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Removal of fluoroquinolone antibiotic, ofloxacine, by adsorption on titaniferous sand

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Abstract

The elimination of fluoroquinolone antibiotic, ofloxacine, was carried out by adsorption on titaniferous sand with a 58% content of TiO_2. Various parameters such as contact time, sand concentration and initial pH influencing the adsorption of the antibiotic were optimized. Thus, the adsorption equilibrium was obtained after 100 minutes and the kinetics followed the second pseudo order model. The removal of the ofloxacine was better at a pH of 6.5 for a sand concentration of 160 g / L. Among the isothermal models tested, to represent the experimental results, the Langmuir model better described the adsorption process with a maximum adsorption capacity of 1.1383 mg/g and a kinetic constant of 0.0389 L / mg.

Keywords: Adsorption, fluoroquinolone antibiotics, ofloxacine, titaniferous sand.

Introduction

The fluoroquinolones are the main antibiotics of the therapeutic armory used to treat several infections due to their powerful bacterial activities[1]. Indeed, fluoroquinolones have a high intracellular and tissue penetration, a large antibacterial spectrum, a good clinical tolerance profile and an excellent oral bioavailability[2]. That's why the fluoroquinolones are the fourth antibiotic among the most prescribed in the world[3]. Nevertheless, more than half of these antibiotics can't be removed easily. Then, they remain under their original form[4] and can also be found in aquatic environment[5]. Although, recent studies showed the presence of antibiotics in several types of water: wastewater[6], surface water[7], groundwater[8] and even in drinking water[9]. The fluoroquinolones are among the antibiotics which have a low solubility and biodegradability. They are susceptible to be accumulated in water[10]. This accumulation involves toxic effects on aquatic microorganisms and consequently develops genetically resilienceto antibiotics. These antibiotics can be shared between bacteria by a horizontal gene transfer process which lead to their inefficiency[4]. It was showed that the mixture of fluoroquinolones residues with other active pharmaceutical compounds can generate growth inhibitors effects and genotoxicity in aquatic species[1]. However the harmful effect of fluoroquinolones in aquatic ecosystem and human health require the development of treatment technics for their elimination. Several works related these treatment technics and came up with nanofiltration combined with ozonation[11], electrochemical oxidation[12], advanced oxidation processes[13(p)], adsorption[14]. Among these technics, adsorption is generally considered as the only currently promised one[15]. In fact, adsorption is a unit operation, easily feasible technically, and doesn't require high energy consumption[16]. Excellent adsorbents can be used such as activated char coal, silica gel, activated alumina, zeolites, etc. However a recently reviewed literature interestingly highlights the adsorption by titanium oxide[17,18] and other oxides like titaniferous sand, silicium oxide[19], zirconium oxide[20], etc.That's what inspired us to use titaniferous sand as adsorbent. The latter is considered a by-product of the zirconium industry and has a very low commercial value[21]. The adsorption of ofloxacine was experienced on titaniferous sand with a 58% content of titanium oxide. Until recently, there has been no works relating the adsorption of fluoroquinolones antibiotics on titaniferous sand. In this work, the influence of different parameters was studied to optimize the adsorption process.

Materials and methods

The used titaniferous sand was from an ore in Senegal. Its black and metallic aspect (Figure-1). The sand contains 58 % titanium dioxide. In addition to titanium dioxide, it contains other dioxides such as: Fe_2O_3, FeO, V_2O_5, Cr_2O_3, SiO_2, Al_2O_3, P_2O_5, MgO, MnO, CaO …The characteristics of the titaniferous sand were a porosity of 38.33%, a density of 4054 $kg.m^{-3}$ and a specific surface of 11.84 $g.m^{-2}$.

Trials of adsorption were carried out by a « MULTISTIRRER 15 » agitator and a series of Erlenmeyer flasks. The experiment was based on making contact with agitation for a given time a mass of titaniferous sand (M_{STF}) and a given volume ofloxacine in solution. When the contact between the sand and the pollutant was established, the run time was set. The follow-up of the adsorption in time was handled by sampling 10 mL using a disposable syringe. The samples were filtrated on a 0.45 µm HA millipore membrane. The reduction of the antibiotic concentration was followed by measuring the chemical oxygen demand with the reflux method using a « BLOC DIGEST » multipostes heating system. The retained amount of ofloxacine by the sand at the equilibrium time and the rate of elimination were found by the following relationships:

$$Q_e = \frac{(DCO_0 - DCO_e).V}{M_{STF}} \quad (1)$$

$$\text{yield \%} = \frac{(DCO_0 - DCO_e)*100}{DCO_0} \quad (2)$$

COD_0: Initial Chemical Oxygen Demand of the antibiotic in solution (mg/L); V: volume of the antibiotic solution (L); M_{STF}: Mass of the titaniferous sand (g); CODe: Equilibrium Chemical Oxygen Demand of the antibiotic in solution (mg/L).

