SIMULTANEOUS ADSORPTION OF TETRACYCLINE AND AMOXICILLIN BY CLADOPHORA AND SPIRULINA ALGAE BIOMASS

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ABSTRUCT

Adsorption studies were performed at different initial Tetracycline (TC) and Amoxicillin (AMO) concentration, different biomass dosage and type, contact time, agitation speed, and initial pH. In the batch mode were investigated. The optimum pH of solutions is 6.5 for TC and 5 for AMO, agitation speed 200 rpm and concentration 50 ppm. The results in FTIR showed that there were -OH and amides (N-H) and other functional groups on the surface of Cladophora and Spirulina algae. The equilibrium isotherm data were modeled with Freundlich, Temkin, and Langmuir isotherm models. The data best fitted with the Langmuir model. The maximal adsorption capacity from the Langmuir model was (9.86, 20. 5 mg/g) for TC and (7.89, 17.4 mg/g) for AMO on Cladophora and Spirulina algae, respectively. Finally, the pseudo-second-order kinetic model was best fitted the experimental kinetic data of TC and AMO onto Cladophora and Spirulina algae biomass with a high coefficient of determination between 0.97 and 0.99. Cladophora and Spirulina algae, low-cost and eco-friendly adsorbents, can be used to adsorb the TC and AMO from the solution.

Keywords: Tetracycline, Amoxicillin, batch, kinetic, isotherm

امتزاز التتراسايكلين والاموكسيسلين بواسطة كتلة الطحالب الحيوية الكلادوفورا والسبارولينا

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المستخلص

تم دراسه امتزاز نظام الوجبة الواحدة عند تراكيز مختلفة من التتراسايكلين (TC) والاموكسلين (AMO) ،كمية المادة المازة ونوع الطحالب ، زمن التلامس ، سرعة الاهتزاز و الرقم الهيدروجيني. أفضل ظروف عند حامضية pH= 6.5 للتتراسايكلين و pH=5 للاموكسيسلين، زمن تلامس 2.5 ساعات، سرعة اهتزاز 200 rpm و التركيز الأولي للملوثين 50 ملغم/لتر. تم تشخيص المواد المازة المستخدمة بأستخدام جهاز محلل (FTIR) طيف الاشعة تحت الحمراء وتم ايجاد المجاميع الفعاله (-OH) ,amides (N-H) على سطح الطحالب الخضراء Cladophora والطحالب الخضراء المزرقة Spirulina. كانت البيانات متطابقة مع الموديلات الثلاثة المستخدمة Temkinو Langmuir و Freundlich . وتم اختيار افضل موديل رياضي يُمثل النتائج العملية فوجد ان موديل لانكَمير (Langmuir) هو افضل الموديلات وكانت قابليه الامتزازفي موديل لانكمر (9.86، 20. 5 mg/g) للتتراسايكلين و (7.89، 17.4 mg/g) للاموكسيسلين على سطح Cladophora و Spirulina بالتعاقب. البيانات الحركية اتبعت موديل الحركية من الدرجة الثانية للمضاد الحيوي حيث معامل الارتباط (Correlation coefficient) 0.97–0.99. الطحالب الخضراء Cladophora والطحالب الخضراء المزرقة Spirulina قليلة الكلفه ومادة مازة صديقه للبيئة لامتزاز التتراسايكلين والاموكسيسلين.

الكلمات المفتاحية: التتراسايكلين، الاموكسيسلين، نظام الوجبة الواحدة، الحركية، الايسوثرم.

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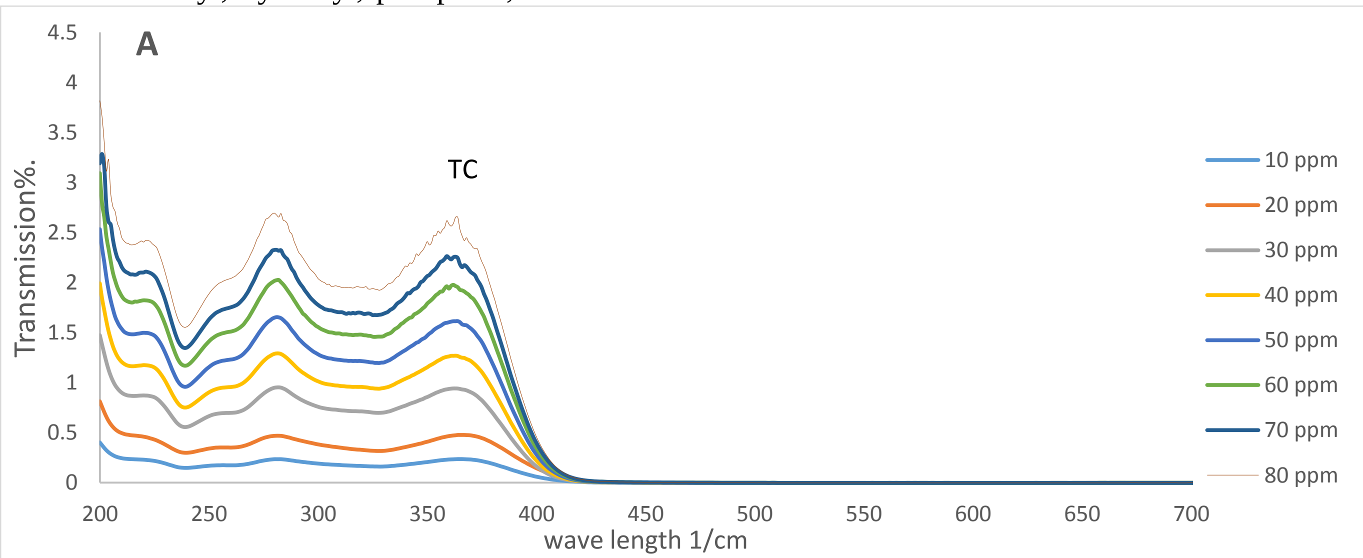
INTRODUCTION

Various concentrations of pharmaceutical products were found in the effluent of a wastewater treatment plant. Water purification is affected by antibiotic-resistant bacteria in water sources (**8**). The engineering structures (wastewater treatment plant) are not designed to eliminate antibiotics nor microorganisms (24)**.** Hence antibiotics are regarded as toxic and hazardous chemicals. Before discharging wastewater into the environment, it is highly important for antibiotic residues to be removed before treated wastewater disposal to surface water, but it usually involves high cost (3). The adsorption process is being widely used by vario.us researchers for the removal of antibiotics from waste streams, offering significant advantages like the low cost, availability, profitability, ease of operation, and efficiency, in comparison with conventional methods, especially from economic and environmental points of view (2). The lack of information about using algae biomass to remove antibiotics from wastewater needs to be studied. So that in this work, the ability of algae biomass to remove antibiotics from wastewater will be explored. It has been found in many kinds of research that algal biomass is rich in functional groups, such as carboxyl, hydroxyl, phosphate, amine groups, and so on. Therefore algae biomass was the target to investigate its ability to remove different types of antibiotics from aqueous solutions (26). For that, the current research aims to prepare and characterize the algae biomass for removing TC and AMO from wastewater.

