Assessment of Nanoscale Ni/Fe Bimetallic Particle for Removal of Tetracyclines

Sibel ASLAN, Hande TÜRK, Özge HANAY

***Abstract*—** Bimetallic nanoparticles (BNPs) are combination of nanoscale zero valent iron (nZVI) with a noble metal catalysts like Pd, Ni, or Cu and they are generally more reactive than nZVI alone. Tetracyclines (TCs) are the second most common antibiotic group in both production and usage throughout the world. The aim of this study was to investigate the removal efficiency of tetracycline (TC) and chlortetracycline (CTC) from aqueous solution using nanoscale Ni/Fe bimetallic particles. For this purpose, batch experiments were carried out at different experimental conditions such as pH, bimetallic particle dosage, initial concentration of tetracyclines, reaction time, and temperature. Removal efficiencies of TC and CTC at optimal conditions were above 95%. Moreover, the degradation products of TCs were also analyzed and determined that the dominant degradation products for TC and CTC were 4-epitetracycline (ETC) and anhydrochlortetracycline (ACTC), respectively. Adsorption kinetics followed closely the pseudo-second-order kinetic model. Adsorption equilibrium data were also fitted by different isotherm models such as Langmuir and Freundlich and it was seen that Langmuir adsorption model provided the best fits to the adsorption equilibrium data of TC and CTC.

***Keywords*—**Bimetallic nanoparticle, chlortetracycline, Ni/Fe, tetracycline.

I. Introduction

Pharmaceuticals constitute a large group of human and veterinary medicinal compounds which have long been used throughout the world and therefore frequently detected in natural surface water and groundwater [1, 2, 3]. The most important pharmaceuticals found in the waters are antibiotics, analgesics, painkillers, and hormonal drugs [2]. Among pharmaceuticals, antibiotics are widely used for the therapy of infectious diseases in human and veterinary medicine [4] and as growth promoters in livestock and aquaculture operations [5]. Antibiotics are of particular concern, as they are considered to pose a potential threat to ecosystem and human health due to ecotoxicity and the development of antibiotic resistance genes, even at low concentrations [6, 7].

The tetracyclines, which were discovered in the 1940s, are broad-spectrum agents, exhibiting activity against a wide range of gram-positive and gram-negative bacteria, a typical organisms such as chlamydiae, mycoplasmas, and rickettsiae, and protozoan parasites [8]. As tetracyclines are poorly metabolized or absorbed by human and animals after intake, large fractions are excreted through urine and feces as unmodified parent compound and could emit to environment [5, 7, 9]. Tetracyclines are designed to be stable and biorefractory, and their removal by conventional water treatment methods is ineffective, therefore they have been widely detected in soils, surface waters, ground water, and even drinking water [7, 10]. Tetracyclines have been shown to disrupt microbial soil respiration, Fe(III) reduction, nitrification, and phosphatase activities [11].

Bimetallic nanoparticle (BNP) contains Fe or Zn as reductant for water and the second metal Pd, Pt, Ag, or Ni, as a catalyst [12]. The noble metal promotes iron oxidation and may act as a catalyst for electron transfer and hydrogenation [13-16]. BNP has some advantages such as cost effectiveness, good corrosion stability, high reactivity, and faster contaminant degradation [15, 17].

In this study, nanoscale Ni/Fe bimetallic nanoparticles was used for the efficient removal of tetracyclines from water. TC and CTC were selected as model tetracyclines. The influencing factors, including pH value of solution, bimetallic particle dosage, initial TCs concentration, reaction time and temperature, were investigated. Degradation products of TC and CTC were examined at optimal conditions. In addition, the adsorption isotherms and kinetics were also evaluated.

