The Pharmaceutical and Chemical Journal, **2016, 3(2):12-17**

Available online www.tpcj.org

Research Article

ISSN: 2349-7092
CODEN(USA): PCJHBA

Canola Residual as a Biosorbent for Antibiotic Metronidazole Removal

Davoud Balarak*, Ferdos Kord Mostafapour

Department of Environmental Health, Health Promotion Research Center, School of Public Health, Zahedan University of Medical Sciences, Zahedan, Iran

*Corresponding author: Email id: dbalarak2@gmail.com

Abstract Significant concerns have been raised over pollution of antibiotics including metronidazole (MNZ) in aquatic environments in recent years. dried Canola biomass is a potential effective absorbent for metronidazole antibiotics and can be used to remove them from aqueous solution. The adsorption isotherm fits Langmuir and Temkin models well, and the theoretical maximum of adsorption capacity calculated by Langmuir model is 21.42 mg/g, which is approximately in a close agreement with the measured data. Higher adsorption percentages were observed at lower concentrations of MNZ and Maximum antibiotic was removed within 90 min after the beginning for every experiment.

Keywords Canola, Metronidazole, Adsorption, Isotherm

Introduction

For several decades now antibiotics have been used in veterinary and human medicine, yet these compounds when released into the environment have potential risks for aquatic and terrestrial organisms [1-3]. The antibiotics are excreted in large quantities with more than 75% of them are being unmetabolized and are therefore likely to end up in domestic wastewater in significant quantities [4, 5]. Pharmaceutical ingredients are actually found as residues in water and have been recognized as part of the hazardous chemical substances able to alter the natural equilibrium system of the surrounding environment [6, 7]. Recently, antibiotics were quantified in hospital sewage water and wastewater, in rivers and in wastewater treatment plants [8-10]. Metronidazole (MNZ) with antibacterial and anti-inflammatory properties is a kind of nitroimidazole antibiotic, which is commonly used in clinical applications and widely used for the treatment of infectious diseases caused by anaerobic bacteria and protozoans, such as Giardia lamblia and Trichomonas vaginalis [11, 12]. Aside from being widely used as antibiotics for humans, MNZ is also abused as an additive in poultry and fish feed to eliminate parasites. As a result, MNZ was accumulated in animals, fish farm water, and effluents from meat industries [13]. Recently, adsorption of antibiotic onto bentonite and activated carbon has been investigated, and results show that the adsorption of amoxicillin onto activated carbon plays an important role [14]. However, the most used adsorbents in this process are activated carbons (GACs) which are costly [15]. Consequently, there is much interest in finding alternative adsorbents that are inexpensive to implement [16, 17]. The canola stalk is one of lignocellulosic wastes that are widely produced in Iran and all of the world due to the growth of the production and consumption of vegetable oils; therefore, the Canola stalk is easily available and due to its characteristics has been used in several studies to remove the pollutants [18-20]. The objective of this study is to investigate the capability of this lignocellulosic waste material, for the removal of metronidazole from aqueous solutions in batch system. The effects of different process parameters like biosorbent dose, initial MNZ concentration, Contact time and temperature on the biosorption of MNZ are studied. The equilibrium and kinetic data of biosorption studies are processed to understand the mechanism of MNZ onto Canola biomass.

Materials and Methods

Preparation procedure of adsorbent: In this study, the Canola was used as low cost natural or agricultural wastes for MNZ removal from aqueous solutions. The stalks of Canola(C) were collected from research farm of Tabriz agricultural school. The stalks were washed several times with water to remove the contaminant, dried in the oven at 105 ℃ for 5 h. The biomass was then treated with 0.5M H_2SO_4 for 2 h followed by the washing with distilled water and then was oven dried at 105 ℃ for 5 h. After drying, adsorbent were sieved to obtain particle size of 18 mesh prior to being used for adsorption studies.

MNZ ($C_6H_9N_3O_3$; 99% chemical reagent) was supplied by the Merck Company. Standard MNZ was supplied by the National Institute for the Control of Pharmaceutical and Biological Products and was used for calibration.