MATERIALS AND METHODS

Sorbate (Tetracycline, Amoxicillin)

Powdered Tetracycline (TC) used in this study and Amoxicillin (AMO) were obtained from a general company in the drugs industry (Samarra, Iraq) (original manufacturer: Merck, Germany), Fig. 1 (A, B) sho.ws the scan UV-V (visible spectrophotometer) was used to measure the concentration of antibiotics in the solution (Model: Cary-100 conc., Varian, USA), for the TC and AMO, respectively at AlKhawarizmi University lab at wavelength 360 nm for TC and 230 nm for AMO. Table 1 summarizes antibiotic characteristics. Wavelength scanning at different TC concentrations yielded the respective adsorption spectra, the determination of TC (21). Stock standard solutions were prepared by adding 1 g of the pure substance and dissolving it in distilled water to obtain TC and AMO concentration 1000 mg/L. The pH value measured by (pH meter: ISOLAB).



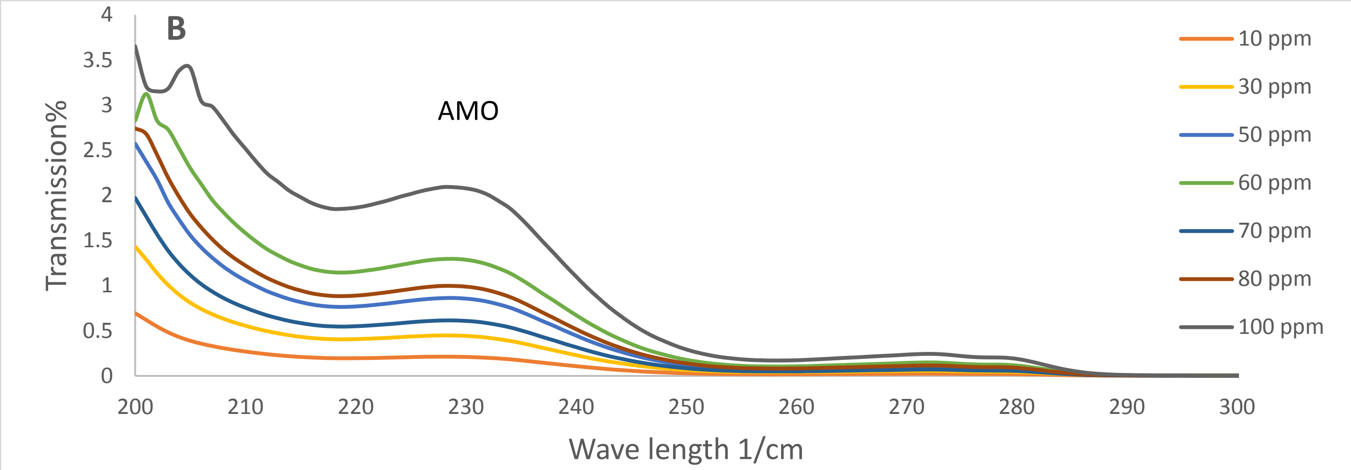
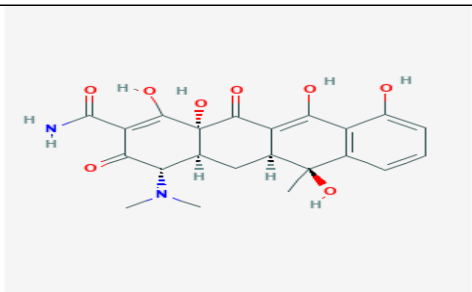
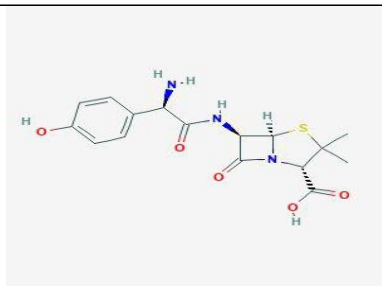


Fig. 1. Full scan UV-V is spectrum of A) TC, B) AMO

Table 1. Characteristics of TC and AMO. (14)

Property	TC	AMO
Chemical structure	 $C_{22}H_{24}N_2O_8$	 C16H19N3O5S
Color	**yellow**	**white**
molecular weight	**480.9 g/mol**	**365.4 g/mol**
purity	**98%**	**97.5%**
pKa with different pH value	**p*K*a1 =3.30** **p*K*a2 = 7.70** **p*K*a3 = 9.27**	**p*K*a1 =2.67** **p*K*a2 = 7.11** **p*K*a3 = 9.55**

Sorbent (algae biomass preparation)

Two kinds of algae biomass were used; the first one was local algae biomass [Cladophora]. It was used in this work as biosorbent for TC and AMO removal from aqueous solution. A mass of wetted algae collected from the artificial irrigation canal near the College of Engineering at the University of Baghdad in March of 2019. The water in this canal fed from the Tigris River. Fig. 2 shows the collected algae. A random sample of the collected wet mix algae was analyzed for their species and content percentage of each type by using a microscope at the laboratories of the Biology Department, Science College, the University of Baghdad as given in Table 2.

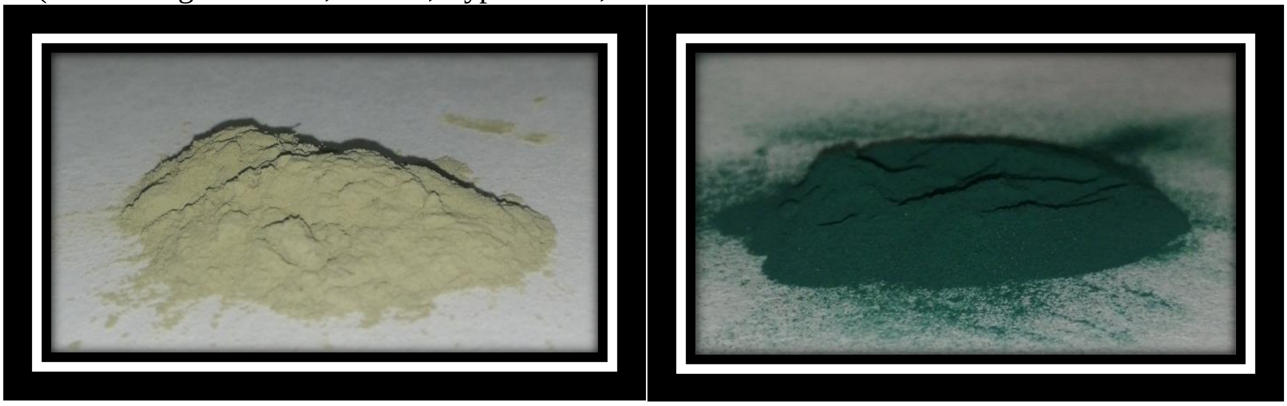
Fig. 2. The algae collection location (Cladophora)

Table 2. The genus, species and percentage weight for mixed algae

Algal species	Percentage ٪
Cladophora	**85**
Microalgae	**10**
Impurities	**5**

Two types were found in this sample, Cladophora algae were the highest percentage.