II. Materials and Methods

A. Chemicals

Tetracycline hydrochloride (molecular weight: 480.90 g mol^{-1}; molecular formula: $C_{22}H_{24}N_2O_8.HCl$) and chlortetracycline hydrochloride (molecular weight: 515.34 g mol^{-1}; molecular formula: $C_{22}H_{23}ClN_2O_8.HCl$) were purchased from Applichem and Sigma. Anhydrotetracycline (ATC), 4-epitetracycline (ETC), 4-epianhydrotetracycline (EATC), anhydrochlortetracycline (ACTC), 4-epichlortetracycline (ECTC), 4-epianhydrochlortetracycline (EACTC) were obtained from the European Pharmacopoeia Reference Standard and Dr. Ehrenstorfer GmbH. Methanol, acetonitrile, and formic acid from Merck were all liquid chromatography–mass spectrometry (LC–MS) and HPLC grade. All other reagents used were of analytical grade. HCl and NaOH were used to adjust solution pH. Reagent water was produced from a Millipore Milli-Q Ultrapure Gradient 3 V

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purification system. Solutions for other uses in this study were prepared with deoxygenated water. The stock solutions of tetracyclines were prepared by dissolving each compound in deionized deoxygenated water. They were stored at 4°C in the refrigerator before use.

B. Preperation of nZVI Particles and Nanoscale Ni/Fe Bimetallic Particles

nZVI particles used in this study were prepared according to method given by Hwang et al. [18]. nZVI synthesis conditions were as following; reductant delivery rate: 20 mL min^{-1}, $[Fe^{3+}]$: 71.7 mM and $[BH_4^-]$: 358.5 mM. Bimetallic particle was prepared according to method given by Fennelly and Roberts [19].

C. Experimental Procedure for Batch Experiments

Batch experiments for removal of TC and CTC by Ni/Fe bimetallic particles were carried out at predetermined temperature in 120 ml glass beaker containing 100 ml of TC or CTC solutions. Different factors that influence the reaction of TCs with Ni/Fe bimetallic particles were investigated, including initial pH value of solution, Ni/Fe bimetallic particle dosage, initial TCs concentration, reaction time, and temperature. The reaction mixtures were shaken at 150 rpm using a constant temperature orbital shaker (Gallenkamp) for different reaction times. At the end of the predetermined time intervals, the samples were withdrawn and analyzed for TC and CTC. The experiments were performed twice and average results were presented.

D. Analytical Methods

The concentration of TC and CTC in the solution was analyzed using High Performance Liquid Chromatography (HPLC, Shimadzu). Column: AllureBiPh 5µm, 150x4.6 mm; mobile phase: a mixture of ammonium dihydrogenphosphate /acetonitril/ (20/80, v/v); flow rate: 1.2 mL min^{-1}; sample size: 100 µL; detector: diode-array detector at 269 nm. The retention time for TC and CTC was found to be 3.90 and 7.07 min, respectively.

Samples were withdrawn at designated times and filtered through Millipore 0.22 µm filters prior to analysis. The removal of TC and CTC was calculated using (1):

$$\text{Removal (\%)} = [(C_0 - C_t)/C_0]*100 \quad (1)$$

The amount of TC or CTC adsorbed per gram of Ni/Fe bimetallic particle at any time, q_e was calculated as (2);

$$q_e = [(C_0 - C_t)*V]/m \quad (2)$$

where V is the volume of solution (L), C_0 and C_t are the concentrations of TC or CTC before and after the reaction, respectively (mg L^{-1}); m is the mass of Ni/Fe bimetallic particle (g).

The degradation products of TC and CTC were analyzed by LC-MS-MS (Shimadzu LC-20 AD) with Venusil XBP C18 column (3µm, 100 Å, 2.1x50mm). Mobile phase: a mixture of ultrapure water (A) and methanol containing 0.1% formic acid (v/v) (B); flow rate: 0.3 mL min^{-1}; sample size: 100 µL; column temperature:40 ^oC; injection volume was 100 µL.

pH measurements of solutions were done by pH meter (Orion 3 STAR).

E. Adsorption Isotherms

Adsorption isotherm studies were carried out in 100 ml aqueous TC or CTC solution at increasing concentrations (20 to 100 mg L^{-1}) treated with the appropriate amount of bimetallic particle. The suspensions were placed in orbital shaker at temperatures of 30, 45, 60 ^oC. Then, samples were withdrawn from the glass beakers.