Figure-1: Sample of titaniferous sand used as an adsorbent.

Results and discussion

Adsorption kinetics of ofloxacine on the titaniferous sand: The adsorption kinetics of the antibiotic is showed in Figure-2. The experiment was based on determining the optimal duration to reach the adsorption equilibrium.

The kinetics highlighted 100 minutes of duration. The retention of ofloxacine was 57.14% in operational conditions consistent of an adsorption capacity of 0.41 mg/g.

To better describe the adsorption mechanism of ofloxacine on titaniferous sand, two kinetics models were used. These are the models of the first pseudo order and the second pseudo order. Their respective linear equations are as follows.

$$\ln(Q_e - Q_t) = -K_1.t + \ln Q_e \quad (3)$$

$$\frac{t}{Qt} = \frac{1}{K_2\,Qe^2} + \left(\frac{1}{Qe}\right)t \quad (4)$$

Where: Q_t: adsorption capacity at time in (mg/g); K_1: rate constant of pseudo first order adsorption in (min^{-1}); K_2: rate constant of pseudo second order adsorption in ($g.mg^{-1}.min^{-1}$); Qe: Equilibrium adsorption capacity (mg/g).

The results of the kinetics modeling are displayed in Figure-3 and Figure-4.

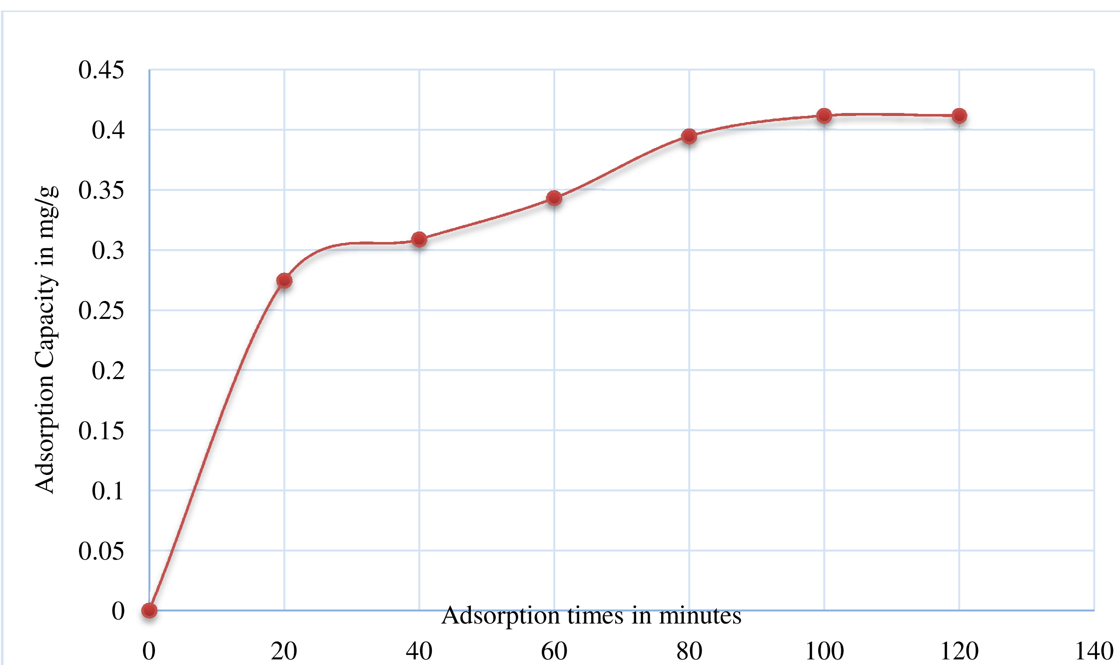

Figure-2: Effect of contact time on the adsorption of the ofloxacine: COD_0=201.6 mg/L; pH=7.5; M_{STF}=70 g; T=24°C; V=250 mL.