Various experimental conditions which may influence on biosorption of MNZ by dried Canola, including contact time**,** biosorbent dosage and initial MNZ concentration were assessed in batch experiments. Initial MNZ solutions with different concentrations were prepared by diluting of MNZ stock solution (1000 mg/L) with distilled water. The pH was adjusted using either diluted 0.1M HCL or 0.1M NaOH solution. The experiments in batch system were carried out in a 100 ml Erlenmeyer flask. The resulting solutions were then shaken at 180 rpm and the samples were taken at fixed time periods (10-150 min) in order to study the kinetics of the adsorption process. Preliminary experiments showed that this time length was sufficient for adsorption of MNZ onto Canola sorbent. The samples were subsequently filtered off through 0.45 µm cellulose filter and the residual MNZ concentration in the filtrate was determined using Spectrophotometer (DR 5000) at wavelength of 340 nm [21].

The percentage of adsorption of MNZ from the solution was calculated from the relationship [22]:

$$\%R = (Co - Ce)/Co \times 100 \quad (1)$$

Where Co corresponds to the initial concentration of MNZ ions and C_e is the residual concentration after stirring for a definite time. The metal uptake q_e (mg/g) was calculated as [23]:

$$q = [(Co - Cr)/m].V \quad (2)$$

Where m is the quantity of sorbent (mg) and V the volume of the suspension (ml).

Results and Discussion

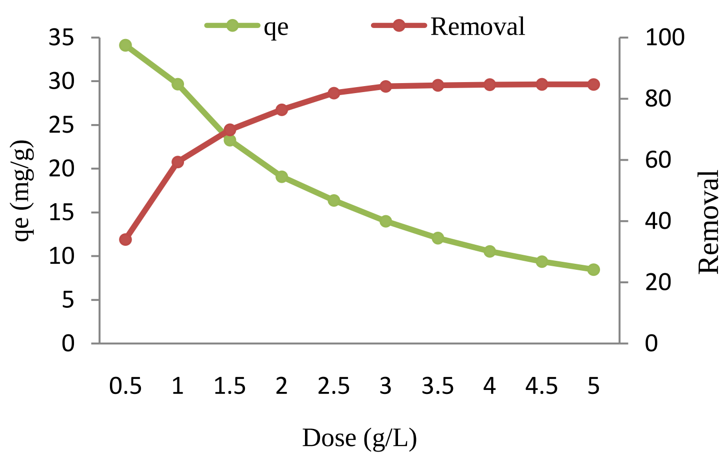

Figure 1: Effect of biomass dose on MNZ biosorption

(C_0 = 50 mg/L, pH=7, Contact time=90 min and Temp: 25 °C)

Changes in the amount of adsorbent during the adsorption process (Fig. 1) showed a general trend of increase in percentage removal as the adsorbent dose increased from 0.5 to 3 g. This phenomenon according to balarak et al [24], is expected since the Amoxicillin uptake capacity of the adsorbent increases with the increase in dosage as the number of active sites available for metal increases with increase in the amount of adsorbent. Malakootian et al [25]., similarly reported that increasing adsorption with adsorbent weight can be attributed to increased number of unsaturated active sites on the adsorbents as well as high accessibility of the various ions to the binding sites.

Adsorption isotherms for MNZ with Canola as adsorbent are presented in Fig. 2a. C_e (mg L^{-1}) denotes the equilibrium concentrations in aqueous phase after the adsorption of MNZ on Canola. The equilibrium adsorption capacity (q_e, mg g^{-1}) of Canola is the variation between initial (C_0) and equilibrium concentration (C_e) caused by per unit weight of the adsorbent, Canola. In short, q_e is calculated by $(C_0–C_e)/C_{canola}$. As shown in Fig. 3a, adsorption capacities increase with the increase in equilibrium concentration of adsorbates and the slopes of adsorption isotherms decrease gradually. When initial concentration is lower than 25 mg L^{-1}, the final equilibrium concentration is lower than 1.04 mg L^{-1} and the removal efficiencies are higher than 94.8%. In the present work, the Langmuir, Freundlich, and Temkin models, three classic adsorption models, were used to describe the adsorption equilibrium. The mathematical representations of the Langmuir, Freundlich, and Temkin models are given below [26-28]:

$$\frac{C_e}{q_e} = \frac{1}{q_{max} K_L} + \frac{C_e}{q_{max}}$$

$$\text{Log } q_e = \frac{1}{n} \log Ce + \log K_F$$

$$q_e = K_t \ln (A) + K_t \ln C_e$$

Where q_{max} is the theoretical maximum adsorption capacity per unit weight of the adsorbent (mg g^{-1}), K_L, K_F, K_T are adsorption constants of Langmuir, Freundlich, and Temkin models, respectively, and n is the Freundlich linearity index. Langmuir model is an ideal model, which possesses perfect adsorbent surface and monolayer molecule adsorption. As an empirical model, Freundlich model is used widely in the field of chemistry. Temkin model is a proper model for the chemical adsorption based onstrong electrostatic interaction between positive and negative charges [29-30].

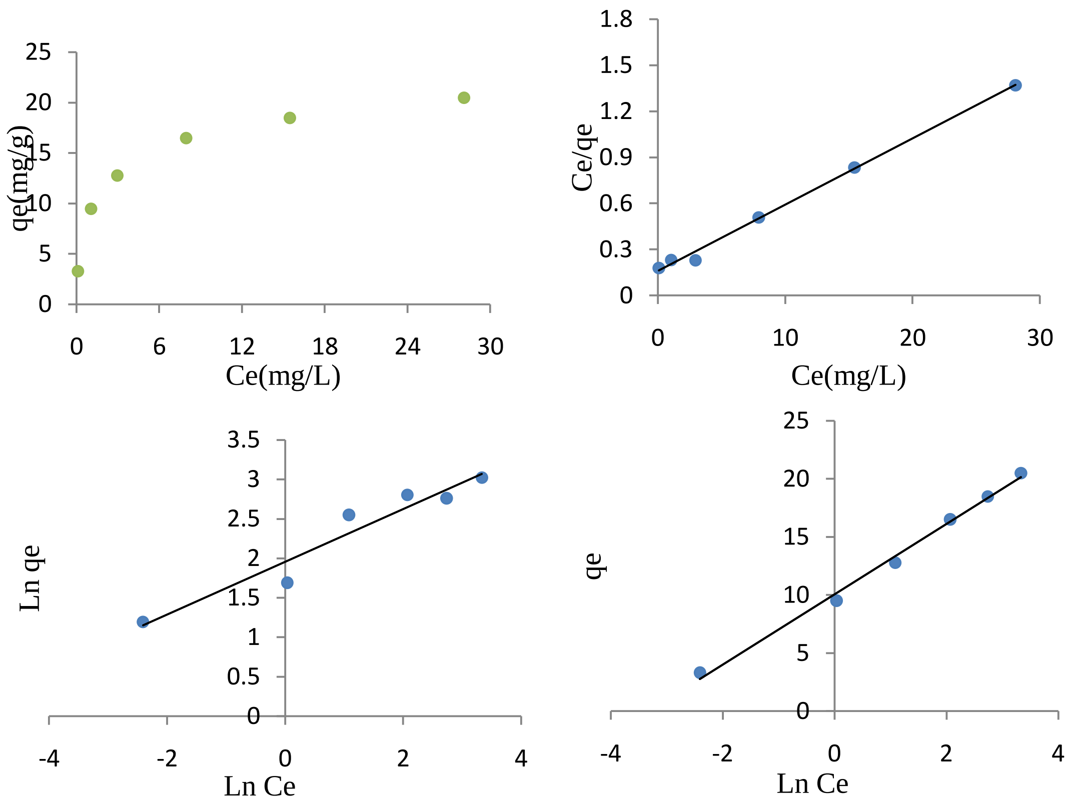

Figure 2: Adsorption isotherms of MNZ on Canola (a); Langmuir (b); Freundlich (c), and Temkin (d) model fitting for the adsorption of MNZ on Canola. Experiment condition: pH 7; 25 ℃; dose biomass 3 g/L and contact time 90 min.