After the collected step, algae were washed many times with tap water to g.et rid of impurities, dirt and other unwanted materials such as (non-vertebrate animals, small worms, crustaceans, bird feathers), then with distilled water twice to ensure clearness (12, 7). The washed algae were left under the sun for three days to dry (2). Fig. 3A Shows the dried Cladophora algae biomass was cut off, ground in (Grinder Agate mortar, Retsch, Type BB1A, Ma.sch.Nr.4323, Germany). And sieved in (RETSCH sieves) to get grain size powder or <63 µm for biosorption in batch experiments. Fig. 3 B shows the second type used in this study was a pure Spirulina Algae biomass (supplied from amazon) was used in this work as biosorbent for TC and AMO removal from aqueous solution. As powder less than 63 µm in particle size.



(A) (B)

Fig. 3. A. Powder size of Cladophora dried algae biomass. B. Pure Spirulina algae powder

RESULTS AND DISCUSSION

FTIR analysis of algae biomass

The adsorption capacity of solid adsorbents not only depends on the surface area but also on chemical surface functional groups. The purpose of the FTIR analysis is to identify the different functional groups found on the algae cell surface of biomass that is responsible for the adsorption process. The adsorbent functional groups impact the action, as well as control the mechanism of adsorption (23). The peaks shown in the FTIR spectrum were allocated to several active sites according to their wavenumbers. **Figure 4.** shows the FTIR spectrum of Cladophora and Spirulina algae biomass as powder algae before sorption. The wavenumber was measured within the range of 400–4000 cm^{-1}. Among the active sites, aromatic, amine, hydroxyl, and carboxylic acid have been suggested to be responsible for the adsorption of antibiotics on the adsorbent surfaces. These negative charge groups like sulfate, carboxyl, amino, and hydroxyl groups can be credited to the contaminant uptake of biomass (22).

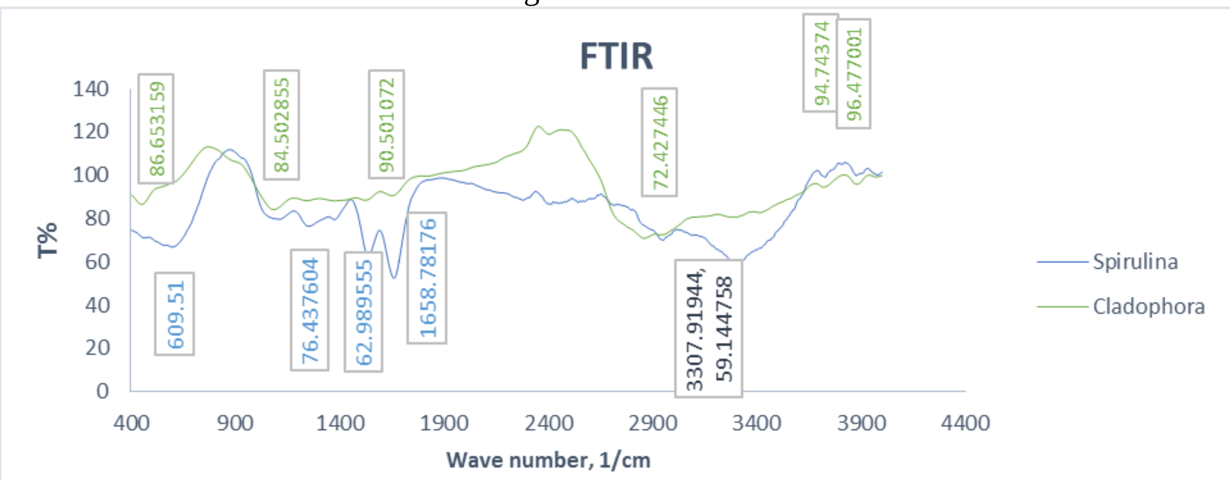


Figure 4. FTIR spectrum of pure algae biomass (Cladophora ,Spirulina)

Effects of parameters in batch system.

Effect of Initial concentration

Biosorption efficiency as a function of initial concentration for TC and AMO ranged from 10 to 70 mg/l was studied by adding the biosorbent dosages into 100 ml of aqueous phase. Figure 5 shows that the removal efficiency of TC and AMO onto the algae biomass as powder. The removal efficiency decreased from higher values (> 90 .%) to lower values (< 50 %) as a function of antibiotic concentration.(20). In contrast, small reduction in the removal efficiency of TC and AMO onto the algae biomass (powder, beads) for (20-50 mg/l) range of initial concentration was observed. This can be attributed to large active (binding) sites available in the biosorbent dosage (0.2-0.5g/ 100 ml) Spirulina and Cladophora powder respectively, 200 rpm and 2.5 hr used in this set of experiments. pH= 6.5 for TC experiment sets, pH=5 for AMO experiment sets. H.ence, the initial concentration (Ci) of 50 mg/l was used for remaining batch experiments. Reduction in the efficiency explained by the saturation of the available reactive adsorption sites on the sorbent surface while increasing initial concentration (9).