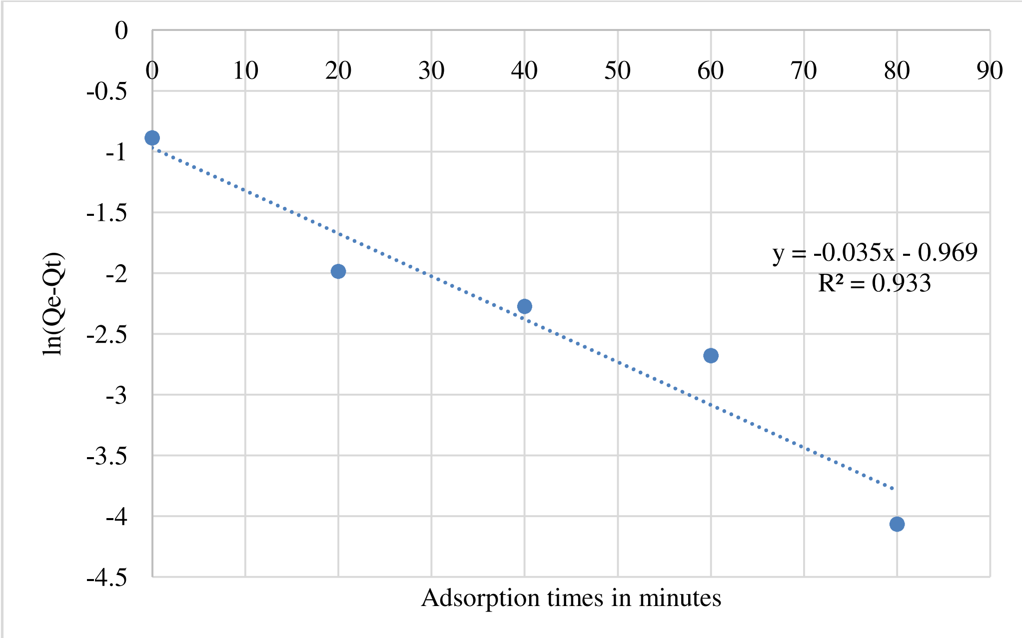

Figure-3: Linearization according to the pseudo first order model.

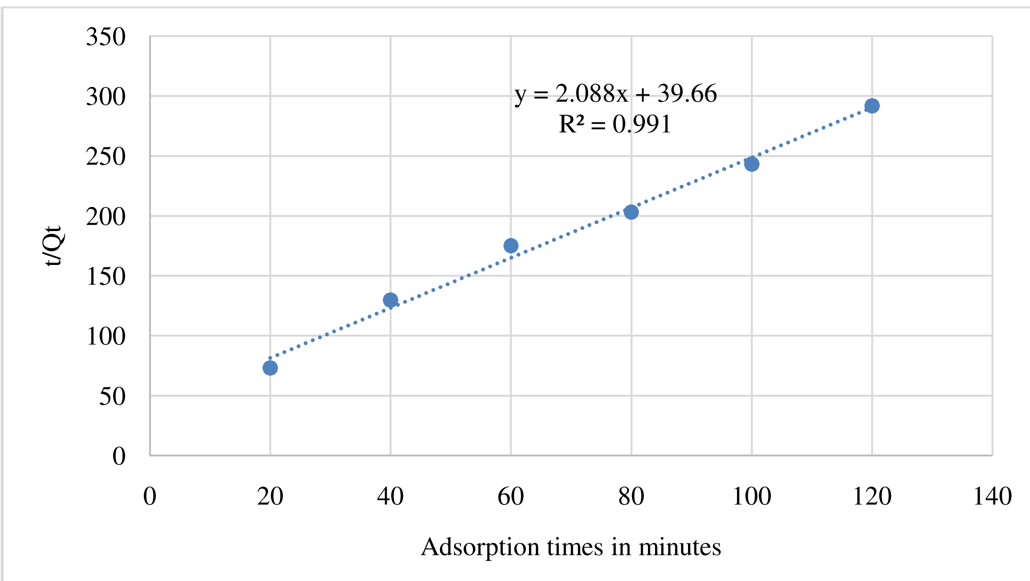

Figure-4: Linearization according to thepseudo second order model.

Based on the obtained correlation coefficients R^2, the two kinetics models were consistent with the experimental results. However, the pseudo second order model better described the adsorption kinetics. Thus, the adsorption of the antibiotic on the titaniferous sand is chemical. The kinetic parameters of the model are displayed in Table-1.

