REMOVAL OF ANTIBIOTIC WASTES BY ADSORPTION METHOD

[1]UMRANTEZCANUN, [2]S. EREN ÖCAL, [3]AYŞE GÜL

[1,3]Anadolu University Department of Environmental Engineering, Turkey
[2]Anadolu University Department of Chemistry Engineering, Turkey
E-mail: [1]utezcan@anadolu.edu.tr; [2]eocal@anadolu.edu.tr; [3]aysegul@anadolu.edu.tr

Abstract - Antibiotics are chemical compounds used as treating medicine for human and animal while also being consumedforagricultural use. These compounds have different decomposition times and are stablein the environment. In this study removal of tetracycline antibiotic, which has been found to be present in wastewater in considerableconcentrations, by adsorption method using actived carbon in a batch reactor was studied. Effects of operating parameters like initial pH (3,5,7 and 9), temperature (20,30,40 and 50°C), adsorbent dosage (0.025,0.050,0.1,0.15 and 0.2g),initial antibiotic concentration (25,50,100 and150 mg/L) and agitation time (1,2,3,5,8 and 24h) were investigated. The highest chemical oxygen demand (COD) removal of %91.2 was obtained at a pH value of 5, working temperature of 20 °C with 0.15 g activated carbon and 100 mg/L initial tetracycline concentration after 24 hour adsorption time.Considering the results, it was concluded that adsorption of tetracycline antibiotic from wastewater using activated carbon can be used as an effective treatment method.

Index Terms - Activated carbon,Adsorption, Antibiotics

I. INTRODUCTION

Antibiotics being considered as a significant type of environmental contamination, have studied by many researchers using different techniques for their removal from waste water.[1].The occurrence of antibiotics in the environment has received great attention in the past decade due to their wide usage and the growing demand for medical treatment of both animals and humans with drugs [2].

Antibiotic pollution is a potential threat confronting human health so that their abatement from the environment is a very important issue .A variety of methods have been studied for antibiotics removal such as ion exchange [3],biological treatment [4], electrochemical treatment [5], adsorption [1]-[6] and membrane process [7]. The term “adsorption” is the accumulation of matter from a gas or liquid phase to the surface of an adsorbent, which could involve physical and/or chemica ladsorption. Adsorption technology is a well-known physicochemical process which is fast, efficient and economical so that extensively used in waste water treatment.[1]-[8].

Tetracycline is a pharmaceutical considered safe and effective medicine fortreatment of many bacteria linfections.

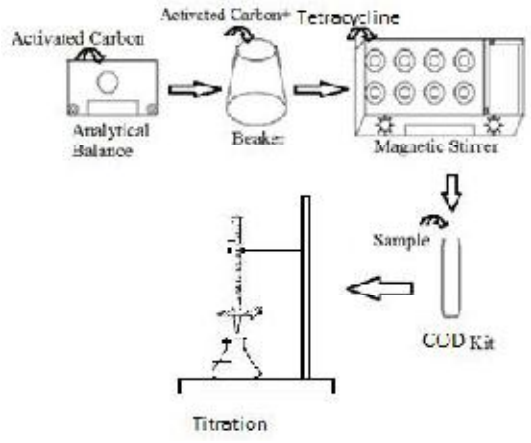
Tetra-cycline (TC) is also a common medicine prescribed for animals care. Tetra-cycline isbeing added to animals feed for growth improvement which finally results into soil and aquatic environment contamination with TC residues due to their high aqueous solubility.[9]- [10].

In this study, removal of TC by adsorption with activated carbon was investigated.

The main objective was to investigate the effectiveness of adsorption method and to determine the removal efficiency of COD for the removal ofTC. Effects of initial pH, adsorbent dosage, temperature, initial antibiotic concentration and agitation time on the removal of COD were studied.

II. EXPERIMENTAL PROCEDURE

The stock solution of TC was prepared in the laboratory using analytical reagent grade TC supplied by AppliChem Panreac by dissolving 0.1 g TC in one litter of water. The solution was prepared using deionized water. The pH of the sample was adjusted to the desired value using H_2SO_4 or NaOH. Reagents used in the study were of analytical grade quality. Activated carbon supplied by Sigma Aldrich was used as adsorbent in the adsorption process.Cas-No:7440-44-0.The pH of the active carbon used in the experiment wasbetween 6.0 and 9.0. The relative density was0.250-0.600 g / cm^3. The surface area wasapproximately 750 m^2 / g and the maximum amount of moisture was 22%. Batch adsorption studies were carried out using the batch contact method.The synthetically preparedwastewater had an initial COD value of 1000mg/L. The pH was measured using SevenGo pH meter and the COD values were determined usingHach Lange COD analysis kit with a measurable range of 0-1500 mg/L.The experimental setup isshown in Figure 1.