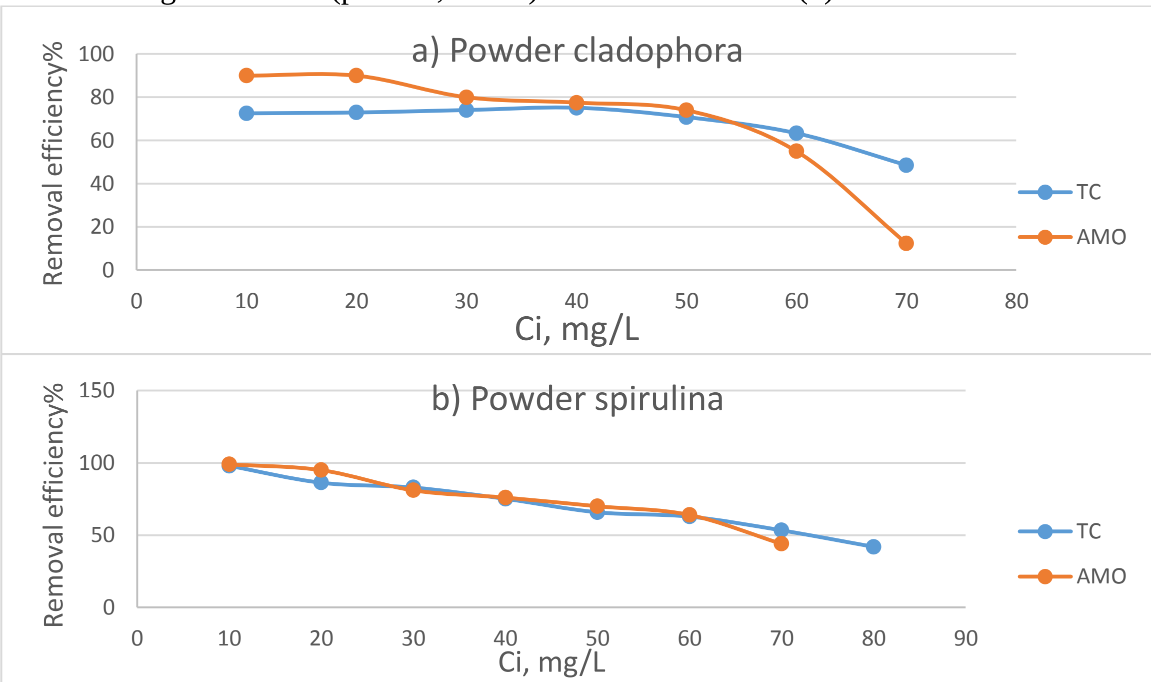


Fig. 5. Effect of in.itial concentration on the re.moval efficiency of antibiotic by a) cladophora and b) spirulina algae biomass as powder (pH_{TC} 6.5, pH_{AMo} 5, $mass_{(cladophora)}$= 0.5 g/100ml, $mass_{(spirulina)}$= 0.2 g/100ml, 25°C, speed= 200rpm and time=2.5hr)

Effect of algae biomass dosage

The effect of varying the adsorbent dose (mass) on the adsorption of antibiotic are shows in Figure 6. The biomass dosage is a significant parameter used to determine the capacity of biosorbent for specific initial concentration, it is one of the mos.t essential factors that effected the biosorption process (4). In this work various amount of algae biomass as powder (0.05-1.25 g/100 ml) were used. By increasing the amount of algal biomass, the pollutants may be fully adsorb or reach an equilibrium state when reaching a plateau at a fixed concentration of each pollutant (1). It is clearly seen that the removal efficiency of antibiotic increases by Cladophora and Spirulina from 10 to 98%, and from 20 to 98 %, respectively, as the algae mass (m) (powder) increases from 0.05 to 1.25 g, respectively. An increase in the biomass weight generally increases the amount of solute biosorbed, due to the increased surface area of the biosorbent, which in turn increases the number of vacant binding sites (16). Increasing biomass concentrations positively increase final bio-removal, although it negatively affects biosorption capacity due to the fact that fixed initial concentration led to unsaturated active site on biomass surface and an increase in the biomass concentrations cause particle aggregation (25). At low biomass doses, the surfaces became saturated faster because all locations were totally exposed to the pollutant, a higher value of qe.

Nevertheless, at higher dose of the biomass, the availability of higher energy, decreased as the fraction of lower energy sites occupied increased, resulting in a lower qe value (22). Increasing of removal efficiency with algae dose may be as a result of the increased surface area results in existence of greater quantity of sorbent sites available for antibiotics sorption (14). Based on these results, 1.25, 0.5 g /100mLwas selected as the best dose of cladophora powder, spirulina powder, respectively, for the next experiments.

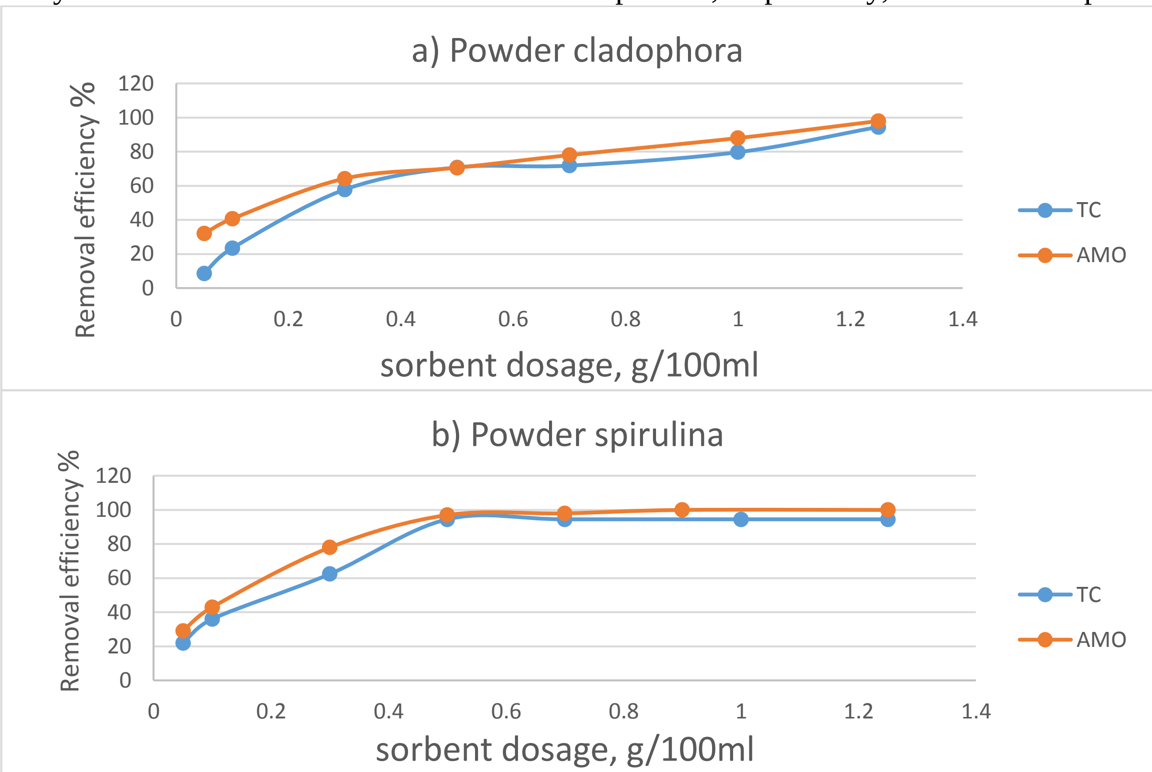


Figure 6. Effec.t of sorbent am.ount on th.e remo.val efficiency of antibiotic by a) cladophora and b) spirulina algae biomass (pH_{TC} = 6.5, pH_{AMo} = 5, 25˚C, Co.= 50 mg/L , speed= 200 rpm and time=2.5hr)