Table-1: Kinetic parameters of the pseudo second order model.

Kinetic parameters	Qe (mg/g)	K_2 (g.mg^{-1}.min^{-1})	R^2
Values	0.4788	0.1100	0.9915

Influence of the titaniferous sand concentration: The influence of the titaniferous sand was experienced to determine the minimum amount of titaniferous sand for having the maximum retention of ofloxacine. Therefore, it is inferred that adsorption is a process which is strongly influenced by the mass of the adsorbent.

To find out the influence of the titaniferous sand concentration, a 200 mg/L solution of ofloxacine was preparedand a volume of 250 mL was sampled in which a titaniferous sand mass of 0 to 100 mg was added. The results of this experiment are displayed in Figure-5.

The results showed that the adsorption yield became higher when the mass of titaniferous sand increased. The maximum yield was obtained with a mass of 40g which meant a concentration of 160 g/L in an aqueous solution. This solution allowed a 57.14% deduction rate of the COD after 100 min of adsorption. The mass of 40 g was used for the following tests.

Influence of the ofloxacine solution initial pH: Adsorption of organic compounds is influenced by the initial pH of the solution[22]. In fact, the pH acts on the charge of the adsorbent surface[23]. Then, in order to find out this impact, the value of the pH was shifted from 3 to 9. Figure-6 showed how the adsorption capacity of ofloxacine was depending on the initial pH of the solution.

The results highlighted the important role played by the pH in the ofloxacine fixation on the titaniferous sand. Indeed, the adsorption capacity of ofloxacine became higher when the pH increased to reach a maximum value of 0.72 mg/g at pH of 6.5. Nonetheless, a decrease of the adsorption capacity was noticed when the pH became higher than 6.5. The maximum value of the adsorption capacity at a pH of 6.5 would be explained by the charge missing on the TiO_2 surface. Elsewhere the pH_{PZC} (pH zero charge point) is ranged between 5.5 and 6.6[24]. However, the adsorbent surface is positively charged when the pH is less than 6.5 while it is negatively charged when the pH is higher than 6.5 because of the adsorption ions of H^+ and OH^-[25]. The presence of these ions in the adsorbent surface put back the antibiotic molecules which reduce their adsorption efficiency. Similar results were obtained on the adsorption of organic molecules by other authors[26,27]. Then, since the maximum adsorption capacity was obtained at a pH of 6.5, the adsorption isotherms were carried at this value.

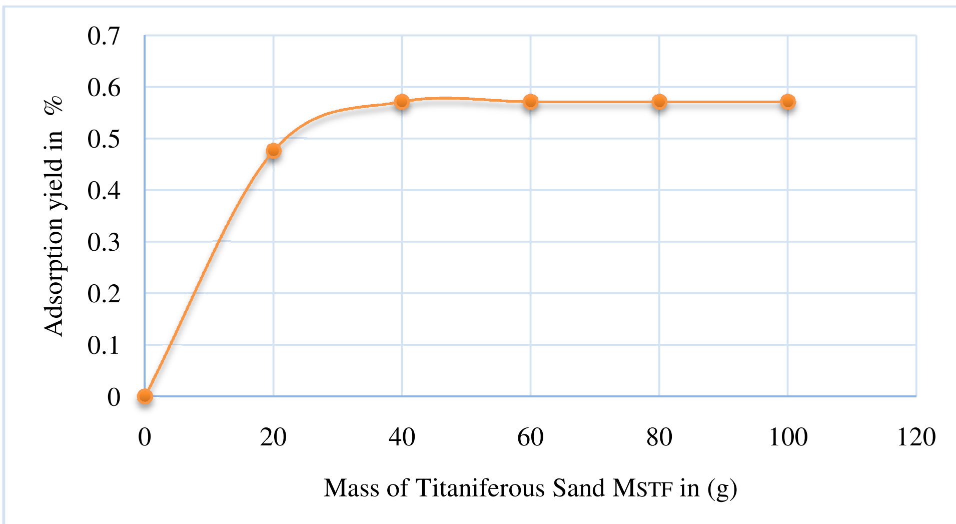

Figure-5: Variation of the adsorption yield in terms of the titaniferous sand mass: COD_0=201.6mg/L; pH=7.5; T=24°C; V=250 mL; t=100 min.

