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Research Article

Nanoparticle for safe for environment

Investigating the Efficiency of Zirconium Oxide Nanoparticles in Removal of Ciprofoxacin from Aqueous Environments

Davoud Balarak[1], Marzieh Baniasadi[2] and Kethineni Chandrika[*3]

[1] *Department of Environmental Health, Health Promotion Research Center, Zahedan Universityof Medical Sciences, Zahedan, Iran.*

[2] *Student Research Committee, Zahedan University of Medical Sciences, Zahedan, Iran.*

[3]*Associate Professor, Department of Petroleum Engineering, Koneru Lakshmaiah Education Foundation, Vaddeswaram, Guntur, Andhra Pradesh, India*

Abstract: Antibiotics as emerging contaminants are of global concern due to the development of antibiotic resistant genes potentially causing superbugs. The inefficiency of conventional purification processes in the complete removal of antibiotics increases the resistance of microorganisms in humans and the environment, hence new and low-cost technology is needed. Adsorptive materials have been extensively used for the conditioning, remediation and removal of inorganic and organic hazardous materials. Zirconium oxide is a widely used inorganic material which is chemically stable, non-toxic and not soluble in water. Thus it could be an attractive candidate for drinking water puri? cation. In this study, Zirconium Oxide Nanoparticles (ZrO_2NP)has been used as the adsorbent for the possibility of removing Cipro? oxacin (CIP) from aqueous solution using the batch adsorption technique under different conditions of initial CIP concentration (25, 50, 75, 100 mg/L), adsorbent dose (0.1, 0.2, 0.3, 0.5, 0.7, 0.9 and 1 g/L) and contact time (10-150 min). The percentage of CIP adsorbed increased with increase in the mass of the adsorbent dose from 0.1 to 1 g/L. Kinetics study for sorption was evaluated using diffusion models, pseudo-first order kinetic and pseudo-second order kinetic. Results show that pseudo second-order kinetic model gave the best description for the adsorption process. The experiments showed that the highest removal rate was 96.5% under optimal conditions. The sorption of CIP on ZrO_2NP was rapid during the first 30 min and the equilibrium attained within 75 min. The results suggest that ZrO_2NPcould be a good candidate to remove CIP from wastewater containing different amounts of antibiotic.

Keywords: ZrO_2NP, Adsorption, Kinetics, Cipro? oxacin, Aqueous solution

***Corresponding Author**

Kethineni Chandrika , Associate Professor, Department of Petroleum Engineering, Koneru Lakshmaiah Education Foundation, Vaddeswaram, Guntur, Andhra Pradesh, India

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1. INTRODUCTION

In recent years, antibiotics have been widely used to treat bacterial infections in humans and animals [1-2]. Antibiotics are known as biodegradable materials. Residues of antibiotics in soil environments can lead to increased resistance of microorganisms[3-4]. As a broad-spectrum antibacterial, Ciprofloxacin (CIP) is one of the most frequently detected fluoroquinolone antibiotics which pose a serious threat to the ecosystem and human health by inducing proliferation of bacterial drug resistance [5, 6]. Although the CIP concentration in the environment is low, it can induce chronic allergic reactions and antibiotic resistance in bacteria [7].Antibiotics are potentially unchanged during the activity of conventional wastewater treatment plants [8-9]. These materials enter the surface and underground waters through various means. Therefore, the development of purification technologies in order to remove this pollutant is a necessity [10, 11]. Adsorption and chemical oxidation, together with biological treatment and precipitation are the most popularly known methods of removing antibiotics from aqueous solutions [12]. Other popularly known methods of removing antibiotics from aqueous solutions include distillation, solvent extraction, and ion exchange, as well as membrane processes, microbial fuel cells, reverse osmosis, and electrochemical methods [13-14]. There has been an increase in the demand for organic compounds removal that includes antibiotics due to increasing in industrial wastewaters [15]. Adsorption, a physio-chemical process, plays a vital role in the contaminants' transport and fate in engineered and natural aquatic systems by physical and chemical interactions[16-17]. Adsorption, in the systems of engineered treatment, is seen as a most cost-effective treatment approach in the reduction of dissolved contaminants to levels that are extremely low [18]. The simple nature of the adsorption systems makes their capital and operational costs, as well as their fouling problems low, thereby shielding them from being affected by toxic harmful substances [19-20]. For this purpose, various adsorbents have been examined, including zero-valent iron, activated carbon, goethite, Zeolite, red mud, and fly ash.[21-22] Because of their large surface areas and preferred surface properties, synthesized metal oxides at nano-size have demonstrated effective antibiotics adsorption[23]. Zirconium oxide is a widely used inorganic material which is chemically stable, non-toxic and not soluble in water[24]. Thus it could be an attractive candidate for drinking water purification. Compared with extensively studied oxides based on aluminum, iron and titanium, there are limited reports on using zirconium based oxides for the removal of organic compounds[25, 26]. There is no report on using nano structured ZrO_2 to remove antibiotics from water. Due to the inefficiency of conventional purification processes to remove CIP antibiotic in hospital, urban and Pharmaceutical Industries sewage, the use of ZrO_2NP as a new adsorbent and due to their excellent ability to remove various organic and inorganic pollutants in sewage, has attracted widespread attention. The purpose of this study is to investigate the use of ZrO_2-NP to evaluate CIP adsorption potential from aqueous solutions.

