: Maximum adsorption capacity (q_m) of various adsorbents for TC

| Adsorbent | q_m (mg/g) | Reference |
|---|--------------|------------|
| F-ACF | 58 | This study |
| Fe ₃ O ₄ Nanoparticles@graphene Oxide | 603 | 22 |
| Pumice stone | 20 | 23 |
| Graphene oxide | 212 | 10 |
| Kaolinite | 4.3 | 24 |
| Activated sludge | 72 | 25 |

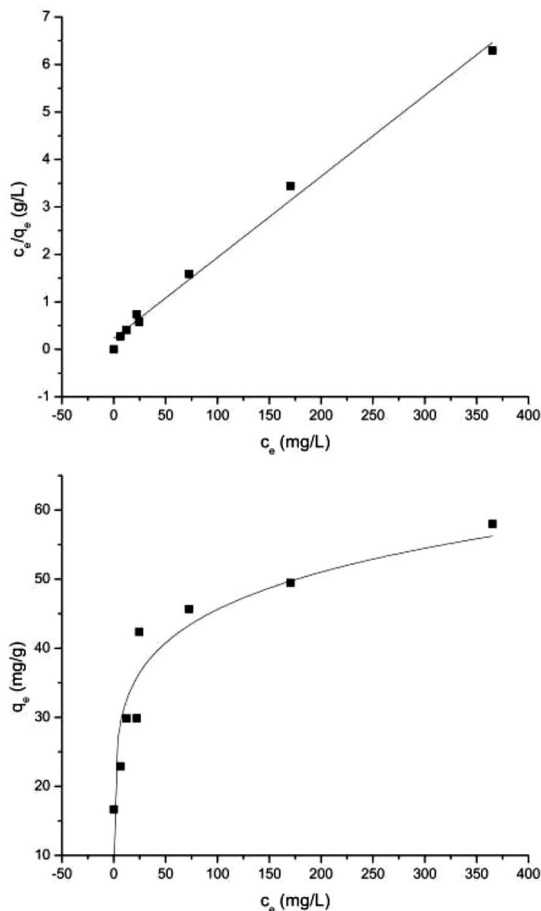


Figure 5: Langmuir and b) Freundlich equation plots for TC adsorption onto F-ACF

4 CONCLUSIONS

Fe₃O₄/activated carbon fiber (F-ACF) was successfully prepared using a simple precipitation method. The SEM, XRD and EDS characterizations of F-ACF and ACF show the Fe was loaded on the surface of ACF in the form of Fe₃O₄. The analysis of BET of F-ACF and ACF indicates F-ACF has a lower surface area, which is due to the introduction of Fe₃O₄ over the surface of F-ACF. The increase in pH has a negative effect on the removal rate of TC. In addition, interfering metal ions have a certain effect on the removal of TC. The adsorp-

tion behavior of TC on F-ACF was fitted best with the pseudo-second-order kinetics model. The equilibrium of TC on F-ACF agrees well with the Langmuir models. The maximum Langmuir adsorption capacity was found to be 58 mg/g. The results of this paper show that F-ACF is a practical and economical adsorbent for TC in agriculture wastewater.

