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Tetracycline Remove from Synthetic Wastewater by Using Several Methods

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ABSTRACT
Tetracycline (TC), a commonly utilized drug for human and animal therapy, is one of the most widespread antibiotic residues existing in the environment. The lack of sophisticated techniques for the removal of residual tetracycline from wastewater indicates an actual environmental risk. In this study, three methods for tetracycline removal from synthetic wastewater were utilized. Pillared clay was used as adsorbent (alone) and with coagulant (alum) in a hybrid technique. Coagulation and flocculation technique was the first method. The best operation conditions were alum dose of 2.5 mg/L, pH 7 and tetracycline concentration of 10 mg/L. The second method was the adsorption on Al-Fe pillared clay, the optimum operating conditions were found to be pH 4.5, time 120 minutes, tetracycline dose 90 mg/L, and the amount of Al-Fe pillared clay adsorbent 400 mg/L. In the third method (hybrid method), the optimum conditions for the above methods were used. The highest removal efficiency of tetracycline by using coagulation and flocculation only as a coagulant reached 60%. In turn, by using Al-Fe pillared clay it was 90% and in the case of the hybrid method, it was 94%. Thus, the hybrid technique improves the removal of tetracycline from synthesized wastewater.

Keywords: adsorption, coagulation and flocculation, hybrid method, pillared clay, tetracycline removal.

INTRODUCTION

Today, the appearance of drugs in the aquatic environment has become a global case of growing environmental worry [Kimura et al, 2007]. Worldwide, there is an abundance of pharmaceutical products used and existing at very small concentrations (µg/L to ng/L range) [Vona et al, 2015; Utrilla et al, 2013]. They enter the environment by diverse human activities, including direct disposal of unutilized medication liberates from pharmaceutical plants [Utrilla et al, 2013]. Pharmaceutical products could be a menace to both human health and the environment [Quesada et al, 2009] as a result of their physical and chemical properties, especially polarity, microbial resistance [Wang et al, 2010], persistence, water solubility, and bioaccumulation in the food chain [Lúcia et al, 2010]. Tetracycline, in addition to other contaminants, cannot be removed totally in traditional treatment plants [Wu et al, 2014]. The evolution of new clean techniques according to progressively demanding environmental laws requires creative adsorbents, or catalyst supports; in this concept, clays are considered as a resource for materials research [Sergio et al, 2006]. The efficiency of pillared clay minerals (PILCs) to adsorb organic pollutants and herbicides was proven because of their structural pores are geometrically compatible with the volume of the chemical molecules, besides their certain interactions with the pillars and layers of the clay mineral [Cheknane et al, 2010]. Tetracycline, a traditional drag is utilized in the urinary tract, respiratory system, and intestine infections cases. The usefulness of many old antibiotics has been reduced by the development and spread of the antibiotics-resistant strains of the targeted microorganisms, for example tetracycline once was a very effective antibiotic against many types of infections like chlamydia that cause granulomatous conjunctivitis, urethritis, typhus fever, as well as many sexually transmitted diseases and veterinary diseases. They have been now much less effective and fallen out of favor because of the development of drug resistance. However, it still might be able to decrease the duration and intensity of cholera [Boxali et al, 2003]. Worldwide, the utilization of antibiotics as well as the secretion of their metabolites in their original form have been greatly increased in the last decade. Most of ingested antibiotics are imperfectly metabolized, so that a portion of them (25–75%) may exit from human bodies in an unaltered form after use [Khan, Ongerth, 2004].

The main part of utilized antibiotics is secreted to the environment from hospitals, industrial wastewater, urine, and feces [Tran et al, 2019]. Lately, the antibiotics pollution in the environment has led to intense concern, as they are difficult to metabolize by animals and difficult to biodegrade, causing their persistence in the environment. Various processes were utilized for the removal of contaminants, such as coagulation, sedimentation, ion exchange, oxidation, and other. The traditional treatment processes are generally inefficient in antibiotics removal [Al Aukidy et al, 2014]. The costly antibiotics removal needs more suitable, convenient and low-cost removal techniques of antibiotics, for a safer environmental system, hence minimizing the passive effects of the residue antibiotics and their metabolites on aquatic life. In recent years, there have been many studies to find out the magnitude of the antibiotic contamination problem and to evaluate the best methods for treatment of these environmental pollutants utilizing many different treatment techniques. These physical, chemical, and biological processes like adsorption, membrane filtration, chemical oxidation, ozonation, activated sludge, and membrane reactor have been used for eliminating antibiotics residue, including tetracycline. However, these treatment techniques are condition-dependent (e.g., pH and molar ratio) with high cost based on the degree of the pollution in the environmental source that has to be treated [Pan, et al, 2015; Rayaroth, et al 2016].