2. MATERIALS AND METHODS

2.1 Preparation of CIP Solution

This study is an applied research which is empirical and done on an experimental scale. All chemicals used in this study except Zirconium Oxide Nanoparticles, which is the product of Sigma Aldrich, were supplied from Merck Co., Germany. Ciprofloxacin (CIP) antibiotics, ($C_{17}H_{18}FN_3O_3$·HCl, purity >98%) with a molecular weight of 696.6 g/mol was purchased from Sigma-Aldrich and used without further purification. The molecular structure of Ciprofloxacin is given in Figure 1.Stock solution of CIP was prepared by dissolving 1 g of the CIP in 1L of distilled water to obtain concentration of 1000 mg/L. The serial dilutions of the stock was performed to obtain 25, 50, 75 and 100 mg/L. The pH of CIP solutions was adjusted with 0.1 M NaOH or HCL using a pH meter.

2.2 Batch Adsorption Experiments

Batch experiments were carried out in orbital shaker at a constant speed of 120 rpm at 20^{0}C in 250 mL conical flasks. Varied dosages (0.1, 0.2, 0.3, 0.5, 0.7, 0.9 and 1 g/L) of ZrO_2-NP, varied initial CIP concentration (25, 50, 75 and 100 mg/L) were used for the adsorption studies at predetermined time intervals (10-150 min) at fixed pH=7. The adsorbent was separated from the solution by centrifugation at 2000 rpm for 10 minutes. The residual CIP concentration after adsorption was determined spectrophotometrically using UV-Vis spectrophotometer at λ_{max}=276 nm. The temperature of the solution was maintained at 20 °C. The CIP concentration was measured until the equilibrium reached. The removal efficiency (%R) of the CIP was calculated using the equation below

$$\% R = \left[\frac{C_0 - C_e}{C_e}\right] \times 100$$

Where, Co and Ce are the initial and equilibrium concentrations of CIP (mg/L), V is the volume (L) of the CIP solution used.

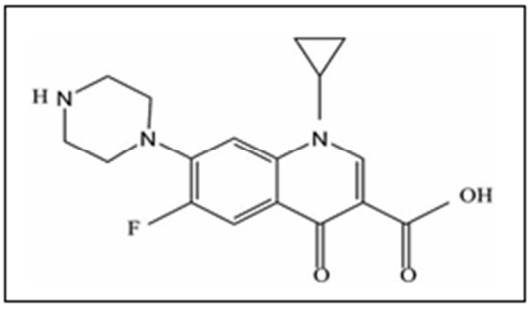

Fig 1. The structure of CIP

3. RESULTS AND DISCUSSION

3.1 Effect of the contact time

Contact time is an important factor that affects uptake efficiency in batch adsorption process. Fig. 2 reveals that the maximum adsorption of CIP occurred at around 75 min with percentage removal of 96.5%. The rate of the adsorption process increased rapidly in the first 30 min and then grew more slowly as the agitation time increased beyond 30 min. The rapid removal of CIP at the initial stage may be attributed to the rapid attachment of CIP molecules to the surface of the adsorbent and the increased number of binding sites available, consequently leading to an increase in driving force of the concentration gradient between adsorbate in solution and adsorbate-adsorbent interaction [27, 28]. This implies that the adsorption process nearly reached equilibrium within the first 75 min of agitation. This observation is similar to literature reports on the adsorption of CIP.