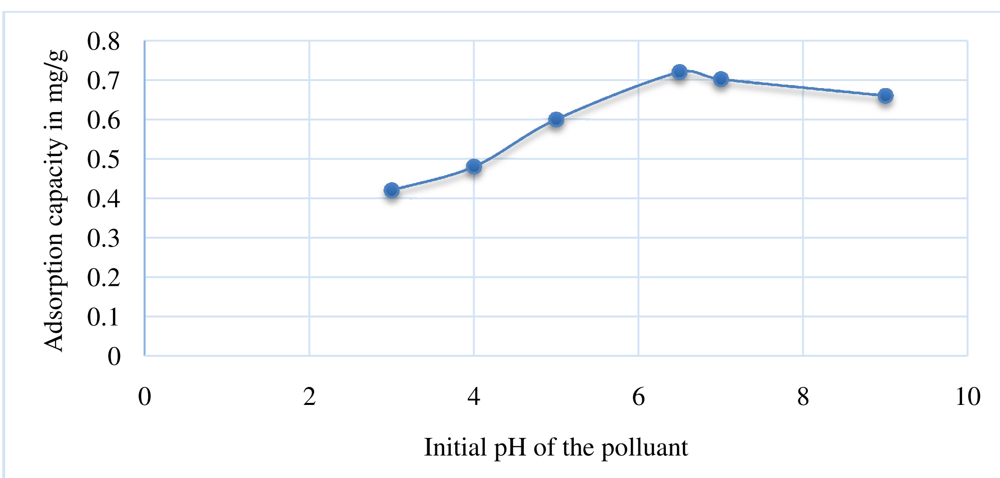

Figure-6: Variation of the adsorption capacityof ofloxacine in terms of the solution pH: COD_0=201.6mg/L; M_{STF}=40g; T=24°C; V=250 mL; t=100 min.

Modeling the adsorption isotherms: The Langmuir (Equation-5) and Freundlich (Equation-6) models were used to explore the relationship between the adsorption capacity and the equilibrium concentration.

$$\frac{1}{Q_e} = \frac{1}{Q_{max}K_L}\frac{1}{C_e} + \frac{1}{Q_{max}} \quad (5)$$

$$\text{Log}Q_e = \text{Log } K_f + n \text{ Log } C_e \quad (6)$$

Q_{max}: Maximum adsorbent amount (mg/g); K_L: Langmuir constant (L/mg); K_f:Freundlich constant (m^3/g); n:empiric constant depending on the studied system (adsorbant/molecule) and physical and chemical conditions of the area (T, pH...).

The isotherms were studied at 24°C with solutions of ofloxacine which concentrations varied from 50 to 250 mg/L at a pH of 6.5. The results are displayed in Figure-7 and Figure-8. Langmuir model gave the highest correlation (R^2 = 0.9757) implying that ofloxacine adsorption on titaniferous sand followed Langmuir isotherm which bring out a single type of adsorption sites (monolayer adsorption). This result is in accordance witch others indicate that the adsorption of organic compounds on titanium dioxide generally follow the Langmuir model[28,29]. The parameters of the Langmuir isotherm are given in Table-2. Then, the maximum adsorption capacity of the antibiotic on the titaniferous sand was 1.1383 mg/g.