Pillared clays, manufactured from bentonites, are micro-mesoporous materials with the obvious features of a high specific surface area, lasting porosity, and more hydrophobic than the raw material [Gil et al, 2011]. In addition to the consideration of PILC as alternate catalysts to zeolites, they have been vastly utilized as catalysts and as catalyst supports; they have demonstrated to be efficient adsorbents of different contaminants [Hou et al, 2011]. Pillared clay forms a new category of microporous materials that can be utilized as catalysts [Joel, 2000]. There are some studies that investigate the different method of tetracycline removal. Qingdong Qin et al. studied the combined existence of tetracycline and Cu(II) and used coconut shell-based granular activated carbon (GAC) treated with nitric acid to attain simultaneous removal of these pollutants from water [Qingdong et al, 2018]. Kinetics studies revealed that in spite of the decrease in the removal rate of coexisting tetracycline and Cu (II), the ultimate removal efficiency was boosted in the binary system. Jannat et al. reported the high adsorption efficiency of synthetic zeolite 13X, which was modified utilizing Fe (III), to adsorb tetracycline by a batch system [Jannat et al, 2019]. Moreover, the removal of tetracycline utilizing bentonite and red mud as the major materials and pine sawdust as the additive was investigated by Yanting et al. [Yanting et al, 2020]. Characterization (XRD and SEM analyses) results showed a microporous structure with some crystal strength ingredient. Neutral condition and high temperature were indicated to lead to increased efficiency of tetracycline removal. The results revealed that the effect of coexisting ions (Na+ or Ca2+) on the removal efficiency of tetracycline using bentonite, red mud, and pine sawdust was negative.

In this study, pillared Iraqi clays were prepared by adding $ALCl_3$ and $FeCl_3$ to silt clay, which were used to remove Tetracycline (TC) from synthetic wastewater. Lime (Al $SO_4.18H_2O$) was used as a coagulant –flocculent to remove Tetracycline from synthetic wastewater. Finally, the hybrid (adsorption and coagulation and flocculation) technique was used for the removal of Tetracycline from synthetic wastewater.

MATERIALS AND METHODS

Materials

Tetracycline medicine was the main material in this study. The natural silty clay utilized in the present work was collected from Anbar, Iraq. Aluminum chloride ($AlCl_3$), ferric chloride ($FeCl_3$), sodium hydroxide (NaOH), sulfuric acid (H_2SO_4), were bought from Thomas Baker Chemicals (made in India) and utilized as received.

Preparation of pillared clay

The pillared was prepared as in Figure 1. Several tests (XRD, XRF, SEM, BET and pore volume and pore size) were carried out to characterize the prepared pillared clay.

Preparation of synthetic wastewater

To prepare synthetic wastewater with suitable tetracycline concentration, the shell of Tetracycline capsulate was removed, and then 160g of Tetracycline was dissolved in 500L of distilled water.

Coagulation and Flocculation method

For the coagulation flocculation method, three parameters were used to choose the appropriate operating conditions (pH, change of alum, and change of tetracycline) with constant temperature.

The initial concentration of tetracycline solution was measured using a UV spectrophotometer device. The jar test device was used, which consisted of four 500-liter jars used for this purpose. Tetracycline was placed in each jar (beaker), and H_2SO_4 or NaOH was used to adjust the pH to the relative value. The operation was carried out at a high speed (350 rpm per minute), after which the speed was reduced to 50 rpm for 15 minutes, left to sediment for an hour according to the procedure (ASTM Designation: D 2035 – 80) (Standard Method, 1998). The effect of alum dose, pH, and tetracycline concentration on the removal rate of tetracycline were studied. The pH values ranged from 2 to 12 (2, 4, 6, 7, 8, 10, 12), tetracycline concentrations were 10, 20, 40, 60, 80, and 100 mg, and alum dose was from 0.75 to 4.25 mg/L. The samples were taken from each jar to check immediately the final concentration, find the removal rate by the equation (1); then, the pH that gives the best removal was chosen.