3.2 Effect of the adsorbent dose

The effect of adsorbent mass on the adsorption study is shown in Fig. 3. The figure reveals that percentage removal is a function of the mass of the adsorbent used. The percentage of CIP adsorbed increased with increase in the mass of the adsorbent dose. This behavior can be attributed to increased adsorbent surface area which invariably increases the number of adsorption sites available for adsorption [29, 30]. Results similar to this have been reported by several authors [31, 32].

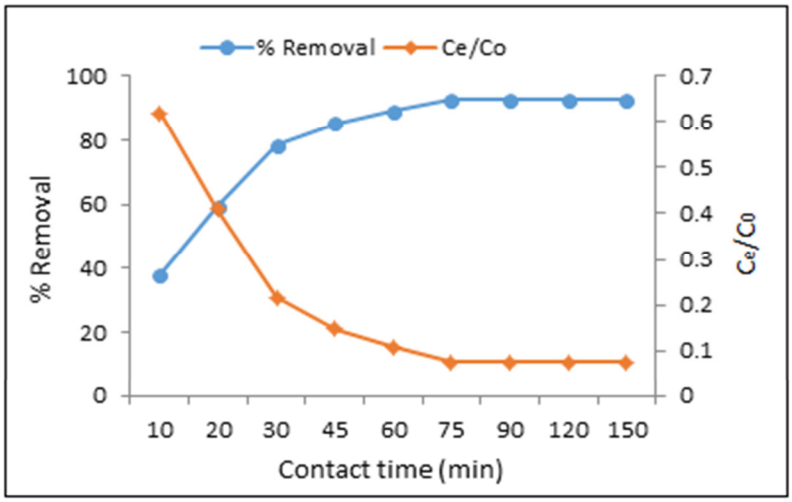

Fig 2. Effect of contact time on CIP removal by ZrO_2-NP (pH =7, C_0=100 mg/L, Adsorbent dosage 1 g/L and temperature= 28±2°C)

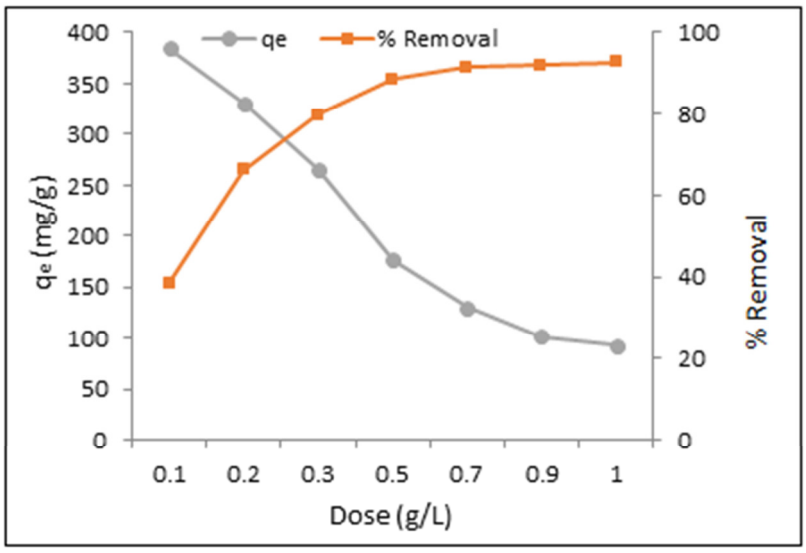

Fig 3. Effect of adsorbent dosage on CIP adsorptionby ZrO_2NP (C_0 = 100 mg/L, contact time = 75 min, pH = 7, temperature= 28 ± 2°C)

3.3 Adsorption Kinetics

A study of the kinetics of adsorption is desirable as it provides information about the mechanisms and characteristics of adsorption which is important for efficiency of the process. The Pseudo-first-order and Pseudo-second-order kinetic models were tested at different concentrations in this study to determine which model is in good agreement with experimental q_e