Cont.act time and . pH of solu.tion

The influence of contact time and initial pH on the sorption of TC using Using (1.25, 0.5) g of cladophora powder, spirulina powder respectively, for 100 ml of contaminated solution at 25°C is illustrate in the Figure 7. The adsorption process was quick at the beginning, (nearly at the first 90 min), and then a small increase occurs until the adsorption attained equilibrium. Rapid adsorption at the earlier contact time often be attributed to the active sites existence on the adsorbent, in another hand, slow adsorption rate is likely due to the adsorbate slow diffusion molecule into the adsorbent bulk (19). 2.5 hr was chosen as equilibrium time, since the adsorption process attained equilibrium at that time. The experimental results proved that the biosorption performance is affected significantly by the initial pH of the liquid phase. Clearly, the adsorbed amounts of each antibiotic onto algae biomass was increased with pH increasing from (5 to 7) for TC and from (4 to 6) for AMO, and subsequently it was decreased with below or above this value of pH, this is due to high concentration of hydrogen ions (11). These ions can be competed the active groups for binding with available sites on the algae biomass. Higher TEC removal efficiency (98.21%) was obtained at pH 6.5, after this value, the efficiency decreased from 98.21 to 29 % as shown in Fig. (8 a) .Such adsorption behavior can be explained according to the electrostatic interactions between antibiotic molecules and surface of algae biomass. TEC molecule has several ionizable functional groups like dimethylammonium, tricarbonylamide and phenolic diketone groups (14). These active groups undergo protonation–deprotonation reactions. Zwitterion species of H2TEC0 are formed in case of the solution pH were from 3.3 to 7.7. At pH > 7.7, anion species of HTEC−/TEC2−

were dominant in the aqueous solution (13) The pHpzc (Point Zero Charge) of the cladophora and spirulina algae biomass was determined to be (7-7.8) respectively (10). Oppositely at pH < pHpzc, ions of H+ are transferred to the particle surface and combined with OH- groups leading to a positive charge algae surface. Under these circumstances, the net surface charges of the algae biomass at pH < 7were positive, thus the electrostatic attraction may take place among them and negatively charged tr.icarbonylamide groups of TEC which is resulting to high TEC removal efficiency. When the pH was below 5, the electrostatic repulsion between the positively charges of algae surface and cationic moieties of TEC was behind the decreasing in the TEC adsorption efficiency (14). Same results were obtained in case of AMO adsorption onto algae biomass, maximum removal efficiency was 98% at pH 5 (Fig 8).

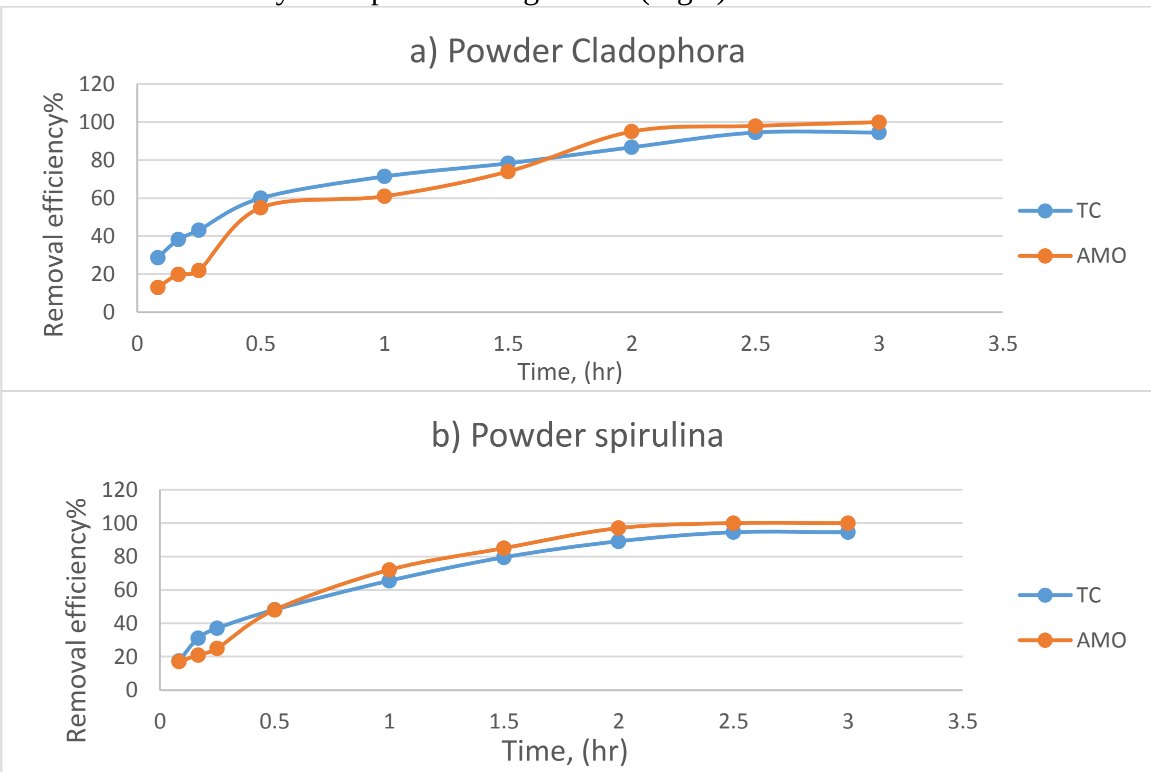


Figure 7. E.ffect of ti.me on the removal efficiency of antibiotics by cladophora and spirulina algae biomass (pH_{TC} = 6.5, pH_{AMo} = 5, $mass_{(cladophora)}$= 1.25 g/100ml, $mass_{(spirulina)}$= 0.5 g/100ml,25°C, at speed= 200 rpm, Co =50 mg/L).