$$\text{Tetracycline removal} = \frac{C_0 - C_e}{C_0} \quad (1)$$

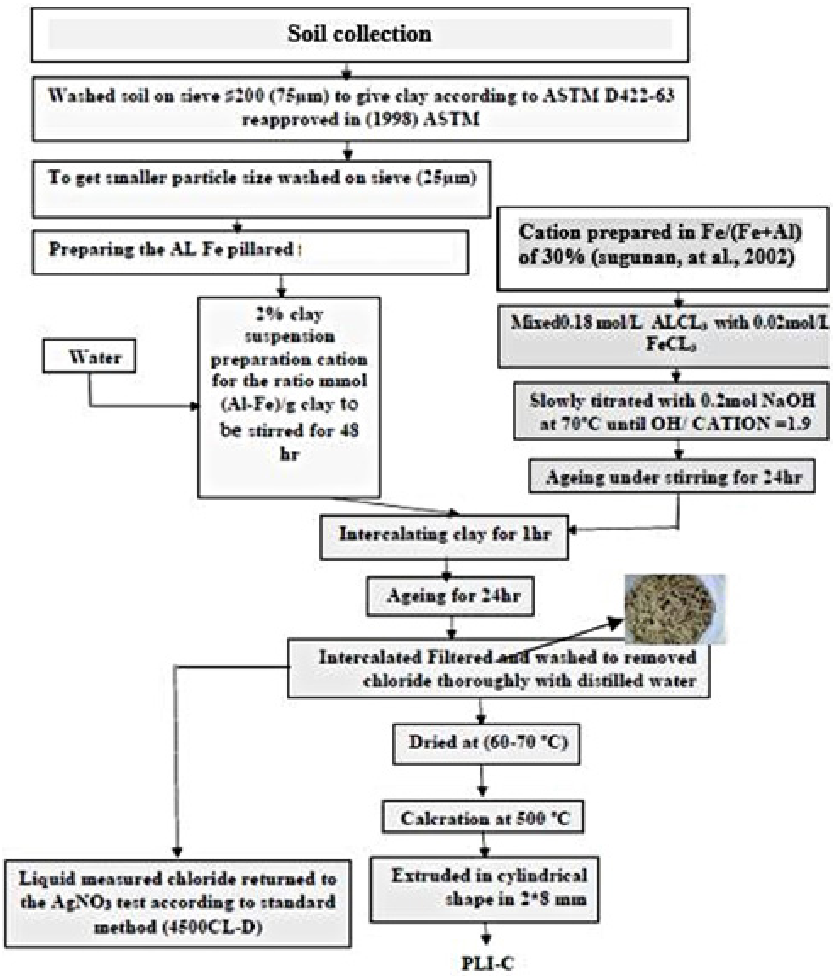

Figure 1. Preparation of pillared clay

Adsorption on pillared clay method

For the adsorption method, three parameters were measured to choose the appropriate operating conditions (change of pH, change of alum dose, and change of tetracycline concentration) with constant temperature. In the same way, the tetracycline solution was prepared, and the jar test device was utilized to perform the adsorption assay. The variables were changed, including pH (from 3 to 11), tetracycline concentration (90, 110, 150, and 200 mg/l) and pillared clay concentration were (200, 400, 750, and 1000 mg/L). The device was running at a speed of 50 rpm for a period of four hours. The samples were collected every half hour until it reached a stable state. The samples were filtered by Whitman filter paper to remove the suspended solid and immediately test by UV spectrophotometer. The removal efficiency is found by eq. (1) [AL Ani et al, 2019; AL-Kindi and Hussam, 2021].

Isotherm models

The variables of isotherm models can be utilized to detect the relation between the adsorbate and adsorbent, describing the surface properties, efficiency of the adsorbents, and the adsorption process mechanism [Kadhum et al, 2021].

The Langmuir model characterized the equilibrium of the adsorption system, where the adsorption process occurs at one layer (monolayer). The linear form of Langmuir equation is written as:

$$\frac{C_{eq}}{q_e} = \frac{1}{q_m} C_{eq} + \frac{1}{K_L\, q_m} \tag{2}$$

where: q_m is the adsorbent maximum capacity in (mg g^{-1}), K_L is the adsorption energy in (L mg^{-1}), C_{eq} (mg L^{-1}) is the equilibrium concentration of adsorbate in solution and q_e is the adsorbate concentration at equilibrium onto adsorbent (mg g^{-1}).

The Freundlich model for heterogeneous surface energy systems is reported as:

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_{eq} \tag{3}$$

where: n and K_f are the Freundlich constants, which can be determined from the slop and intercept of the linear plot of ln q_e versus ln C_{eq}.

The Temkin model has been utilized in the following formula:

$$q_e = \beta \ln \alpha + \beta \ln C_e \tag{4}$$

where: β = (RT/b), T is the absolute temperature in Kelvin, R (8.314 J/mol K) is the universal gas constant, and b is the Temkin constant (J mg^{-1}); α and β are calculated from the linear plot of q_e vs. ln Ce which represent slop and intercept.

Adsorption kinetics

The kinetics involves significant relations for investigating the adsorption processes. Pseudo-first order demonstrates the adsorption process which follows the first order mechanism.

$$\ln(q_e - q_t) = \ln q_e - K_1 t \tag{5}$$

where: q_t is the adsorbate adsorbed at time t (mg/g). K_1 is the rate constant of adsorption (min^{-1}), which is found by plot ln ($q_e - q_t$) versus t.

Pseudo-second order assumption is that the ratio of adsorption depends on the available sites on the adsorbent. The linearized form is as follows [Ho, et al, 2000].

$$\frac{t}{q_t} = \frac{1}{K^2 {q_e}^2} + \frac{t}{q_e} \tag{6}$$

Hybrid method

The hybrid method is based on the combination of the coagulation and flocculation method with adsorption, where the test was carried out using a jar inspection device. In this method, the variables used according to the best operations conditions were obtained from previous methods (flocculation and coagulation, and adsorption). These variables (pH, tetracycline concentration, and adsorbent dose) were from the adsorption method; also, the alum dose was added according to the coagulation and flocculation process.

RESULTS AND DISCUSSION

Characteristics of Al-Fe pillared clay

According to ASTM D3663, ASTMD 3908, and ASTM D1993, surface area, pore size, and pore volume were found as shown in Table 1.

Table 1. Surface area, pore volume, and pore size of Al-Fe pillared clay (BET analysis)

Surface area (m^2/gm)	Pore volume (cm^3/gm)	Pore size (Å)
97.8157	0.0962	77.4

The pore sizes of the pillared clay were classified as mesopores, depending on the International Union of Pure and Applied Chemistry (IUPAC) classification which characterize the pore size (Å) as [Nicoleta et al, 2013]:

- macropore (≥ 500),
- mesopore (20 to 500),
- supermicropore (7–20),
- ultra-micropore (≤ 7).

X-ray diffraction (XRD) is a commonly utilized technique for phase identification of crystalline structure and to provide identification for the minerals of finer grained sediments, particularly clays [International Center for Difraction, 1990]. According to the XRD patterns given in Figure 2, montmorillonite (M), quartz (Q), and calcite (C) phases were recognized in the investigated Al-Fe pillared clay sample [28].

Scanning electron microscopy analysis (SEM) was utilized to realize the morphology of Al–Fe pillared clay and conceive the surface reaction. As illustrated in Figure 3, which gives the images of Al–Fe pillared clay, the pores and surface roughness in various scales (5, 10, and 50 µm) and boundaries of crystals regions were described in a circular around it. From the images of pillared clay, the presence of combinations needles, comprising clusters of active ingredients, is dramatically clear.