(adsorption capacity) value, thus suggesting which model that the sorption system follows. The Pseudo-first-order-model can be expressed by following equation [32, 33]

$$\text{Log } (q_e - q_t) = \log q_e - \frac{K_1}{2.303}t$$

Where, q_e,q_t (mg/g) are the masses of the CIP adsorbed at equilibrium (adsorptive capacity), and at any time (t), respectively; K_1, (1/min) is the equilibrium constant of the pseudo-first-order adsorption. The value of $K_1$and $q_e$are determined, respectively from the slope and intercept of the plot of Log (q_e− q_t) versus t. A pseudo-second order equation can be expressed as follows [34-36]:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e}$$

Where, K_2 (mg/g.min), and q_e, are rate constants and adsorption capacity at equilibrium, respectively. The value of q_e is determined from the plot of t/q_t versus time. The values for q_e and K_2 can be calculated from the slope and intercept. The two models described the adsorption data. The agreement between experimental data and model calculated values is expressed by the correlation coefficient R^2. The results are presented in Table 1. Kinetic adsorption of CIP onto ZrO_2-NPfits pseudo-second order model more than pseudo-first-order-model. The correlation coefficients R^2 indicate the applicability of these kinetic equations and the good agreement between the experimental and calculated equilibrium describes correctly the adsorption kinetics.

Table 1. Parameters for CIP adsorption onto ZrO2-NP

CIP Concentration (mg/L)			
25	**50**	**75**	**100**
48.22	94.48	135.6	172.8
11.93	28.58	37.81	69.36
0.176	0.129	0.104	0.083
0.891	0.874	0.869	0.848
48.22	94.48	135.6	172.8
41.96	89.72	129.7	166.4
0.034	0.00145	0.0096	0.0081
0.999	0.998	0.996	0.997

4. CONCLUSION

The effect of contact time on the CIP adsorption showed that the adsorption process increases with increase in contact time, reaching equilibrium in about 90 min. Kinetics of the adsorption shows that the process follows pseudo-second-order kinetic model, indicating that the rate-limiting step of the process could be the chemical reaction. Kinetic studies also showed that the adsorption transport mechanism was particle-diffusion controlled for adsorption of metal ions onto the adsorbents.

5. ACKNOWLEDGMENT

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6. AUTHORS CONTRIBUTION STATEMENT

Eng. Marzieh Baniasadi conceptualized and gathered the data with regard to this work. Dr. Davoud Balarak and Dr. Kethineni Chandrika analyzed these data and necessary inputs were given towards the designing of the manuscript. All authors discussed the methodology and results and contributed to the final manuscript.

7. CONFLICT OF INTEREST

Conflict of interest declared none.

8. REFERENCES

1. Balcıoğlu IA, Ötker M.Treatment of pharmaceutical wastewater containing antibiotics by O_3 and $O3/H_2O_2$ processes.Chemosphere. 2003;50(1):85-95. DOI: 10.1016/S0045-6535(02)00534-9.
2. Oberoi AS. Insights into the Fate and Removal of Antibiotics in Engineered Biological Treatment Systems: A Critical Review Environ. Sci. Technol. 2019;53(13):7234-64. DOI: 10.1021/acs.est.9b01131
3. Adriano WS, Veredas V, Santana CC. Adsorption of amoxicillin on chitosan beads: Kinetics, equilibrium and validation of finite bath models. Biochem Eng J. 2005; 27(2): 132-37. DOI:10.1016/j.bej.2005.08.010
4. Ding R, Zhang P, Seredych M, Bandosz TJ. Removal of antibiotics from water using sewage sludge- and waste oil sludge-derived adsorbents. Water research. 2012; 46(13):4081-90. DOI: 10.1016/j.watres.2012.05.013