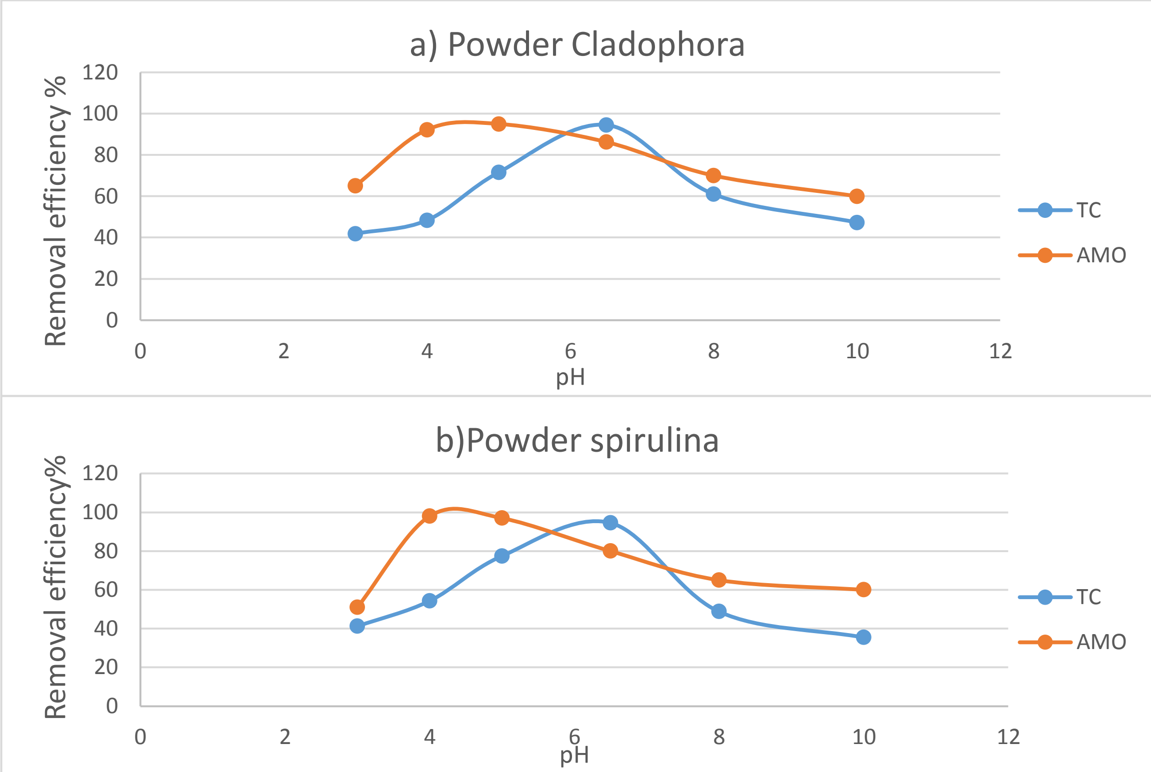


Figure 8. E.ffect of p.H on the removal efficiency of antibiotic by cladophora and spirulina algae biomass (time=2.5hr, mass$_{(cladophora\ )}$= 1.25 g/100ml, mass$_{(spirulina\ )}$= 0.5 g/100ml,25˚C, at speed= 200 rpm Co =50 mg/L).

Effect of agitated speed

Agitation facilitates proper contact between the contaminants in solution and the biomass binding sites and thereby promotes effective transfer of sorbate to sorbent sites (6). The efficiency was increased when the speed of the shaker increased from 100 to 300 rpm, this behavior owing to the rise in turbulence and as a result, the external mass transfer resistance thickness around the biomass particles was decreased with an increase in mixing speed (5). The distribution of antibiotic molecule in solution is affectted by agitation speed and it affects the uptake of antibiotic molecules by disrupting the film resistance surrounding the adsorbent particles (2). At low speed (100 rpm), the particle could not spread sufficiently to provide active binding sites for antibiotic adsorption. The time essential to achieve equilibrium decrease when the shaking speed increased. This action might be because the lack of biomass aggregation that finally rises the biomass surface area, leads to the rapid adsorption of antibiotic (15). Additionally, these results clearly indicate that maximum removal efficiency for antibiotic achieved at 200 rpm mixing speed also 300 rpm obtained maximum removal efficiency for antibiotic as show in Fig. 9 no significant increase was observed because the solution had reached equilibrium. The mixing speed of 200rpm was used for batch experiments instance of 300 rpm to save energy. And from economical view point, longer agitation speed (300) unnecessarily prolonged the treatment for obtaining the similar result.

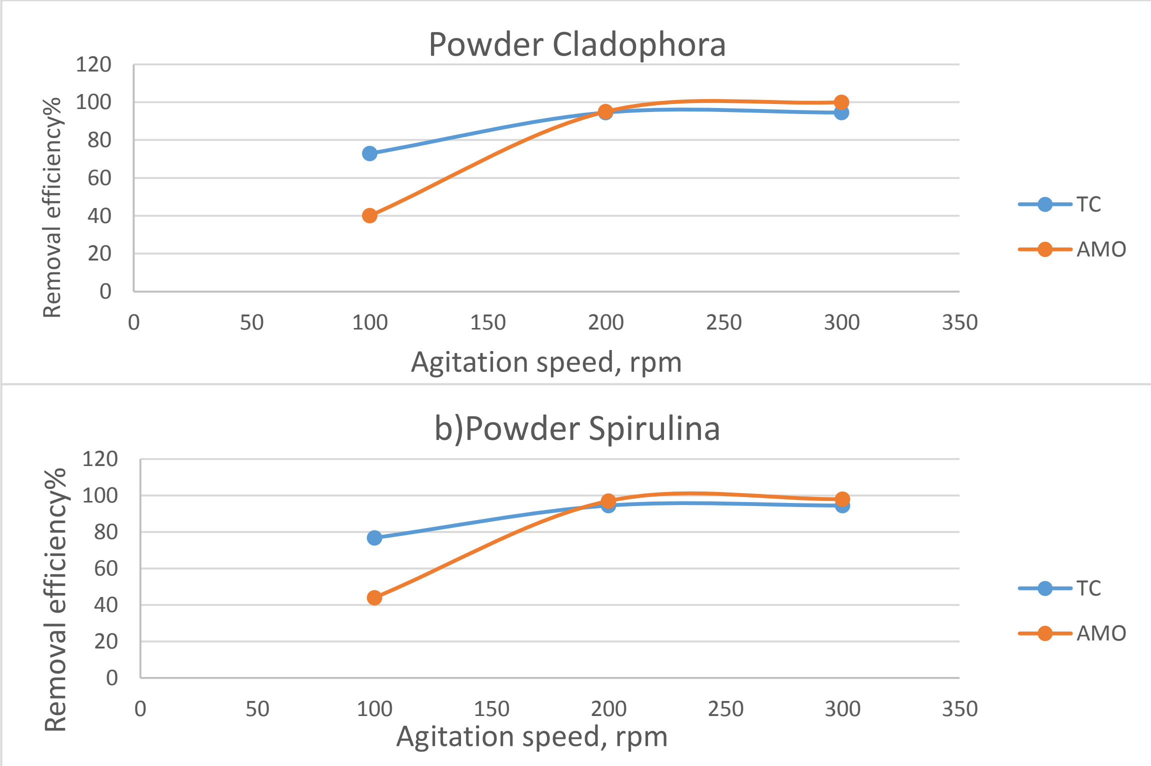


Figure 9. E.ffect of agitation s.peed on the removal efficiency of antibiotic by a) cladophora and b) spirulina algae biomass (pH_{TC}= 6.5, pH_{AMo}= 5, $mass_{(cladophora)}$= 1.25 g/100ml, $mass_{(spirulina)}$= 0.5 g/100ml, 25°C, Co= 50 mg/L and time=2.5hr)

Sorption isotherm study

The sorption process usually studied by using Langmuir, Freundlich, and Temkin isotherm models. The model parameters can be taken further, providing understanding of surface properties, attraction of the sorbent and sorption mechanism as show in Figure 10 and tabulated in Tables 3. From these Figures and Tables one can conclude that the three models represent the data very well recognized by the highest values of (R2). The little. va.lue of SSE ind.icate the better models fitting and the similarity of these models with the experimental data, (14). Since 1/n less than one, so it indicates normal biosorption. The affinity of both pollutants and the algae biomass was strong, because Freundlich constant (n) fills in the range (1-10) (18). From the comparison with other applied model Langmuir isotherm gave butter fitting for the biosorption data at 25°C with a maximum adsorption capacities of AMO and TC on Cladophora algae biomass powder was (20.5, 17.4) respectively, AMO and TC on Spirulina algae biomass powder was (24.6, 19.7) respectively. Isotherms are characterized the interaction between sorbate and sorbent. These relationships are show a rapid rate in first stages and approaching asymptotic at higher concentration. Figure 10 also shows that the powder has a stronger sorptive property as the TC and AMO isotherms are located at an upper position in this plot. Table 3 indicates that the maximum biosorption capacities of Cladophora and Spirulina given by Langmuir equation (*qm*) were found of AMO greater than of TC.