Adsorption isotherm equations explain how adsorbate molecules distribute between adsorbent and solution after the system equilibrium is reached. Langmuir and Freundlich isotherm models are two most common adsorption models. The Langmuir isotherm assumes that the adsorbate covers homogeneously on the surface of adsorbent, the interaction between adsorbed molecules is negligible. The Langmuir equation is given below:

$$q = (q_m.K_L.C_e)/(1+K_L.C_e) \quad (3)$$

A linear form of Langmuir equation is given as:

$$(C_e/q_e) = (C_e/q_m) + (1/K_L.q_m) \quad (4)$$

where q_e is the amount of TC or CTC per mass of Ni/Fe bimetallic particle (mg g^{-1}); q_m is the theoretical maximum adsorption capacity (mg g^{-1}); C_e is the equilibrium concentration of TC or CTC (mg L^{-1}), and K_L is a constant that is related to the energy of adsorption (L mg^{-1}). A plot of C_e versus C_e/qe is a line with a slope equal to $1/q_m$ and intercept equal to $1/(K_L.q_m)$.

The Freundlich isotherm is based on the assumption that adsorption occurs on a heterogeneous surface, in which the energy varies as a function of the surface coverage. This model can described as the following equation:

$$q_e = K_f.C_e^{1/n} \quad (5)$$

A linear form of the Freundlich isotherm can be written as

$$\ln q_e = \ln K_f + (1/n).\ln C_e \quad (6)$$

where K_f is the empirical constant, n is the adsorption intensity. A plot of $\ln q_e$ versus $\ln C_e$ is a line with a slope equal to 1/n and intercept equal to $\ln K_f$.

F. Kinetic Studies

Kinetic models have been proposed to elucidate the removal mechanism. Pseudo-first-order and pseudo-second-order rate models are used to determine kinetic parameters and describe the adsorption mechanism.

The pseudo-first-order kinetic model is also known as the Lagergren model and is widely used adsorption rate equation for the adsorption of solute from aqueous solution. Lagergren kinetic equation is generally expressed as follows:

$$dq/dt = k_1.(q_e - q) \quad (7)$$

where q_e and q are the adsorption capacities at equilibrium and time t (min) (mg g^{-1}), respectively, k_1 is the pseudo-first-order rate constant for the kinetic model (min^{-1}). Integrating (7) with the boundary conditions of q=0 at t=0 and q=q at t=t, yields

$$\log (q_e-q)=\log (q_e)- (k_1/2.303).t \quad (8)$$

A plot of log (q_e-q) against t should give a linear relationship with the slope of $k_1/2.303$ and intercept of (log q_e).

The pseudo-second-order kinetic model is also based on the adsorption capacity of the solid phase and the assumption that the adsorption process involves chemisorption mechanism. The equation is expressed by the following differential equation:

$$dq/dt = k_2. (q_e - q)^2 \quad (9)$$

Integrating (9) and using again the initial condition q=0 at t=0, the following equation is obtained:

$$t/q = (1/ k_2. q_e^2)+ (1/q_e). t \quad (10)$$

In the case of second-order kinetic equation, the plot of t/q against t should give a linear relationship that the q_e and k_2 could be determined.

III. Results And Discussions

A. Characteristics of Ni/Fe Bimetallic Particles

Fig. 1 shows the SEM image of nanoscale Ni/Fe bimetallic particles. As seen from Fig. 1, the size of synthesized Ni/Fe bimetallic particles was between 710 and 4250 nm.

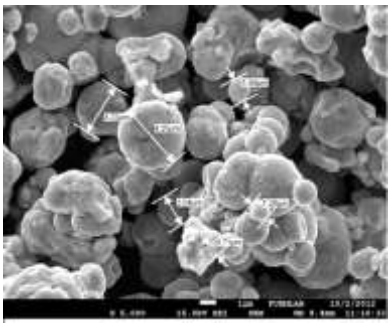


Fig.1. SEM image of nanoscale Ni/Fe bimetallic particles

B. Effect of pH Value

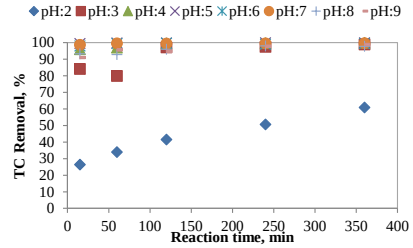
pH of a solution is an important parameter affecting the adsorption process because it affects both aqueous charge distribution and the surface binding site of the adsorbent [20]. The ionic form of TCs and surface charge of the sorbent depend on the solution pH [21]. To study the effect of pH on adsorption, the initial pH of solution was adjusted from 2 to 9 using NaOH or HCl aqueous solutions. Fig. 2 (a, b) represents the effect of pH on the removal of TC and CTC. Generally, the removal of TC and CTC was increased with increase in pH. TC and CTC removal was low at pH of 2. However, the removal efficiencies at pH values above 3 for both of the tetracyclines were close to each other and they were nearly 99%.