Coagulation and flocculation method

The best operating conditions were found by studying the effects of three parameters (pH, change of alum, and change of tetracycline) on the removal rate of tetracycline with constant temperature.

Effect of coagulant dose

The efficiency of the coagulation process can be considerably influenced by surface charge due to the coagulant mass. Furthermore, economically, the investigation of the optimum coagulant dosage is an important matter.

The influence of coagulant dose on the removal rate of tetracycline is illustrated in Figure 4. The effect of the coagulant (alum) dose was

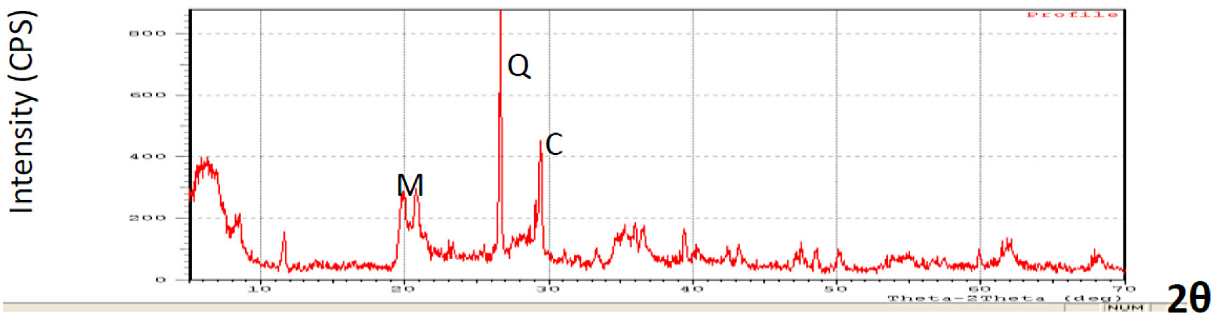

Figure 2. XRD pattern of AL-Fe pillared clay

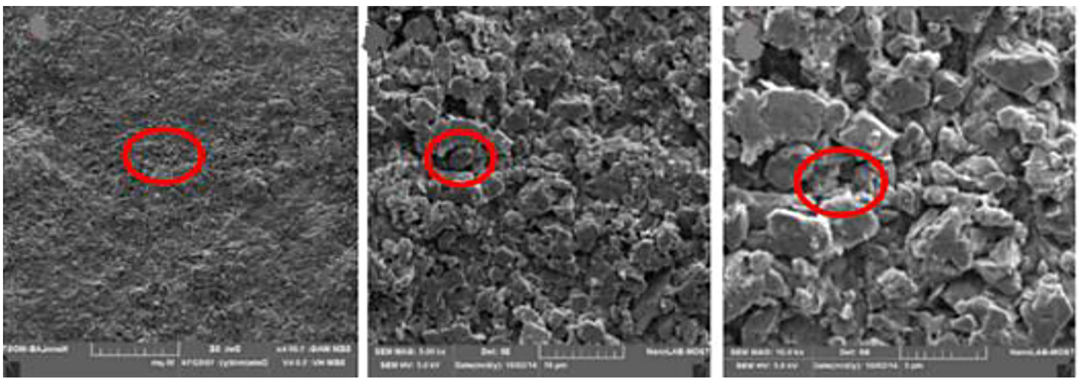

Figure 3. SEM images of Al-Fe pillared clay

studied over the range from 0.75 to 4.25 mg/L. The highest removal rate of tetracycline (56%) was gained with coagulant dose of 2.5 mg/L. As it is obvious in Figure 4, the removal rate of tetracycline increased along with alum dosage. The two probable reasons are the generation of flocs and acidic anion compounds due to electrostatic reactions and the increase in alum dose results in raise in the adsorption sites. At relatively high coagulant dose (> 2.5 mg/L), the continued adsorption of the mono- and polynuclear hydrolysis species of the active group on the surface of alum will invert the surface charge of particles [Kumar et al, 2012].

pH influence

To obtain the optimum pH, the impact of TC solution pH on the removal rate of TC was studied over range (2–12). As seen in Figure 5, as the pH value was raised from 2 to 7, the removal rate of TC increased from 58 to greater than 64%. The proposed cause of this behavior is the increase in OH ions reactions with the Fe and Al species in TC to generate more ferrite polymers, thus enhancing the bridging flocculation. At the same time, the colloids particle charges were reduced by the charge neutralization mechanism, improving the destabilization of the colloidal particles in solution.

At pH value greater than 7, the removal rate of TC decreased with increase in pH until it reached 51% at pH 12. The protonation of TC functional groups at neutral pH improves the coagulation efficiency of TC. Furthermore, for alkaline water, the coagulant would be exposed to hydrolysis, preventing the bridging flocculation [Okuda et al, 2001]. Coagulation of alum in water is heavuly influnced by the solution pH, in order that many