The results of fitting these models are shown in Fig. 2b–d, and the fitting parameters for tetracycline are listed in Table 1. In the range of tested concentration, the Langmuir (R^2 = 0.994) and Temkin models (R^2 = 0.986) fit the adsorption data well, while the Freundlich model (R^2= 0.921) fits reasonably. Although the Langmuir model globally fits well, it does not give apparently a nice fit at high concentration levels, showing the limitation of the hypothesis about a monolayer adsorption. Considering the Temkin model gives the best fitting at all tested concentration levels, we suspected that there was electrostatic interaction in the process of adsorption. From Langmuir model, the ideal maximum adsorption capacity (q_{max}) as a model fitting parameter was determined to be 21.42 mg g^{-1}.

Table 1: The adsorption isotherms constants for the removal MNZ

Langmuir			Freundlich			Temkin		
q_m	K_L	R^2	n	K_F	R^2	K_t	A	R^2
21.42	0.43	0.998	3.57	0.95	0.886	9.85	0.368	0.975

The effect of agitation time on various concentrations of MNZ solutions (10 to 100 mg/L) is presented in Figure 3. The removal rate was rapid during first 30 min of agitation. Then the rate slowed down gradually until it attained an equilibrium beyond which there was no significant increase in the rate of removal. Adsorption equilibrium was obtained at 90 min. Data indicated that the maximum adsorption (q_e) was 3.24, 6.86, 9.21, 13.12, 18.5 and 22.2 respectively, for the initial MNZ concentrations of 10, 20, 30, 50, 75 and 100 mg/L.

The initial high biosorption rate of MNZ on dried Canola within the first 30 minutes was attributed to the high the availability of binding sites on the surface of dried Canola [31, 32], and the subsequent lower biosorption rate after 30 minutes was decreased availability of binding sites on the surface of dried Canola due to the absorption of initial MNZ molecules [33, 34].

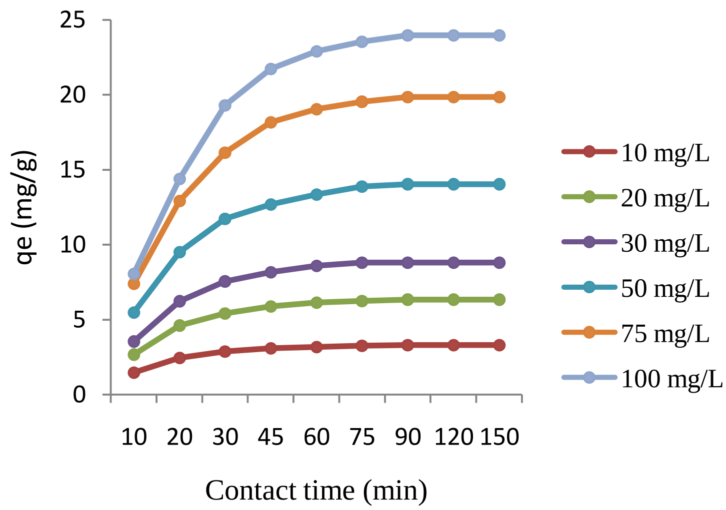

Figure 3: Effect of contact time and initial MNZ concentration(pH = 7, adsorbent dose 3 g/L, Temp: 25 °C)

Conclusions

This study focused on the biosorption of MNZ onto Canola biomass from aqueous solution. The operating parameters, biomass dosage, contact time and initial MNZ concentration, were effective on the biosorption efficiency of MNZ. The percent of MNZ removed by 3 g of biomass at 25 ^oC was nearly 99%. The equilibrium data were analyzed using Langmuir and Freundlich and Tekmin isotherms. Langmuir isotherm fit data very well, which implies the homogenous of surface and that adsorption uptake of MNZ by Canola biomass is mono-layers. Study on the removal of antibiotic MNZ by using canola biomass showed that canola was able to successfully eliminate antibiotic MNZ.