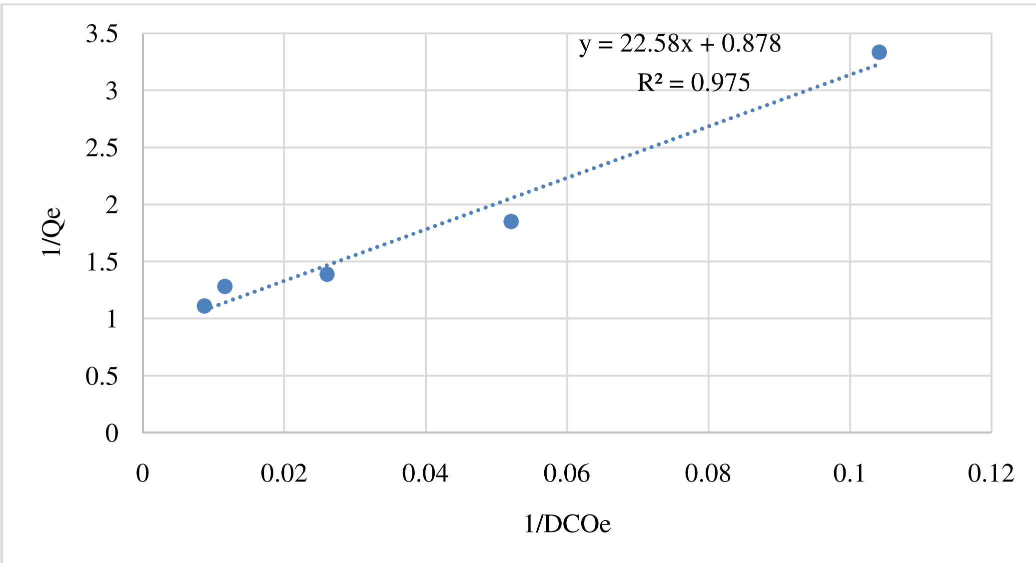

Figure-7: Correlation with Langmuir isotherm.

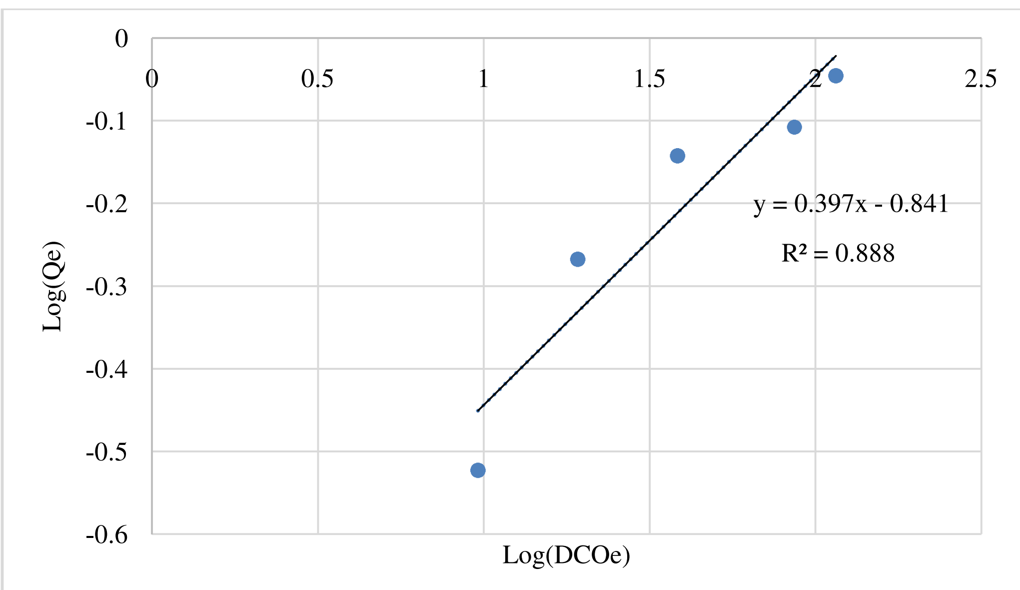

Figure-8: Correlation with Freundlich isotherm.

Table-2: Parameters of Langmuir isotherm for the adsorption of the ofloxacine on titaniferous sand.

Parameters	R^2	Capacité d'adsorption maximale Q_{max} (mg/g)	Constante de Langmuir K_L (L/mg)
Values	0.9757	1.1383	0.0389

Conclusion

This work consisted on studying the adsorption of ofloxacine which is a fluoroquinolone antibiotic by using a titaniferous sand as adsorbent. The adsorption was influenced by several operational parameters such as the mass of titaniferous sand, the pH of the antibiotic solution, etc.the experiment came up with main conclusions: i. the equilibrium was reached after 100 min; ii. the minimum concentration of 160 g/L in titaniferous sand was found out,which was sufficient to obtain a best reduction rate of ofloxacine; iii. a pH of 6.5allowed a maximumadsorption capacity of ofloxacine; iv. the adsorption isotherm is in agreement with the Langmuir model which meant a monolayer adsorption; v. the adsorption kinetics was described by the pseudo second order model. Consequently, the adsorption mechanism of the antibiotic on the titaniferous sand was chemical.

From this study, we can conclude by saying that titaniferous sand could be used successfully for the depollution of contaminated water by pharmaceutical compounds.