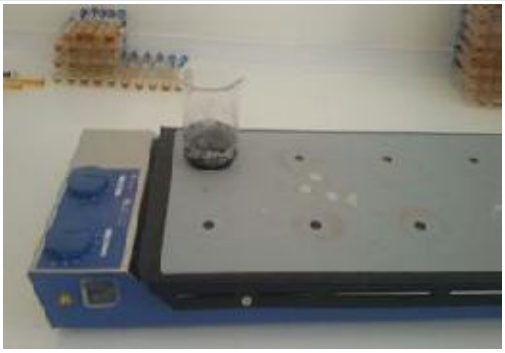


Figure 1. Experimental set-up

2.1.Calculation

The COD removal efficiency (RE %) was calculated after adsorption using following equation:

$RE\ \% = [(C_o\text{-}C)\ /C_o\ ]x100$ (1)

C_o and C are the concentrations of COD before and after adsorption (mg/L).

III. RESULTS AND DISCUSSION

3.1. Effect of pH

It has been confirmed that initial pH is a major important parameter for adsorption process [11].The adsorption is found to be pH-dependent as pH affects the speciation of TC and surface charge of adsorbent [9]. The adsorption of TC, was studied at pH of 3,5,7 and 9 with0.1 g of adsorbent at the room temperature. The initial concentration of TC was 100 mg/L and the contact time was 2h. Theeffect of pH on the COD removal efficiency is shown in Fig. 2.The highest removal efficiency was found at a pH value of 5.

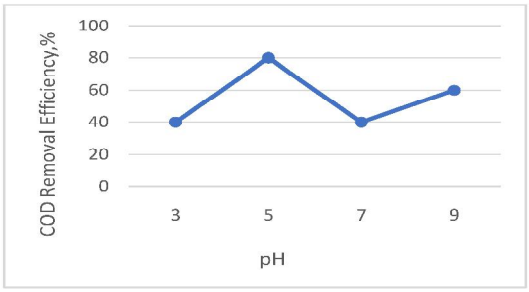


Figure 2.Effect of pH on the COD removal efficiency

As can be seenfromFig. 2 when the initial pH increases from 3 to 5, removal efficiency increases from 40% to 80%. The isoelectric point of tetracyclines is at pH 5 at which zwitter ionic form is dominated. The pH value which result in zero net charge is called the isoelectric point (IEP).The IEP is an important physicochemical parameter can be estimation of surface charges of compound particles and used for characterization of the adsorption properties of materials.

3.2. Effect of Adsorbent Dosage

Activatedcarbon has beencommonlyusedandreported as a highly effective adsorbent due to their large specific surface area, high porosity, and favorable pore size distribution[10].Inordertostudytheeffect of adsorbentdosage on the removal of TC, experiments were carried out at initial concentration of 100 mg/L,pH 5 at room temperature with the contact time of 2h. Different adsorbentdosage including 0.025,0.050,0.1,0.15 and 0.2g were investigated. The effect of adsorbentdosage on COD removal efficiency results are shown in Fig 3.

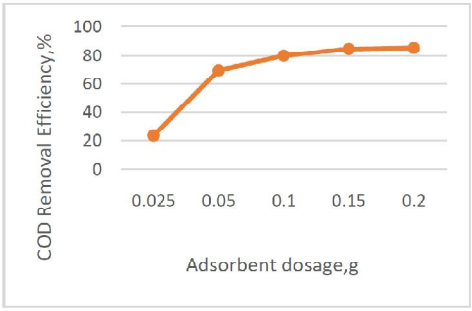


Figure 3.Effect of adsorbentdosage on the COD removal efficiency

As can be seenfromtheFig. 3,with increasing adsorbentdosage, COD removal efficiencyof TC has increased.The removal efficiencies of 23.4%, 69,6%, 80%, 84,8%, 85,5% were obtained for the addition of 0.025g, 0.05g, 0.1g, 0.15g, 0.2g activatedcarbon, respectively. The active surface area of adsorbent is proportional to the amount of adsorbent. There fore the higher removal efficiency was observed as was expected the removal efficiency did not improved significantly when the amount of adsorbent was increased from 0.1 to 0.2 g. This can be related to insulficent rate of mass transfer in diffuse layer at lower concentrations which is the dominated mechanism.