5. Chen WR, Huang CH. Adsorption and transformation of tetracycline antibiotics with aluminum oxide. Chemosphere. 2010; 79(8): 779-85. DOI: 10.1016/j.chemosphere.2010.03.020
6. Igwegbe CA, Ahmadi S, Rahdar S, Ramazani A, Mollazehi AR, Igwegbe CA, Ahmadi S, Rahdar S, Ramazani A, Mollazehi AR. Efficiency comparison of advanced oxidation processes for ciprofloxacin removal from aqueous solutions: Sonochemical, sono-nano-chemical and sono-nano-chemical/persulfate processes. Environmental Engineering Research. 2019;25(2):178-85. DOI: 10.4491/eer.2018.058
7. Liangliang Ji. Adsorption of Pharmaceutical Antibiotics on Template-Synthesized Ordered Micro- and Mesoporous Carbons. *Environ. Sci. Technol.* 2010; 44(8): 3116-22. DOI: 10.1021/es903716s
8. Peng X, Hu F, Dai H, Xiong Q. Study of the adsorption mechanism of ciprofloxacin antibiotics onto graphitic ordered mesoporous carbons. Journal of the Taiwan Institute of Chemical Engineers. 2016; 8; 1–10. DOI: 10.1016/j.jtice.2016.05.016.
9. Ahmed, MJ, Theydan SK. Fluoroquinolones antibiotics adsorption onto microporous activated carbon from lignocellulosic biomass by microwave pyrolysis. Journal of the Taiwan Institute of Chemical Engineers. 2014;45(1): 219-26. DOI: 10.1016/j.jtice.2013.05.014
10. Alexy R, Kumpel T, Kummerer K. Assessment of degradation of 18 antibiotics in the closed bottle test.Chemosphere. 2004; 57(6): 505-12. DOI: 10.1016/j.chemosphere.2004.06.024
11. Choi K.J, Kim SG, Kim SH. Removal of antibiotics by coagulation and granular activated carbon filtration. Journal of Hazardous Materials. 2007; 151(1): 38-43. DOI: 10.1016/j.jhazmat.2007.05.059
12. Ahmed MJ. Theydan SK. Fluoroquinolones antibiotics adsorption onto microporous activated carbon from lignocellulosic biomass by microwave pyrolysis. Journal of the Taiwan Institute of Chemical Engineers. 2014;45(1), 219-26. DOI: 10.1016/j.jtice.2013.05.014.
13. Maria HL, Ribeiro E, Isabel AC. Modelling the adsorption kinetics of erythromycin onto neutral and anionic resins. Bioprocess Biosyst Eng. 2003; 26: 49–55.
14. Balarak D, Mostafapour FK, Bazrafshan E, Saleh, TA.Studies on the adsorption of amoxicillin on multi-wall carbon nanotubes.Watersci technol. 2017; 75(7): 1599-606. DOI: 10.2166/wst.2017.0
15. Erşan M, Bağd E. Investigation of kinetic and thermodynamic characteristics of removal of tetracycline with sponge like, tannin based cryogels. Colloid Surf B. 2013;104(1): 75-82. DOI: 10.1016/j.colsurfb.2012.11.034
16. Bansal P, Verma A, Aggarwal K, Singh A, Gupta S. Investigations on the degradation of an antibiotic cephalexin using suspended and supported TiO2: mineralization and durability studies. Can. J. Chem. Eng. 2016; 94(7): 1269-76. DOI: 10.1002/cjce.22512
17. Bui TX, Choi H. Adsorptive removal of selected pharmaceuticals by mesoporous silica SBA-15. Journal of Hazardous Materials. 2009; 168(2-3): 602–8. DOI: 10.1016/j.jhazmat.2009.02.072
18. Yu F, Li Y, Han S, Jie Ma J. Adsorptive removal of antibiotics from aqueous solution using carbon Materials. Chemosphere. 2016; 153;365-85. DOI: 10.1016/j.chemosphere.2016.03.083
19. Aksu Z, Tunc O. Application of biosorption for Penicillin G removal: Comparison with activated carbon. Process Biochem. 40(2):831-47; 2005. DOI: 10.1016/j.procbio.2004.02.014
20. Ji L, ChenW, Duan L and Zhu D. Mechanisms for strong adsorption of tetracycline to carbon nanotubes: A comparative study using activated carbon and graphite as adsorbents. Environ Sci Technol. 2009; 43(7); 2322–27. DOI: 10.1021/es803268b.
21. Peterson JW, Petrasky LJ, Seymourc MD, Burkharta RS, Schuilinga AB. Adsorption and breakdown of penicillin antibiotic in the presence of titanium oxide nanoparticles in water. Chemosphere. 2012;87(8):911–7. DOI:10.1016/j.chemosphere.2012.01.044
22. Ghauch A, Tuqan A, Assi HA: Antibiotic removal from water: Elimination of amoxicillin and ampicillin by micro scale and nano scale iron particles. Environ Pollut. 2009;157:1626-35;. DOI:10.1016/j.envpol.2008.12.024
23. Balarak D, Azarpira H, Mostafapour FK. Adsorption isotherm studies of tetracycline antibiotics from aqueous solutions by maize stalks as a cheap biosorbent. International Journal of Pharmacy & Technology.2016; 8(3); 16664-75. DOI: 10.1016/j.scitotenv.2018.01.249
24. Chang PH, Li Z, Jean JS, Jiang WT, Wang CJ, Lin KH. Adsorption of tetracycline on 2:1 layered non-swelling clay mineral illite. Appl Clay Sci. 2012; 67;158-63;. DOI: 10.1016/j.clay.2011.11.004
25. Ahmadi S, Banach A, Mostafapour FK, Balarak D. Study survey of cupric oxide nanoparticles in removal efficiency of ciprofloxacin antibiotic from aqueous solution: Adsorption isotherm study. Desalination and Water Treatment.2017; 89: 297-303. DOI: 10.5004/dwt.2017.21362
26. Bergamaschi VS, Carvalho FMS, Rodrigues C, Fernandes DB. Preparation and evaluation of zirconium microspheres as inorganic exchanger in adsorption of copper and nickel ions and as catalyst in hydrogen production from bioethanol. Chemical Engineering Journal. 2005;112(1-3):153-8;. DOI: 10.1016/j.cej.2005.04.016.
27. Awual MR, Jyo A, Ihara T, Seko N, Tamada M, Lim KT. Enhanced trace phosphate removal from water by zirconium(IV) loaded fibrous adsorbent. Water Research. 2010; 45, 4592-4600. DOI: 10.1016/j.watres.2011.06.009
28. Cui H, Li Q, Gao SA, Shang JK. Strong adsorption of arsenic species by amorphous zirconium oxide nanoparticles.Journal of Industrial and Engineering Chemistry. 2012; 18: 1418-27. DOI: 10.1016/j.jiec.2012.01.045
29. Ren ZM, Shao LN, Zhang GS.Adsorption of phosphate from aqueous solution using an iron-zirconium binary oxide sorbent.Water Air Soil Pollution. 2012; 223, 4221-31. DOI: 10.1007/s11270-012-1186-5
30. Rostamian R, Behnejad H. A comparative adsorption study of sulfamethoxazole onto graphene and graphene oxide nanosheets through equilibrium,