C. Effect of Ni/Fe Bimetallic Particle Dosage

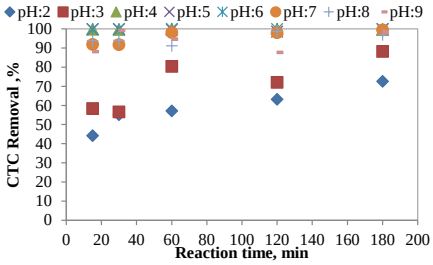
To study the effect of Ni/Fe bimetallic particle dosage on adsorption, different amounts of Ni/Fe bimetallic particle was added tetracycline solutions. Fig. 3 (a, b) illustrates the effect of Ni/Fe bimetallic particle dosage on the removal of TC and CTC from solution. As seen from Fig. 3 (a, b), the removal efficiencies of TCs increased when bimetallic particle dosages increased due to the increase in active adsorption sites of bimetallic particle. The optimum particle dosages for TC and CTC were 0.1 and 0.4 g L^{-1}, respectively.

D. Effect of Temperature

The effect of temperature on the removal of TCs is shown in Fig. 4 (a, b). It can be seen that the effect of temperature was more important for TC compared to CTC.

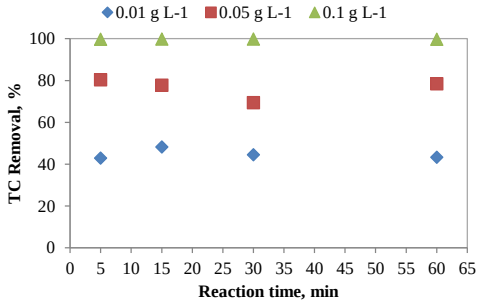


(a)

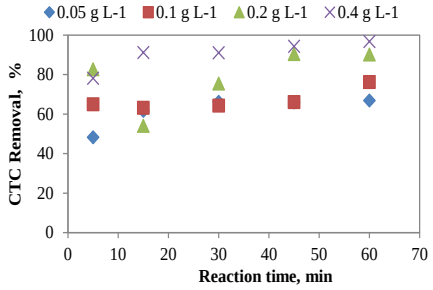


(b)

Fig. 2. Effect of initial solution pH on removal of TC (a) and CTC (b) (Conditions: Ni/Fe bimetallic particle dosage= 0.4 g L^{-1}, C_0= 60 mg L^{-1}, T= 30 ^oC)

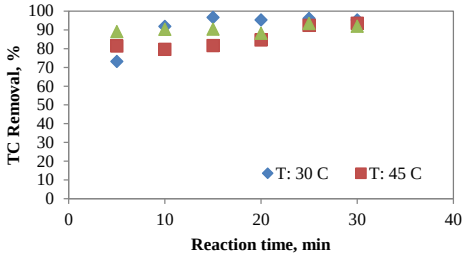


(a)

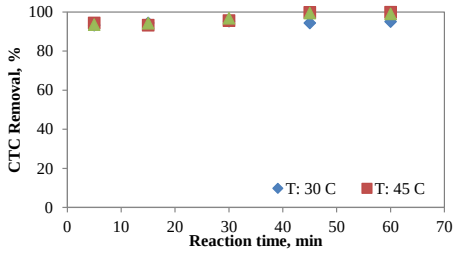


(b)

Fig. 3. Effect of Ni/Fe bimetallic particle dosage on removal of TC (a) and CTC (b) (Conditions: pH=5 (for TC) and pH=6 (for CTC), C_0= 60 mg L^{-1}, T= 30 °C)



(a)



(b)

Fig. 4. Effect of temperature on removal of TC (a) and CTC (b) (Conditions: pH=5 (for TC) and pH=6 (for CTC), C_0= 60 mg L^{-1}, Ni/Fe bimetallic particle dosage=0.1 g L^{-1} (for TC) and 0.4 g L^{-1} (for CTC)).