References

1. Xu WH, Zhang G, Zou SC, Li XD, Liu YC. Determination of selected antibiotics in the Victoria Harbour and the Pearl River, South China using high-performance liquid chromatography electrospray ionization tandem mass spectrometry. Environ. Pollut. 2007;145, 672-679.
2. Alexy R, Kumpel T, Kummerer K. Assessment of degradation of 18 antibiotics in the closed bottle test. Chemosphere; 2004 ; 57, 505–512.
3. Zhang W, He G, Gao P, Chen G: Development and characterization of composite nanofiltration membranes and their application in concentration of antibiotics. Sep Purif Technol 2003, 30:27–35.
4. Choi KJ, Kim SG, Kim SH. Removal of antibiotics by coagulationand granular activated carbon filtration. J. Hazard. Mater.2008; 151;38–43.
5. Zhang L, Song X, Liu X, Yang L, Pan F, Lv J. Studies on the removal of tetracycline by multi-walled carbon nanotubes, Chem. Eng. J. 2011; 178;26–33.
6. Zhu XD, Wang YJ, Sun RJ, Zhou DM. Photocatalytic degradation of tetracycline in aqueous solution by nanosized TiO_2. Chemosphere. 2013; 92; 925–932.
7. Gómez-Pacheco CV, Sánchez-Polo M, Rivera-Utrilla J, López-Peñalver J. Tetracycline removal from waters by integrated technologies based on ozonation and biodegradation. Chem. Eng. J. 2011; 178 ;115–121.
8. Parolo ME, Savini MC, Vallés JM, Baschini MT, Avena MJ. Tetracycline adsorption on montmorillonite: pH and ionic strength effects, Appl. Clay Sci. 208;40;179–186.
9. Ocampo-Pérez R, Rivera-Utrilla J, Gómez-Pacheco C, Sánchez-Polo M, López-Peñalver JJ. Kinetic study of tetracycline adsorption on sludge-derived adsorbents in aqueous phase, Chem. Eng. J. 2012; 213; 88–96.
10. Gulkowsk A, Leung HW, So MK, Taniyasu S, Yamashita N. Removal of antibiotics from wastewater by sewage treatment facilities in Hong Kong and Shenzhen, China. Water research. 2008;42:395-403.
11. Bendesky A, Menendez D, Ostrosky-Wegman P. Is metronidazole carcinogenic? Mutat. Res. 2002; 511;133–144.
12. Lanzky PF, Haning-Snrensen B. The toxic effect of the antibiotic metronidazole on aquatic organisms. Chemosphere.1997; 35; 2553–2561.
13. Johnson MB, Mehrvar M. Aqueous metronidazole degradation by UV/H_2O_2 process in single-and multi-lamp tubular photoreactors: kinetics and reactor design, Ind. Eng. Chem. Res.2008; 47; 6525–6537. .
14. Putra EK, Pranowoa R, Sunarsob J, Indraswatia N, Ismadjia S. Performance of activated carbon and bentonite for adsorption of amoxicillin from wastewater: mechanisms, isotherms and kinetics. Water Res. 2009; 43, 2419-2430.
15. Crisafully R, Milhome MAL, Cavalcante RM, Silveira ER, Keukeleire DD, Nascimento RF. Removal of some polycyclic aromatic hydrocarbons from petrochemical wastewater using low-cost adsorbents of natural origin. Bioresour. Technol. 2008; 99, 4515-4519.
16. Mane VS ,Mall ID. Kinetic and equilibrium isotherm studies for the adsorptive removal of Brilliant Green dye from aqueous solution by rice husk ash, J. Environ. Manage.2007: 84 ;390–400.
17. Aksu Z, Tunc O. Application of biosorption for Penicillin G removal: Comparison with activated carbon. Process Biochemistry. 2005;40(2):831-47.
18. Zazouli MA, Mahvi AH, Mahdavi Y, Balarak D. Isothermic and kinetic modeling of fluoride removal from water by means of the natural biosorbents sorghum and canola. Fluoride. 2015;48(1):15-22.
19. Diyanati RA, Yousefi Z, Cherati JY, Balarak D. Comparison of phenol adsorption rate by modified Canola and Azolla: An Adsorption Isotherm and Kinetics Study.Journal of Health & Development. 2014; 3(3);17-25.
20. Balarak D, Mahdavi Y, Gharibi F, Sadeghi Sh. Removal of hexavalent chromium from aqueous solution using canola biomass: Isotherms and kinetics studies. J Adv Environ Health Res.2014; 2(4);45-52.
21. Naveed S, Qamar F. Simple UV Spectrophotometric Assay of Metronidazole. Open Access Library Journal. 2014;1:615-619.