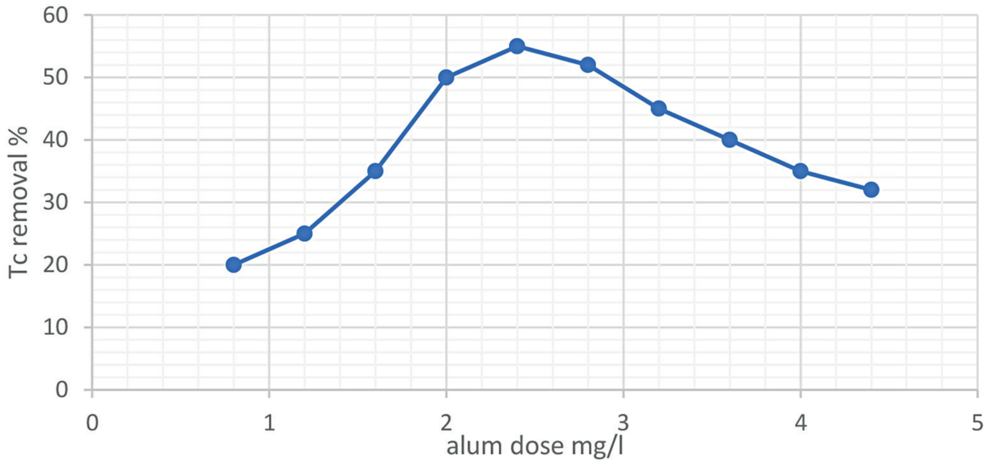

Figure 4. Effect of alum dose on TC removal

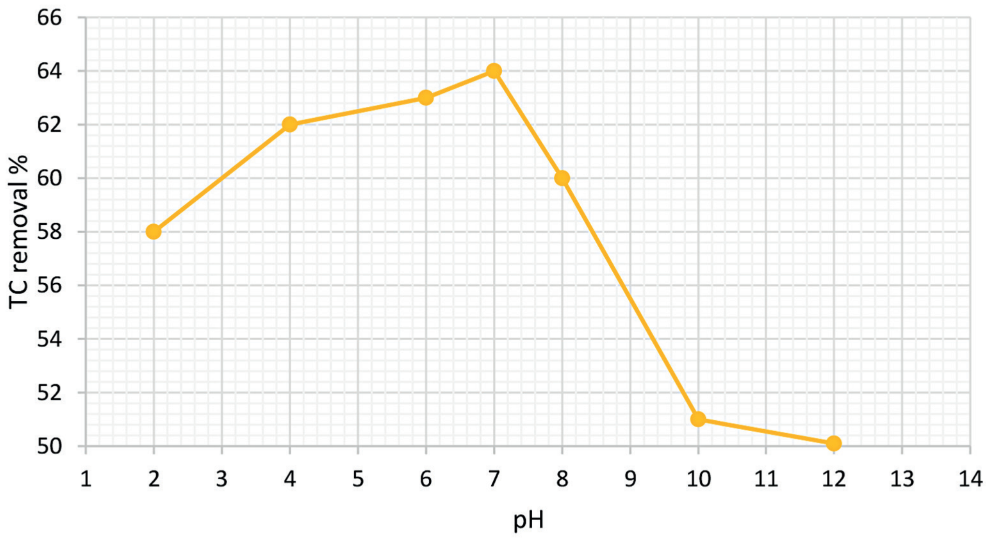

Figure 5. Influence of water pH on TC removal

probable mechanisms of alum coagulation may be suggested. The maximum removal rate of TC was gained at the pH value of 7.

Effects of tetracycline concentrations

The effect of the initial concentration of TC was investigated utilizing a 10–100 mg/L TC concentration. In general, various concentrations result in variations in the driving force. As illustrated in Figure 6, the increase in the TC initial concentration caused a decrease in its removal efficiency due to the excess concentration of TC compared to the constant dosage of alum. A similar result was reported by [Šćiban et al, 2009]. The capability of the alum to act at various TC concentrations might indicate its ability to remediate different waters.

Adsorption on pillared clay and hybrid method

Impact of pH

The effects of media pH on the adsorption of TC onto PILC were assessed over the pH value range from 3 to 11 using HCl or NaOH for pH solutions adjustment, as illustrated in Figure 7. These values were selected depending on the TC solubility, which were investigated in previous study [Roca et al, 2017].

For the PILC, various results were obtained after two hours based on the pillaring agent. At low pH, the adsorption on Al-Fe-PILC as well as adsorption and coagulation (hybrid system) exhibited the highest removal rate of TC, and abruptly decreasing as the pH increased. The proposed cause of this behavior is the interaction between