3.3. Effect of Initial Antibiotic Concentration

In this study the effect of initial antibiotic concentration on the removal efficiency of adsorption process was investigated. Initial concentrations were 25,50,100 and 150 mg/L while other parameters were a pH of 5 working temperature equal to room temperature ,the contact time of 2h and 0.15 g adsorbentdosage. The obtained results are summarized in Figure4.

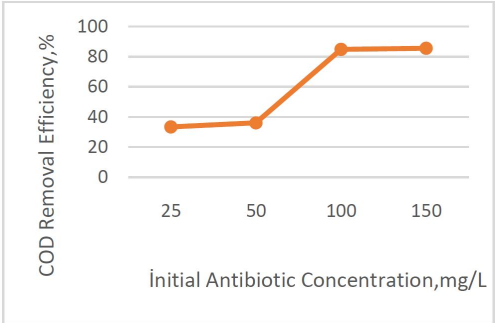


Figure 4. Effect of initial antibiotic concentration on the COD removal efficiency

It was observed that with an increase in initial antibiotic concentration, the COD removal efficiency of TC increased.The removal efficiencies of 33.33%, 36%, 84,8%, 85,6% were obtained for the addition of 25mg/L, 50mg/L, 100mg/L, 150mg/L antibiotic concentration, respectively. Although higher removal efficiency was expected at lower lower antibiotics concentrations, we found that higher antibiotic concentration resulted in higher removal efficiency. Forthe TC molekulesto be absorbed on thesurface of adsorbent. They must diffuse the stagnant layer and then through the pores of adsorbent. Fromtheobservedresult, ıt was calculated that the process was controlled by diffusion step because higher concentration cause increased mass transfer rate.

3.4.Effectof Temperature

Temperature is an effective parameter in the adsorption process [12]. Influence of temperature on the removal efficiency of TC at 20,30,40 and50^{o}C were investigated at pH5 with 0.15 g of adsorbentand 100 mg/L initial concentration. The results are shown in Fig. 5.

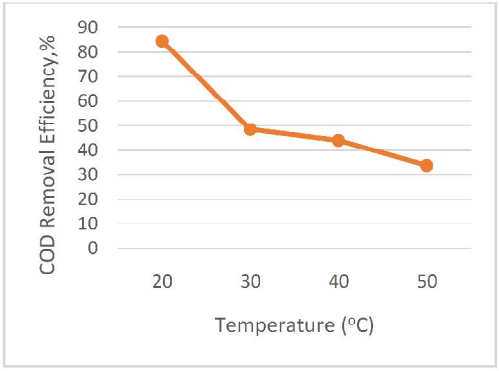


Figure 5. Effect of temperature onthe COD removalefficiency

These results revealed that with an increase in temperature, the COD removal efficiency of TC decreased. This can be related to the physical nature of adsorption process which means a higher temperature makes the molecules to vibrate morestrongly as being so strong to over come the weak Van der Walls bonds and deattach from adsorbent surface. In addition this process is exothermic [13]their fore the increase of temperature decreases the efficiencies.

3.5.Effectof Agitation Time

Agitation time has thevital role that affect the adsorption efficiency. The effect of agitation time on removal efficiency of TC was studied at pH 5 with0.15g ofadsorbent,100 mg/l initial concentration andworkingtemperature of 20 ^{o}C .Influence of theagitation time on theremovalefficiency of TC is shown in Fig. 6and it is clearthatadsorptionefficiencyhas increasedat higheragitationtimes.Almost 55.84% of the TC wasremovedafter 1 hourwherasduringthe rest 24 hrtheremovalefficiency has increasedbyjust 38.77%.This showedthat, theprocessreached a saturationpointthatlongerdetention time was not effective.

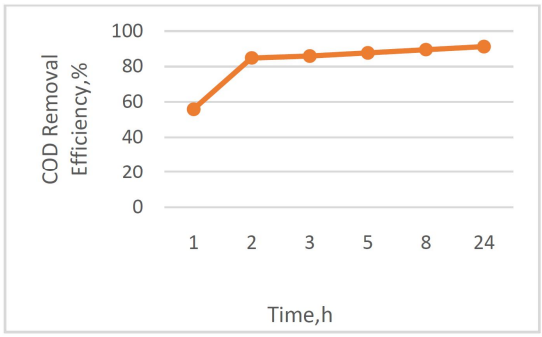


Figure 6. Effect of agitation time onthe COD removalefficiency.

Agitation time is a significantparametertospecifytheequilibrium time of adsorptionprocess. Similarresultswerefound in theliteratüre.[14].