E. Adsorption Isotherms

Langmuir and Freundlich isotherm models were applied to results obtained from experimental studies. Table I represents constants and correlation coefficients of adsorption isotherms for adsorption of TC and CTC. As seen Table I, equilibrium data obtained from our study fitted very well to the Langmuir model.

F. Adsorption Kinetics

The kinetic parameters are helpful for the prediction of adsorption rate, which gives important information for designing and modeling the processes, in order to determine the adsorption mechanism and the potential rate-limiting steps [3]. The Lagergren's pseudo-first-order and pseudo-second-order models were applied to determine the adsorption kinetics and to calculate the specific coefficients of these models. The experimental results well fitted the pseudo-second-order kinetic model, which indicates that the adsorption rate limiting step may be chemisorption and the adsorption of TC and CTC occurs via surface complexation reactions at specific sorption sites. Table II gives k_2, q_e, and correlation coefficients. The calculated q_e values according to pseudo-second-order kinetic model were close to the experimental q_e values.

TABLE I: LANGMUIR AND FREUNDLICH ISOTHERM COEFFICIENTS

Tetracycline type	T (°C)	Langmuir Isotherm Model q_m (mg g^{-1})	K_L (L mg^{-1})	R^2
TC	30	526.32	19.00	0.999
	45	555.56	35.99	0.999
	60	588.24	5.67	0.996
CTC	30	142.86	0.069	0.999
	45	151.51	0.007	0.999
	60	151.51	0.009	0.999
Tetracycline type	**T (°C)**	**Freundlich Isotherm Model K_f (mg g^{-1})**	**n**	**R^2**
TC	30	538.00	6.27	0.210
	45	534.59	3.56	0.480
	60	304.63	2.50	0.760
CTC	30	183.96	2.88	0.972
	45	128.68	5.05	0.070
	60	206.56	6.75	0.410

G. Degradation Products

The degradation products of TCs were investigated at optimum conditions. The determined degradation products of TC were ETC, EATC, and ATC and their concentrations were 262-460 µg L^{-1}, 22-66 µg L^{-1}, 40-66 µg L^{-1}, respectively. The determined degradation product of CTC was only ACTC with its concentration of 5.20-10.25 µg L^{-1}. According to obtained results, it can be concluded that the degradation process was insignificant and the main removal mechanism of TC and CTC was adsorption on Ni/Fe bimetallic particles.

TABLE II: CALCULATED AND EXPERIMENTAL Q_E VALUES ACCORDING TO PSEUDO-SECOND-ORDER KINETIC MODEL FOR DIFFERENT TEMPERATURES

Tetracycline type	T (°C)	$q_{e(exp)}$ (mg g^{-1})	k_2 (g mg^{-1} min^{-1})	$q_{e(cal)}$ (mg g^{-1})	R^2
TC	30	576.76	0.001	588.24	0.997
	45	554.60	0.001	588.24	0.991
	60	560.45	0.004	555.55	0.998
CTC	30	142.00	0.069	142.86	0.999
	45	143.42	0.007	151.51	0.999
	60	145.17	0.010	151.51	0.999

IV. CONCLUSIONS

In this study, the removal of TC and CTC from aqueous solution by nanoscale Ni/Fe bimetallic particle was investigated. The effect of variables such as pH, particle dosage, initial TCs concentration, contact time, and temperature on the removal of TCs was determined. The pseudo-first-order and pseudo-second-order kinetic models were used to analyze the results obtained ant it was seen that pseudo-second-order kinetic

model well fitted the experimental data. Langmuir and Freundlich adsorption isotherm models were used to sorption phenomena and Langmuir isotherm model fitted the experiment data better than Freundlich isotherm model. It can be concluded that TC and CTC can be efficiently removed by adsorption onto nanoscale Ni/Fe bimetallic particle.

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