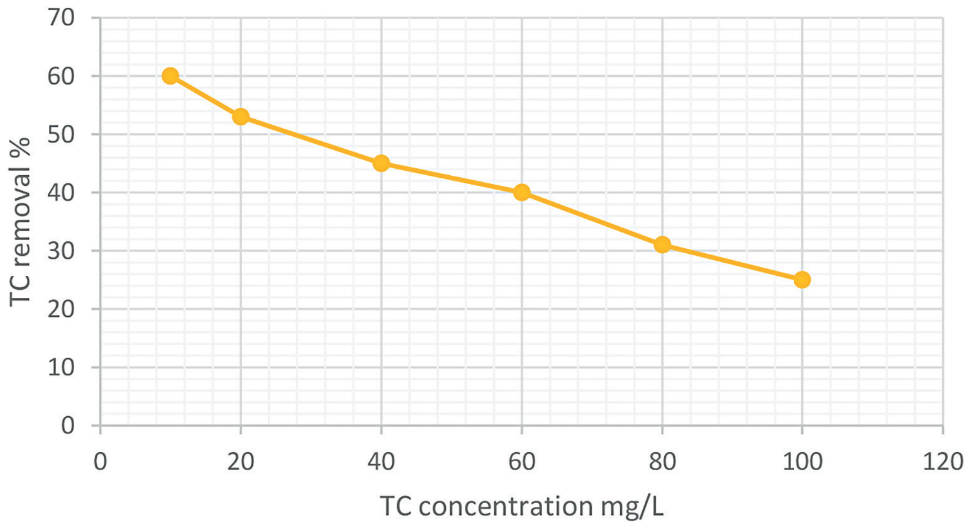

Figure 6. Effect of TC concentration on TC removal

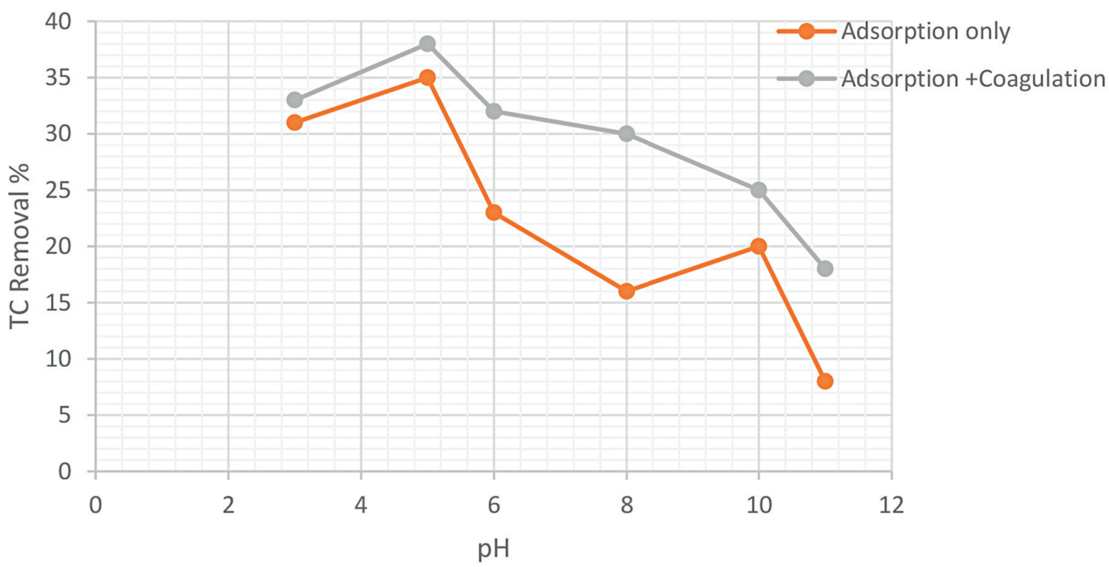

Figure 7. Effect of pH on TC removal by Al-Fe pillared clay adsorption only and with hybrid process

the opposites surface charges (the (-) Al-Fe-PILC and the (+) species of TC) preferring the adsorption at low pH conditions (< 5) [Marco-Brown et al, 2012]. Similar adsorption results were reported for Rhoda mine B and diclofenac on Al-Fe-PILC [Mabrouki, Akretche, 2016; Hou et al, 2011]. With coagulant 2.5 mg/L alum, the TC removal increased slightly with increasing pH.

Effect of Al-Fe pillared clay dose

The influence of various Al-Fe pillared clay doses was studied. The experimental conditions were pH of 4.5, TC concentration of 110 mg/L, ambient temperature, and different of adsorbent doses (200-400-750- and 1000 mg/L). The results showed that the TC removal increased with the adsorbent dose increasing until 400 mg, then it decreased. These results are shown in Figure 8. The removal efficiency of TC was about 69% at 1000 mg/L pillared clay dose, which is related to TC properties. The highest removal rate of TC (90%) was reached with 400 mg/L Al-Fe pillared clay dose. These results may be due to the unsaturated adsorption sites and the probable agglomeration of excess adsorbent particles which lead to decrease the specific surface area of the adsorbent [Kalavathy et al, 2010; Kadhum et al, 2021].

The other group has the same conditions, excluding the addition of 2.5 mg/L coagulant dose. The results demonstrated that the TC removal rate increased along with the adsorbent dosage with coagulant up to 400 mg/L adsorbent dose, and then it decreased. The maximum removal efficiency of TC was 95%. That is attributed to the characteristics of TC.

Effect of tetracycline dose

The effect of the initial concentration of tetracycline on the removal rate of tetracycline was studied using different concentrations of TC (90, 110, 150 and 200) mg/L. The experimental results showed that the TC removal rate increased with the decrease of initial concentration of TC, as illustrated in Figure 9. The maximum removal rate of TC was 90%; that was due to the characteristics of TC [Mayerly et al, 2018].

The effects of the same different doses of TC (90, 110, 150 and 200) mg/L with 2.5 mg/L of alum were investigated. The results demonstrated that the TC removal rate increased with the decrease in TC concentration, and the maximum removal efficiency of TC was 94%, as shown in Figure 9. The same behavior and result were due to the same reason in adsorption with Al-Fe pillared clay.