CONCLUSION

In this study, tetracycline removal from wastewater by adsorption method using activated carbon was investigated. The effect of various operational parameters like pH, temperature, initial antibiotics concentration, adsorbent dosage, and agitation timewas investigated. Removal efficiency of TCwas increased with increasing adsorbent dosage, initial antibiotics concentration, pH and agitation time while it decreased with the increasing temperature. The initial TC COD concentration of 1000 mg/L was reduced to the 88 mg/L corresponding to the removal efficiency of 91,2% at pH 5, 20^{o}C with the 0.15g activated carbonand 100 mg/L initial TC concentration, after 24 hour. Considering the results, it can be said that adsorption of TC from wastewater using activated carbon can be used as an effective treatment method.

REFERENCES

[1] F. Yu, Y. Li, S. Han, J. Ma, “Adsorptive removal of antibiotics from aqueous solution using carbon materials,”Chemosphere vol.153, pp.365-385, June 2016.

[2] K. Chen, L. Liu, W. Chen “Adsorption of sulfamethoxazole and sulfapyridine antibiotics in high organic content soils,”Environmental Pollution vol.231,no. 1,pp. 1163-1171,December 2017.

[3] T. Wang, X. Pan, W. Ben, J. Wang, P. Hou, Z. Qiang “Adsorptive removal of antibiotics from water using magnetic ion exchange resin,”Journal Of Environmental Sciences,vol. 52 pp. 111 – 117, February 2017

[4] Q. Yi, Y. Zhang, Y. Gao ,Z. Tian, M. Yang, “Anaerobic treatment of antibiotic production wastewater pretreated with enhanced hydrolysis: Simultaneous reduction of COD and ARGs”Water Research,vol. 110, pp. 211-217, March 2017.

[5] S. D. Jojoa-Sierra, J. Silva-Agredo, E. Herrera-Calderon, R. A. Torres-Palma, "Elimination of the antibiotic norfloxacin in municipal wastewater, urine and seawater by electrochemical oxidation on IrO2 anodes," Science of the Total Environment, vol.575,no.1, pp. 1228–1238, January 2017.

[6] V. Kårelid, G. Larsson, B. Björlenius, "Pilot-scale removal of pharmaceuticals in municipal wastewater:Comparison of granular and powdered activated carbon treatment at three wastewater treatment plants," Journal of Environmental Management, vol. 193, pp. 491-502,May 2017

[7] T. Tin Nguyen , X. Thanh Bui , V. PhucLuu , P. Dan Nguyen , W. Guo, H. Hao Ngo, "Removal of antibiotics in sponge membrane bioreactors treating hospital wastewater: Comparison between hollow fiber and flat sheet membrane systems," Bioresource Technology, vol. 240, pp. 42-49, September 2017.

[8] M. B. Ahmed, J. L. Zhou, H. H. Ngo, W. Guo, "Adsorptive removal of antibiotics from water and wastewater: Progress and challenges," Science of the Total Environment, vol. 532, pp. 112–126, November 2015.

[9] W.A. Khandaya, B.H. Hameeda, "Zeolite-hydroxyapatite-activated oil palm ash composite for antibiotic tetracycline adsorption,"Fuel vol. 215,pp. 499–505,March2018.

[10] M. J. Ahmed, "Adsorption of quinolone, tetracycline, and penicillin antibiotics from aqueous solution using activated carbons: Review,"Environmental Toxicology and Pharmacology,vol. 50, pp. 1–10,March 2017.

[11] L. A. Rodriguesa, M. L. C. P. Silva, M. O. A. Mendesc, A. R. Coutinhoc and G.P. Thima, "Phenol removal from aqueous solution by activated carbon produced from avocado kernel seeds," Chemical Engineering Journal, vol. 174,no. 1, pp. 49–57, October 2011.

[12] C. I.A. Ferreira , V. Calisto , M. Otero , H. Nadais ,V. I. Esteves, "Removal of tricainemethanesulfonate from aquaculture wastewater by adsorption onto pyrolysed paper mill sludge," Chemosphere,vol. 168 pp. 139-146,February 2017

[13] Turku , T. Sainio, E. Paatero,"Thermodynamics of tetracycline adsorption on silica"Environ Chem Lett, vol.5, pp. 225–228, May 2007.

[14] M. Kilic, E. ApaydinVarol and A. E. Pütün, "Adsorptive removal of phenol from aqueous solutions on activated carbon prepared from tobacco residues: Equilibrium, kinetics and thermodynamics," Journal of Hazardous Materials, vol. 189,no. 1-2, pp. 397–403, May 2011.

★★★