22. Zazouli MA, Balarak D, Karimnezhad F, Khosravi F. Removal of fluoride from aqueous solution by using of adsorption onto modified Lemna minor: adsorption isotherm and kinetics study. Journal of Mazandaran University Medical Sciences 2014;23(109):208-17.
23. Ghauch A, Tuqan A, Assi HA: Elimination of amoxicillin and ampicillin by micro scale and nano scale iron particles. Environ Pollut 2009,157:1626–1635.
24. Balarak D, Mahdavi Y, Azadi NA, Sadeghi SH. Isotherms and thermodynamic study on the biosorption of amoxicillin using canola. International Journal of Analytical, Pharmaceutical and Biomedical Sciences.2016;5(3);8-14.
25. Malakootian M, balarak D, Mahdavi Y, Sadeghi SH, Amirmahani N. Removal of antibiotics from wastewater by azolla filiculoides: kinetic and equilibrium studies. International Journal of Analytical, Pharmaceutical and Biomedical Sciences.2015;4(7);105-113. .
26. Balarak D,Kord Mostafapour F, Joghataei A. Experimental and Kinetic Studies on Penicillin G Adsorption by Lemna minor.International Research Journal of Pure & Applied Chemistry.2016; 10(2): 1-11.
27. Balarak D, Joghataei A, Azadi NA, Sadeghi S. Biosorption of Acid Blue 225 from Aqueous Solution by Azolla filiculoides: Kinetic and Equilibrium Studies. American Chemical Science Journal. 2016; 12(2):1-10.
28. Dianati RA, Balarak D. Ghsemi SM.Survey of efficiency agricultural weast in removal of acid orang 7(AO7) dyes from aqueous solution: kinetic and equilibrium study: Iranian journal of health sciences. 2013;2(1):35-40.
29. Balarak D, Pirdadeh F, Mahdavi Y. Biosorption of Acid Red 88 dyes using dried Lemna minor biomass. Journal of Science, Technology & Environment Informatics.2015; 1(2), 81–90.
30. Zazouli MA, Yazdani J, Balarak D, Ebrahimi M, Mahdavi Y. Removal Acid Blue 113 from Aqueous Solution by Canola. Journal of Mazandaran University Medical Science. 2013;23(2):73-81.
31. Balarak D, Bazrafshan E, Kord Mostafapour F.Equilibrium, Kinetic Studies on the Adsorption of Acid Green 3 (Ag3) Dye Onto Azolla filiculoides as Adosorbent. American Chemical Science Journal.2016;11(1);1-10.
32. Balarak D, Mahdavi Y. Survey of Efficiency Agricultural Waste as Adsorbent for Removal of P-Cresol from Aqueous Solution. International Research Journal of Pure & Applied Chemistry.2016;10(2): 1-11.
33. Yang K, Wu W, Jing Q, Zhu L. Aqueous adsorption of aniline, phenol, and their substitutes by multi-walled carbon nanotubes. Environ Sci Technol. 2008;42:7931-6.
34. Tor A, Cengeloglu Y. Removal of congo red from aqueous solution by adsorption onto acid activated red mud. Journal of Hazardous Materials. 2006;138(2):409-15.