Isotherm models

The adsorption isotherms of tetracycline on PILC are illustrated in Figure 10. Adsorption models (Langmuir, Freundlich, and Temkin) were utilized to fit the experimental results. The parameters of adsorption models are reported in Table 2. The correlation coefficient (R^2) for the Langmuir, Freundlich, and Temkin models are (0.9863, 0.9397, 0.985), respectively. These results denote that the Langmuir isotherm has the greater (R^2) for PILC when compared with the

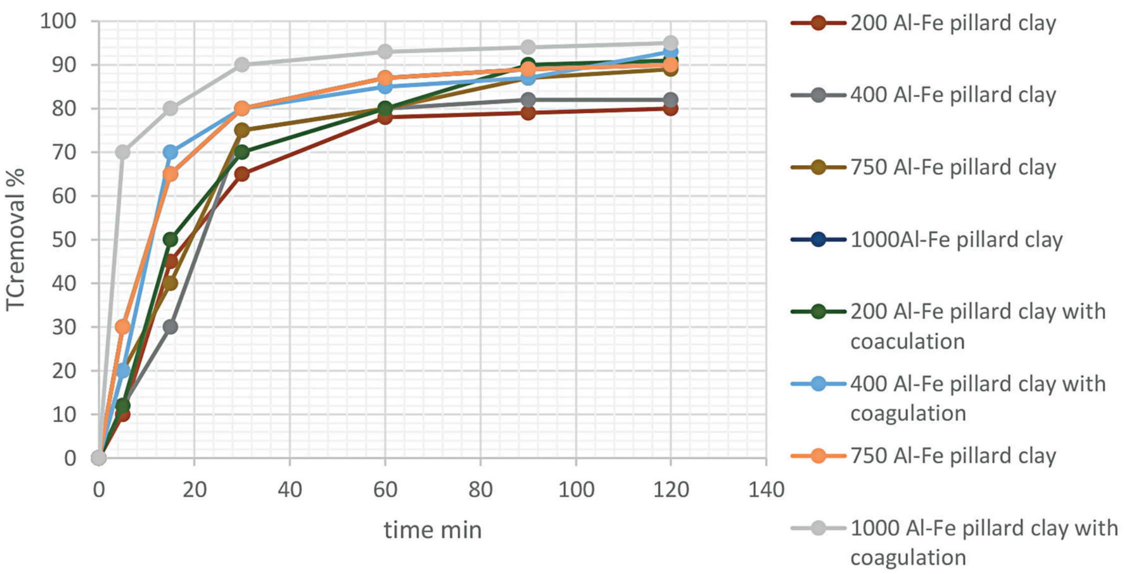

Figure 8. Effect of Al-Fe pillared clay dose and Al-Fe pillared clay with coagulation on TC removal

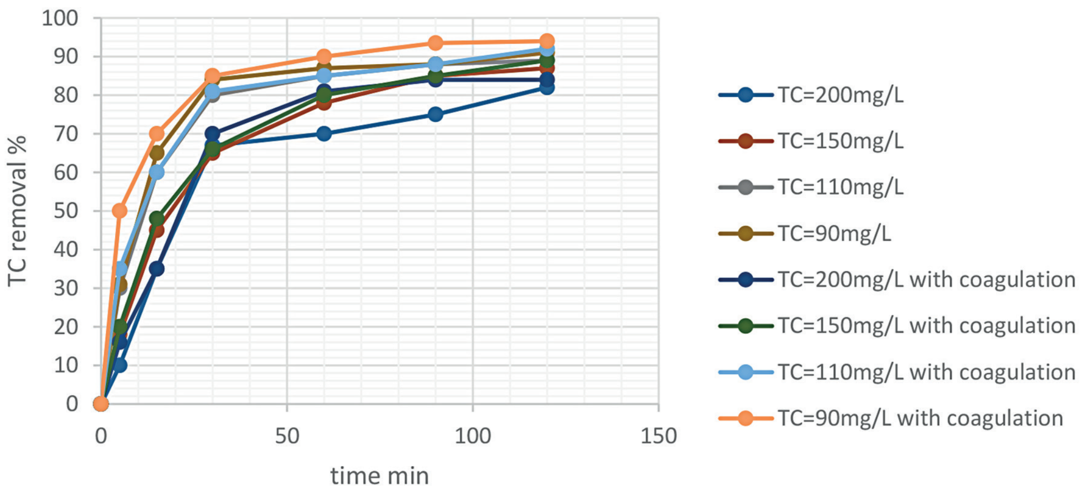

Figure 9. Effect of different TC concentration with Al-Fe pillared clay and Al-Fe pillared clay with coagulation on TC removal