References

1. Feng M., Wang X., Chen J., Qu R., Sui Y., Cizmas L. and Sharma V.K. (2016). Degradation of fluoroquinolone antibiotics by ferrate (VI): effects of water constituents and oxidized products. *Water research*, 103, 48-57. doi:10.1016/j.watres.2016.07.014.
2. de Lastours Victoire and Fantin B. (2015). Impact of fluoroquinolones on human microbiota. Focus on the emergence of antibiotic resistance. *Future Microbiol*, 10(7), 1241-1255. doi:10.2217/fmb.15.40.
3. Van Boeckel T.P., Gandra S., Ashok A., Caudron Q., Grenfell B.T., Levin S.A. and Laxminarayan R. (2014). Global antibiotic consumption 2000 to 2010: an analysis of national pharmaceutical sales data. *The Lancet Infectious Diseases*, 14(8), 742-750.
4. Liu X., Liu Y., Xu J-R., Ren K-J. and Meng X-Z. (2016). Tracking aquaculture-derived fluoroquinolones in a mangrove wetland, South China. *Environ Pollut*, 219, 916-923. doi:10.1016/j.envpol.2016.09.011.
5. Luo Y., Xu L., Rysz M., Wang Y., Zhang H. and Alvarez P.J.J. (2011). Occurrence and transport of tetracycline, sulfonamide, quinolone, and macrolide antibiotics in the Haihe River Basin, China. *Environ Sci Technol*, 45(5), 1827-1833. doi:10.1021/es104009s.
6. Le-Minh N., Khan S.J., Drewes J.E. and Stuetz R.M. (2010). Fate of antibiotics during municipal water recycling treatment processes. *Water Res*, 44(15), 4295-4323. doi:10.1016/j.watres.2010.06.020.
7. Massey L.B., Haggard B.E., Galloway J.M., Loftin K.A., Meyer M.T. and Green W.R. (2010). Antibiotic fate and transport in three effluent-dominated Ozark streams. *Ecol Eng*, 36(7), 930-938. doi:10.1016/j.ecoleng.2010.04.009.
8. Zhang H., Liu P., Feng Y. and Yang F. (2013). Fate of antibiotics during wastewater treatment and antibiotic distribution in the effluent-receiving waters of the Yellow Sea, northern China. *Mar Pollut Bull*, 73(1), 282-290. doi: 10.1016/j.marpolbul. 2013.05.007.
9. Manzetti S. and Ghisi R. (2014). The environmental release and fate of antibiotics. *Mar Pollut Bull*, 79(1–2), 7-15. doi:10.1016/j.marpolbul.2014.01.005.
10. Okay O.S., Li K., Yediler A. and Karacik B. (2012). Determination of selected antibiotics in the Istanbul strait sediments by solid-phase extraction and high performance liquid chromatography. *J Environ Sci Health Part A*, 47(10), 1372-1380. doi:10.1080/10934529.2012.672303.
11. Liu P., Zhang H., Feng Y., Yang F. and Zhang J. (2014). Removal of trace antibiotics from wastewater: A systematic study of nanofiltration combined with ozone-based advanced oxidation processes. *Chem Eng J*, 240, 211-220. doi:10.1016/j.cej.2013.11.057.
12. Liu P., Zhang H., Feng Y., Shen C. and Yang F. (2015). Integrating electrochemical oxidation into forward osmosis process for removal of trace antibiotics in wastewater. *J Hazard Mater*, 296, 248-255. doi:10.1016/j.jhazmat.2015.04.048.
13. Feng M., Qu R., Zhang X., Sun P., Sui Y., Wang L. and Wang Z. (2015). Degradation of flumequine in aqueous solution by persulfate activated with common methods and polyhydroquinone-coated magnetite/multi-walled carbon nanotubes catalysts. *Water Res*, 85, 1-10. doi:10.1016/j.watres.2015.08.011.
14. Hu X., Zhang H. and Sun Z. (2017). Adsorption of low concentration ceftazidime from aqueous solutions using impregnated activated carbon promoted by Iron, Copper and Aluminum. *Appl Surf Sci*, 392, 332-341. doi:10.1016/j.apsusc.2016.09.047.
15. Gao J., Chen J., Li X., Wang M., Zhang X., Tan F. and Liu J. (2015). Azide-functionalized hollow silica nanospheres for removal of antibiotics. *J Colloid Interface Sci*, 444, 38-41. doi:10.1016/j.jcis.2014.12.054.
16. El Bakouri H., Morillo J., Usero J., Vanderlinden E. and Vidal H. (2015). Effectiveness of acid-treated agricultural stones used in biopurification systems to avoid pesticide

contamination of water resources caused by direct losses: mathematical modelling and thermodynamical study. *J Environ Solut*, 3, 11-18.