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5 REFERENCES

- J. Davies, Origins and evolution of antibiotic resistance, *Microbiologia*, 12 (1996) 1, 9–16, doi:10.1128/MMBR.00016-10
- A. L. Giraldo, G. A. Penuela, R. A. Torres-Palma, N. J. Pino, R. A. Palominos, H. D. Mansilla, Degradation of the antibiotic oxolinic acid by photocatalysis with TiO₂ in suspension, *Water Res.*, 44 (2010) 18, 5158–67, doi:10.1016/j.watres.2010.05.011
- R. Hao, X. Xiao, X. Zuo, J. Nan, W. Zhang, Efficient adsorption and visible-light photocatalytic degradation of tetracycline hydrochloride using mesoporous BiOI microspheres, *J. Hazard. Mater.*, 209-210 (2012), 137–45, doi:10.1016/j.jhazmat.2012.01.006
- C. Chen, J. Li, P. Chen, R. Ding, P. Zhang, X. Li, Occurrence of antibiotics and antibiotic resistances in soils from wastewater irrigation areas in Beijing and Tianjin, China, *Environ. Pollut.*, 193 (2014), 94–101, doi:10.1016/j.envpol.2014.06.005
- H. Wu, H. Xie, G. He, Y. Guan, Y. Zhang, Effects of the pH and anions on the adsorption of tetracycline on iron-montmorillonite, *Appl. Clay Sci.*, 119 (2016), 161–169, doi:10.1016/j.clay.2015.08.001
- E. S. Elmolla, M. Chaudhuri, The feasibility of using combined Fenton-SBR for antibiotic wastewater treatment, *Desalination*, 285 (2012) s 1–3, 14–21, doi:10.1016/j.desal.2011.09.022
- C. C. Jara, D. Fino, V. Specchia, G. Saracco, P. Spinelli, Electrochemical removal of antibiotics from wastewaters, *Appl. Catal. B-Environ.*, 70 (2007) 1–4, 479–487, doi:10.1016/j.apcatb.2005.11.035
- Y. Zhao, B. Yin, G. Zhang, W. Shi, Facile fabrication of plate-like Bi₃O₄Cl for visible-light-driven photocatalytic degradation of tetracycline hydrochloride, *Iet. Micro Nano Lett.*, 13 (2018) 1, 9–11, doi:10.1049/mnl.2017.0490
- R. Ocampo-Pérez, J. Rivera-Utrilla, C. Gómez-Pacheco, M. Sánchez-Polo, J. J. López-Peñalver, Kinetic study of tetracycline adsorption on sludge-derived adsorbents in aqueous phase, *Chem. Eng. J.*, 213 (2012) 12, 88–96, doi:10.1016/j.cej.2012.09.072
- Y. Gao, Y. Li, L. Zhang, H. Huang, J. Hu, S. M. Shah, X. Su, Adsorption and removal of tetracycline antibiotics from aqueous solution by graphene oxide, *J. Colloid Interf. Sci.*, 368 (2012) 1, 540, doi:10.1016/j.jcis.2011.11.015
- H. M. Otker, I. Akmehtmetbalcıoğlu, Adsorption and degradation of enrofloxacin, a veterinary antibiotic on natural zeolite, *J. Hazard. Mater.*, 122 (2005) 3, 251–258, doi:10.1016/j.jhazmat.2005.03.005
- E. E. Ghadim, F. Manouchehri, G. Soleimani, H. Hosseini, S. Kimiagar, S. J. P. O. Nafisi, Adsorption properties of tetracycline onto graphene oxide: Equilibrium, kinetic and thermodynamic studies, *Plot One*, 8 (2013) 11, e79254, doi:10.1371/journal.pone.0079254
- S. Yang, T. Xiao, J. Zhang, Y. Chen, L. Li, Activated carbon fiber as heterogeneous catalyst of peroxymonosulfate activation for efficient degradation of Acid Orange 7 in aqueous solution, *Sep. Purif. Technol.*, 143 (2015), 19–26, doi:10.1016/j.seppur.2015.01.022
- G. A. Marafra, G. Mário César, L. C. A. Oliveira, De, D. C. Cinthia Soares, A friendly environmental material: iron oxide dispersed over activated carbon from coffee husk for organic pollutants removal, *J. Environ. Manag.*, 127 (2013) 2, 206–211, doi:10.1016/j.jenvman.2013.05.017
- F. Ogata, N. Kawasaki, Adsorption of Pt(IV) and Pd(II) by calcined dried aluminum hydroxide gel from aqueous solution system, *J. Environ. Chem. Eng.*, 1 (2013) 4, 1013–1019, doi:10.1016/j.jece.2013.08.011
- M. I. El-Khaiary, G. F. Malash, Y. S. Ho, On the use of linearized pseudo-second-order kinetic equations for modeling adsorption systems, *Desalination*, 257 (2010) 1, 93–101, doi:10.1016/j.desal.2010.02.041
- M. Rasouli, N. Yaghobi, M. Hafezi, M. Rasouli, Adsorption of divalent lead ions from aqueous solution using low silica nano-zeolite X, *J. Ind. Eng. Chem.*, 18 (2012) 6, 1970–1976, doi:10.1016/j.jiec.2012.05.014
- T. Ishiyama, S. Matsumoto, T. Sakai, T. Yachi, A new model of phosphorus distribution in the soil structure, *Technical report of Ieice Icd*, 98 (1998) 352, 25–30
- R. Selvakumar, N. A. Jothi, V. Jayavignesh, K. Karthikaiselvi, G. I. Antony, P. R. Sharmila, S. Kavitha, K. Swaminathan, As(V) removal using carbonized yeast cells containing silver nanoparticles, *Water Res.*, 45 (2011) 2, 583–592, doi:10.1016/j.watres.2010.09.034
- C. Gu, K. G. Karthikeyan, S. D. Sibley, J. A. Pedersen, Complexation of the antibiotic tetracycline with humic acid, *Chemosphere*, 66 (2007) 8, 1494–501, doi:10.1016/j.chemosphere.2006.08.028
- A. Li, S. Pi, W. Wei, T. Chen, J. Yang, F. Ma, Adsorption behavior of tetracycline by extracellular polymeric substrates extracted from *Klebsiella sp. J1*, *Environ. Sci. Pollut. Res. Int.*, 23 (2016) 24, 25084–25092, doi:10.1007/s11356-016-7726-6
- X. Hu, Y. Zhao, H. Wang, X. Tan, Y. Yang, Y. J. I. J. o. E. R. Liu, P. Health, Efficient removal of tetracycline from aqueous media with a Fe₃O₄ nanoparticles@graphene oxide nanosheets assembly, *Int. J. Env. Res. Pub. He.*, 14 (2017) 12, 1495, doi:10.3390/ijerph14121495
- U. A. Guler, M. Sarioglu, Removal of tetracycline from wastewater using pumice stone: equilibrium, kinetic and thermodynamic studies, *J. Environ. Heal. Sci. Eng.*, 12 (2014) 1, 79, doi:10.1186/2052-336X-12-79
- Z. Li, P. H. Chang, J. S. Jean, W. T. Jiang, C. J. Wang, Interaction between tetracycline and smectite in aqueous solution, *J. Colloid Interf. Sci.*, 341 (2010) 2, 311–319, doi:10.1016/j.jcis.2009.09.054
- N. Prado, J. Ochoa, A. Amrane, Biodegradation and biosorption of tetracycline and tylosin antibiotics in activated sludge system, *Process Biochem.*, 44 (2009) 11, 1302–1306, doi:10.1016/j.procbio.2009.08.006