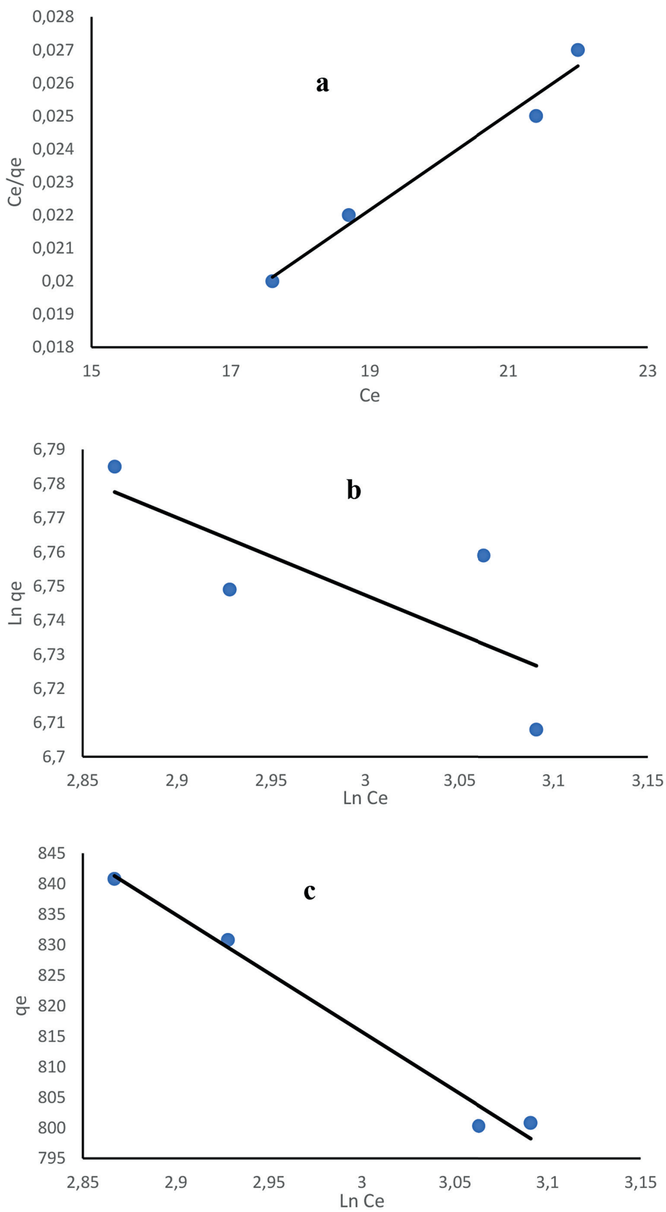

Figure 10. PILC isotherm models: (a) Langmuir, (b) Freundlich, and (c) Temkin

other isotherms. Therefore, the Langmuir isotherm (with the assumption of monolayer and uniform activity onto the adsorbate) gives a better fitting result. The value of RL (0 <RL <1) favor the adsorption of tetracycline onto PILC. According to these results, it can be concluded that PILC show a better fitting model with experimental data [Tonghao et al, 2012].

Table 2. Isotherm's parameters and correlation coefficients for adsorption of tetracycline on PILC

Isotherms	Constants	Values
Langmuir	q_{max} (mg/g)	588.23
	K_L (L/mg)	0.18
	R_L	0.05
	R^2	0.9863
Freundlich	K_f	2.66
	n	0.05
	R^2	0.9397
Temkin	α (L/mg)	1399.6
	b_t (J/mole)	12.89
	R^2	0.985

The kinetics models

The kinetics of tetracycline adsorption onto PILC was studied by utilizing pseudo 1st and 2nd order kinetics models as illustrated in Figure 11. The parameters and correlation coefficients R^2 of kinetic models are reported in Table 3. As shown in this table, the correlation coefficient of pseudo first order (0.9682) is greater than for second order (0.9282). These results indicate that the adsorptions kinetic data can be predicted well by the pseudo 1st order model.

CONCLUSIONS

The hybrid method (coagulation-flocculation and adsorption) was found to be the best technique and a good alternative for the tetracycline removal from synthesized wastewater. The experimental data confirmed a good fit to the Langmuir adsorption isotherm and Pseudo 1st order adsorption kinetics model. For hybrid method, the optimal operating conditions which give maximum

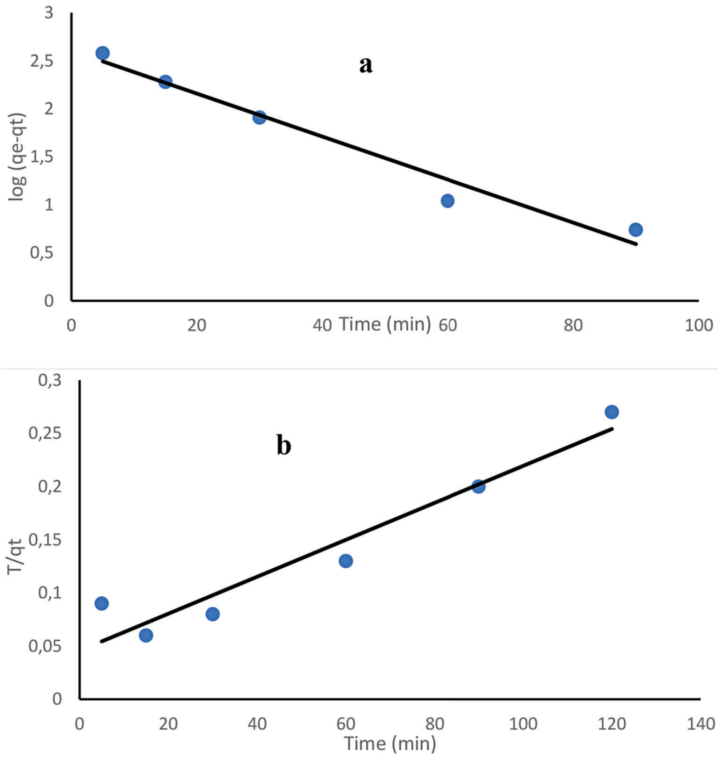

Figure 11. Kinetic for adsorption of tetracycline onto PILC: (a) Pseudo 1st order; (b) Pseudo 2nd order

Table 3. Kinetic parameters for the sorption of tetracycline onto PILC

Pseudo 1st order			Pseudo 2nd order		
qe (mg/g)	K_1 (min^{-1})	R^2	*qe* (mg/g)	K_2 (min^{-1})	R^2
402.7	0.0515	0.9682	588.23	0.00006	0.9282

removal rate of tetracycline (95%) were pH of 4.5, the Al-Fe pillared clay dose of 450 mg/L, and alum dose of 2.5 mg/L.

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