17. Ahmad A., Razali M.H., Mamat M., Mehamod F.S.B. and Amin K.A.M. (2017). Adsorption of methyl orange by synthesized and functionalized-CNTs with 3-aminopropyltriethoxysilane loaded TiO2 nanocomposites. *Chemosphere*, 168, 474-482. doi:10.1016/j.chemosphere.2016.11.028.

18. López-Muñoz M.J., Arencibia A., Segura Y. and Raez J.M. (2017). Removal of As(III) from aqueous solutions through simultaneous photocatalytic oxidation and adsorption by TiO2 and zero-valent iron. *Catal Today*, 280, Part 1, 149-154. doi:10.1016/j.cattod.2016.05.043.

19. Givens B.E., Xu Z., Fiegel J. and Grassian V.H. (2017). Bovine serum albumin adsorption on SiO2 and TiO2 nanoparticle surfaces at circumneutral and acidic pH: A tale of two nano-bio surface interactions. *J Colloid Interface Sci*, 493, 334-341. doi:10.1016/j.jcis.2017.01.011.

20. Hernández-Ramírez E., Wang J.A., Chen L.F., Valenzuela M.A. and Dalai A.K. (2017). Partial oxidation of methanol catalyzed with Au/TiO2, Au/ZrO2 and Au/ZrO2-TiO2 catalysts. *Appl Surf Sci*, 399, 77-85. doi:10.1016/j.apsusc.2016.12.068.

21. Lv J-F., Zhang H-P., Tong X., Fan C-L., Yang W-T. and Zheng Y-X. (2017). Innovative methodology for recovering titanium and chromium from a raw ilmenite concentrate by magnetic separation after modifying magnetic properties. *J Hazard Mater*, 325, 251-260. doi:10.1016/j.jhazmat.2016.11.075.

22. Loosli F., Coustumer P.L. and Stoll S. (2014). Effect of natural organic matter on the disagglomeration of manufactured TiO2 nanoparticles. *Environ Sci Nano*, 1(2), 154-160. doi:10.1039/C3EN00061C.

23. Sbaa M., Chergui H., Melhaoui M. and Bouali A. (2011). Tests d’adsorption des métaux lourds (Cd, Cu, Ni, Pb, Zn) sur des substrats organiques et minéraux de la ville d’Oujda. *Rev Marocaine Sci Agron Vét*, 21(2), 109-119.

24. Giraldo A.L., Peñuela G.A., Torres-Palma R.A., Pino N.J., Palominos R.A., Mansilla H.D. (2010). Degradation of the antibiotic oxolinic acid by photocatalysis with TiO2 in suspension. *Water Res*, 44(18), 5158-5167. doi:10.1016/j.watres.2010.05.011.

25. Bulut Y. and Aydın H. (2006). A kinetics and thermodynamics study of methylene blue adsorption on wheat shells. *Desalination*, 194(1), 259-267. doi:10.1016/j.desal.2005.10.032.

26. Deng H., Yang L., Tao G. and Dai J. (2009). Preparation and characterization of activated carbon from cotton stalk by microwave assisted chemical activation—Application in methylene blue adsorption from aqueous solution. *J Hazard Mater*, 166(2–3), 1514-1521. doi:10.1016/j.jhazmat.2008.12.080.

27. Benjwal P., Sharma R. and Kar K.K. (2016). Effects of surface microstructure and chemical state of featherfiber-derived multidoped carbon fibers on the adsorption of organic water pollutants. *Mater Des*, 110, 762-774. doi:10.1016/j.matdes.2016.08.030.

28. Kim S-H, Ngo H.H., Shon H.K. and Vigneswaran S. (2008). Adsorption and photocatalysis kinetics of herbicide onto titanium oxide and powdered activated carbon. *Sep Purif Technol*, 58(3), 335-342. doi:10.1016/j.seppur.2007.05.035.

29. Alahiane S., Qourzal S., El Ouardi M., BELMOUDEN A.A. and AIT-ICHOU Y. (2013). Adsorption et photodégradation du colorant indigo carmine en milieu aqueux en présence de TiO2/UV/O2 (Adsorption and photocatalytic degradation of indigo carmine dye in aqueous solutions using TiO2/UV/O2). *J Mater Env Sci*, 4(2), 239-250.