kinetic and thermodynamic modeling. Process Saf Environ Prot. 2016; 102: 20-29.
DOI: 10.1016/j.psep.2015.12.011

31. Gao Y, Li Y, Zhang L, Huang H, Hu J, Shah SM, Su X. Adsorption and removal of tetracycline antibiotics from aqueous solution by grapheme oxide.J Colloid Interface Sci. 2012; 368; 540-46.
DOI: 10.1016/j.jcis.2011.11.015
32. Gao J and Pedersen JA. Adsorption of Sulfonamide Antimicrobial Agents to Clay Minerals. Environ Sci Technol. 2005; 39(24): 9509-16;.
DOI: 10.1021/es050644c
33. Moussavi SP, MohammadianFazli M. Acid violet 17 Dye Decolorization by Multi-walled Carbon Nanotubes from Aqueous Solution. J Hum Environ Health Promot. 2016;1(2):110-17. Available from: http://zums.ac.ir/jhehp/browse.php?a_id=35&sid=1&slc_lang=en
34. Rasoulifard MH, TaheriQazvini N, Farhangnia E, Heidari A, DoustMM. Removal of direct Yellow 9 and Reactive Orange 122 from contaminated water using chitosan as a polymeric bioadsorbent by adsorption process. J Color Sci Technol. 2010; 4:17-23. Available from: http://ijhe.tums.ac.ir/browse.php?a_id=97&sid=1&slc_lang=en
35. Lanhua Hu. Oxidation Kinetics of Antibiotics during Water Treatment with Potassium Permanganate. Environ. Sci. Technol. 2010; 44(16): 6416-42.
DOI: 10.1021/ es101331j
36. Castiglioni S. Removal of Pharmaceuticals in Sewage Treatment Plants in Italy. Environ. Sci. Technol. 2006; 40(1): 357-63. 2006. DOI: 10.1021/es050991m
37. Balarak D, Mostafapour FK. Photocatalytic degradation of amoxicillin using UV/Synthesized NiO from pharmaceutical wastewater. Indonesian Journal of Chemistry.2019; 19(1), 211-18.
DOI: 10.22146/ijc.33837