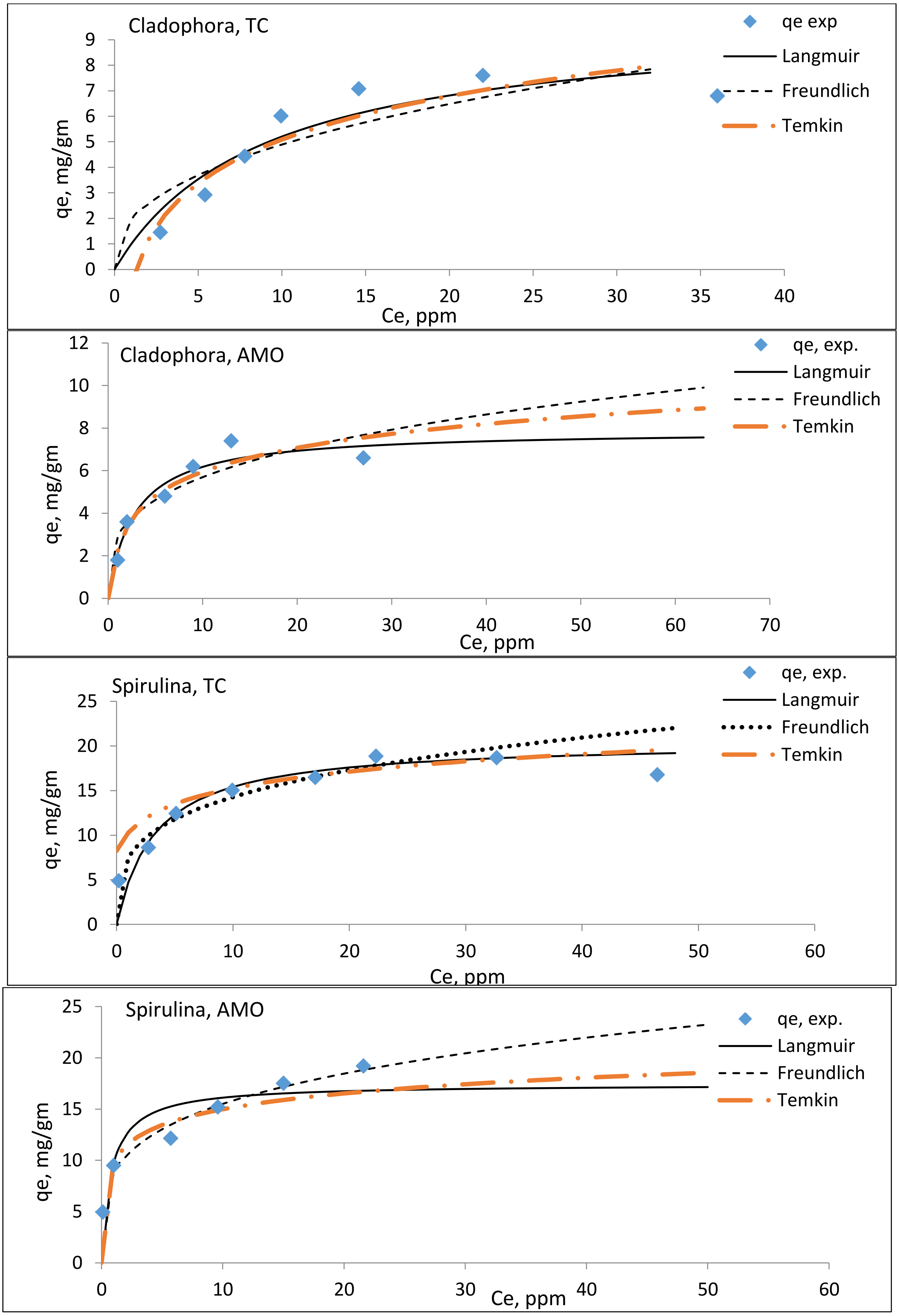


Figure 10. Isotherm model for sorption of TC and AMO on algae biomass as powder

Table 3. Isotherm parameters of TC and AMO on algae biomass as powder

Model	parameters	TC Cladophora powder	TC Spirulina powder	AMO Cladophora powder	AMO Spirulina powder
Langmuir Model $q_e = [q_{max.} * b * C_e/(1+b * C_e)]$	$q_{max.}$ (mg/g)	17.4	19.7	20. 5	24.65
	b (L/mg)	1.22	0.350	0.3	0.112
	R^2	0.99	0.98	0.98	0.97
	SSE	26.3	10.4	16	28
Freundlich Model $q_e = k * C_e^{1/n}$	k (mg/g)	8.6	7.1	7.5	4.8
	n	3.98	3.3	3.6	2.4
	R^2	0.98	0.95	0.97	0.94
	SSE	2.6	26.7	5.15	55.3
Temkin Model $q_e = \frac{RT}{b} \ln(k_T C)$	K_T(mg/g)	86.4	3.9	17	0.78
	B=RT/b (L/mg)	2.2	4.04	2.9	6.15
	R^2	0.97	0.97	0.97	0.96
	SSE	11.6	15.05	11.19	31.5

Sorption Kinetics Model

The kinetics of TC and AMO adsorption onto algae biomass was investigated using pseudo first order, pseudo second order, using the experimental data at various time. The values of R^2 (coefficient of determination) and qe calculated from the second order kinetic model show a well fit with the experimental data compared to other mentioned model. The linear plot of each biosorbent did not pass through the origin, as a result, intraparticle diffusion was not the rate-limiting step (14). While, the second order kinetic model expected that the rate limiting step may be chemical sorption (19). From the kinetic model data in Fig. 11, 12 and Table 4 for the adsorption of TC and AMO, it can be concluded that da.ta are good fitted to the kinetic model. The calculated values obtained from the application of these models are tabulated in Table 4. However, the second-order kinetic model Fig. 12, which expresses the presence of chemisorption process (10).

Ta.ble 4. Kinetic parameters of various models fitted to TC, AMO sorption experimental data

Kinetics m.odels	Param.eters	Cladophora (TC)	Spirulina (TC)	Cladophora (AMO)	Spirulina (AMO)
Experimental	qe	3.79	9.45	3.92	9.88
Pseudo first order	qe	4.278	22.2	6.5	13.69
	K1	0.032	0.051	0.009	0.03
	R2	0.87	0.82	0.95	0.92
Pseudo second order	qe	3.78	11.1	5.5	11.86
	K2	0.025	0.003	0.003	0.0013
	R2	0.97	0.99	0.96	0.98

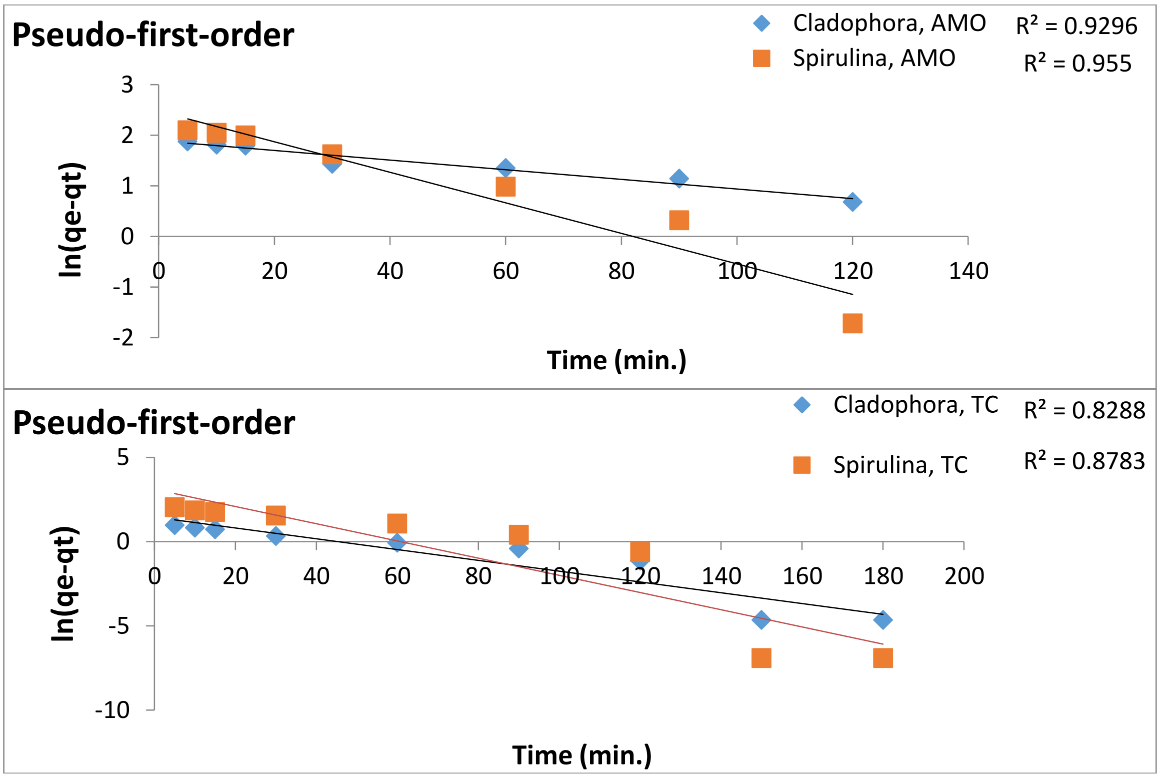
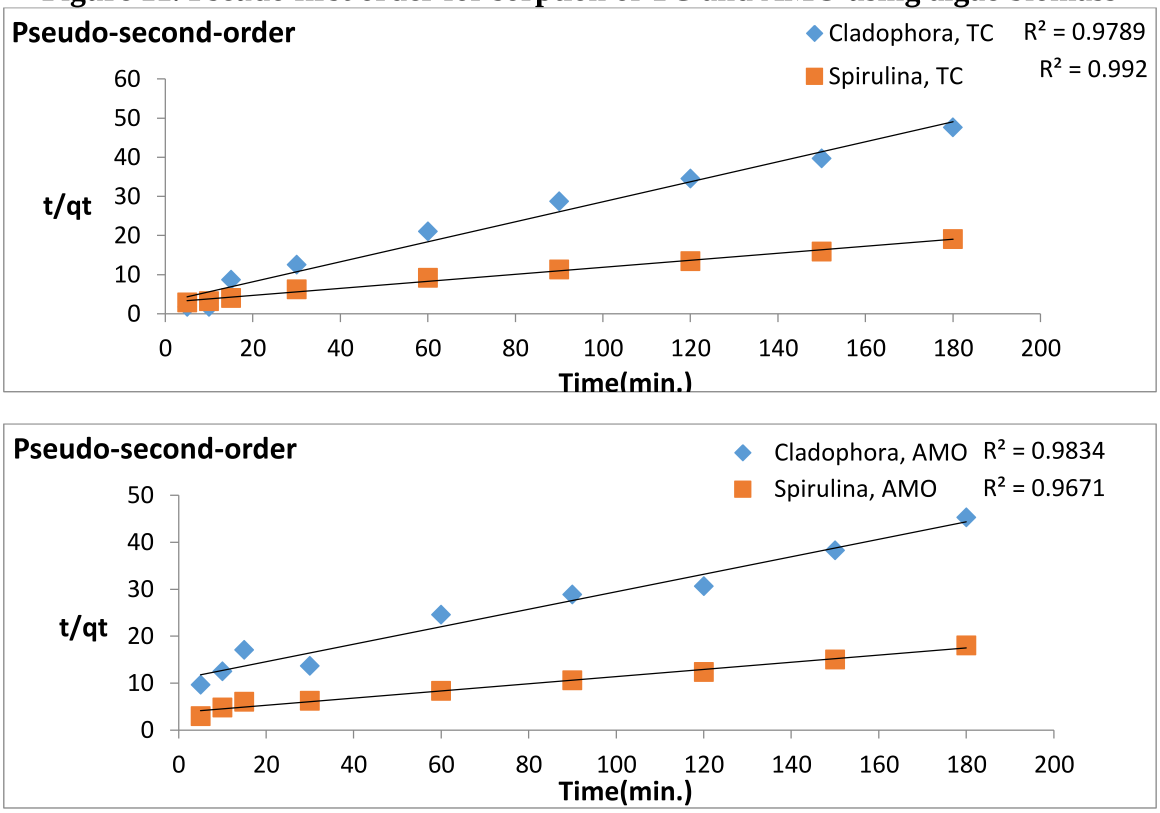


Figure 11. Pseudo first order for sorption of TC and AMO using algae biomass



Figur.e 12. Pseudo s.econd order f.or sorption of TC and AMO using algae biomass

CONCLUSION

The ability of Cladophora and Spirulina biomass to remove TC and AMO from water samples reached 98%. Moreover, TC and AMO removal reached equilibrium within 2.5 hour contact time for both type of algae. The optimum pH of solutions is 6.5 for TC and 5 for AMO, agitation speed 200 rpm and concentration for both antibiotic 50 ppm. Nevertheless, algal biomass cladophora and spirulina dose of 1.25 g/100 ml and 0.5 g/100 ml respectively were shown to be the optimum. The data best fitted with the Langmuir model. . The maximal adsorption capacity from the Langmuir model was (17.4, 19.7 mg/g) for TC and (20.5, 24.6 mg/g) for

AMO on Cladophora and Spirulina algae, respectively. According to the fitness of the data to the second-order kin.etic model, chemisorption adsorption of TC and AMO by Cladophora and Spirulina biomass.

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