

Adsorption of penicillin by decaffeinated tea waste

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Removal of penicillin has been investigated using decaffeinated tea waste (DCTW). Decaffeination of tea waste was investigated using different methods. Results indicate that ozonation was the most effective process for removal of penicillin. Batch adsorption experiments were completed at various temperatures (20, 30, and 40°C), DCTW dosages (2, 4, 6, 8, and 10 g per 250 mL), penicillin concentrations (4, 10, and 14 mg/L), and pH (3, 7, and 10) conditions. Studies showed that adsorption reaches equilibrium within 40 min. The main factor affecting adsorption of penicillin was the solution pH, with maximum adsorption occurring at pH 3. Higher adsorbent dosages and lower penicillin concentrations also resulted in higher percentages of penicillin removal. Results show that data obeyed the pseudo-first-order kinetic and Freundlich isotherm models. This process proves that low-cost DCTW could be used as a high performance adsorbent for removing penicillin from aqueous solutions.

Keywords: adsorption, caffeine, penicillin, isotherm, kinetic.

INTRODUCTION

Water is a precious environmental resource because it is used by nearly all living organisms; therefore, pollution of water resources may be a serious problem in all parts of the world. The pharmaceutical industry produces compounds that are toxic at trace concentrations if released to the environment in water or soil. Antibiotics are a sub-category of pharmaceuticals that may be released to the environment¹. Methods for removing antibiotics from water or soil are being actively investigated; methods include coagulation & GAC filtration², biodegradation³, biosorption⁴, and adsorption⁵, among others. Adsorption is a simple and economic method for removal of trace-level pollutants⁶. In recent years, adsorption onto effective and less expensive adsorbents has received more attention. If biomass is used as the adsorbent (i.e., bioadsorbent), the process is termed as bioadsorption. A desirable adsorbent would be natural, organic and abundant as a waste product from another process⁷. Many bioadsorbents such as bacteria, algae, yeasts, and fungi⁸, chicken feathers⁹, chitosan, and peat¹⁰ are used to remove organic and inorganic contaminants from aqueous solutions. Tea is a natural ingredient for popular drinks, worldwide; therefore, many tons of tea wastes are produced each year. Previous research demonstrated the capacity of tea wastes to adsorb pollutants, such as dyes^{11, 12} and heavy metals^{13, 14}, from aqueous solutions.

The purpose of this research is to study the removal of penicillin (PC) from aqueous solutions using decaffeinated tea waste (DCTW). This is studied by first removing caffeine from tea leave wastes to create DCTW, then investigating the use of DCTW as an adsorbent.

EXPERIMENTAL

Material

Tea waste was provided from commercial black tea of Lahijan, Iran. Caffeine, HCl, and NaOH were purchased from Merck, CNTs were purchased from Research Institute of Petroleum Industry (RIPI) of Iran, and penicillin was obtained from Kimidaro Company, Iran.

Other analytical grade chemicals used in the experiment were obtained from various chemical suppliers.

Preparation of tea waste

In this study, DCTW was used as a bioadsorbent for removal of PC from aqueous solutions. Initially, samples of tea waste were washed several times with hot (90°C) water to remove of color and soluble components.

Because of overlapping of caffeine with PC peaks in the UV region, it is necessary to remove caffeine from the tea waste. Methods for removal of caffeine from tea waste were investigated, including ozonation (flow = 5 L/min), ultrasonic (frequency = 20 Hz), UV radiation (30 watt), and adsorption onto SWCNTs (200 mg/L), MWCNTs (200 mg/L), SWCNTs-COOH (200 mg/L) and MWCNTs-COOH (200 mg/L). By comparing the results of decaffeination of tea, ozonation was found to be the most effective method. After drying of DCTW in 100°C for 1 hour, it was ground and stored in a dry place.

Methods

Adsorption experiments were done in a 250 mL Erlenmeyer flask on a stirrer. A solution with PC concentration of 5000 mg/L was prepared in distilled water. Generally, 2 g of DCWT were used with 10 mg/L of PC, and HCl and NaOH were used to adjust pH of the solution. The effects of parameters such as pH (3, 7, 10), contact time, PC concentration (4, 10, 14 mg/L), DCTW dosage (2, 4, 6, 8, 10 g/250 mL) and temperature (20, 30, 40°C) were studied.

Analytical methods

All of the experiments were done on a magnetic stirrer for a period of 40 min. Samples were withdrawn every 5 min, then filtered using filter paper. The remaining PC concentration could be analyzed using a UV-Vis spectrophotometer (HACH-DR5000) at maximum wavelength of PC ($\lambda_{\max} = 255$ nm). q_e , q_t , and % Removal were obtained using the following equations:

$$q_t = \frac{(C_0 - C_t)}{m} \times V \quad (1)$$

$$q_e = \frac{(C_0 - C_e)}{m} \times V \quad (2)$$

$$\% \text{Removal} = \frac{(C_0 - C_t)}{C_0} \times 100 \quad (3)$$

RESULTS AND DISCUSSION

Decaffeination of tea waste leaves

Different physical and chemical methods (adsorption onto CNTs, O₃, ultrasonic, UV) were investigated for their capacity to remove caffeine from tea waste. A solution containing 10 mg/L of caffeine was prepared and % removal of caffeine was analyzed by different methods (Fig. 1).

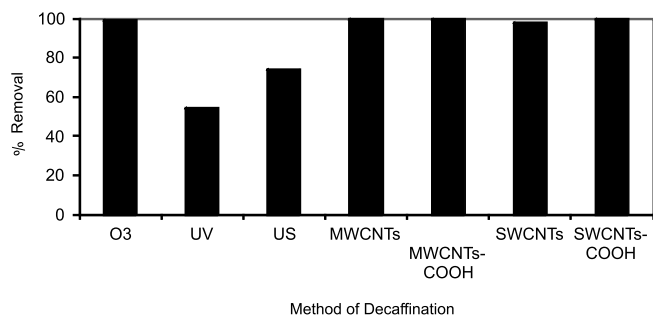


Figure 1. Comparative study of decaffeination of tea waste

Nearly 100% of the caffeine was removed by ozonation and CNTs after 30 min (shown in Fig. 1). Because the by-product of ozonation is O₂, ozonation is selected as a preferred method for removal of caffeine from tea waste. After decaffeination of tea waste by ozonation, it was ground and dried in an oven for an hour. Then used as a bioadsorbent for removal of PC.

Adsorption of PC onto DCTW

Removal of PC by DCTW was evaluated at various contact times, pH values, concentrations of PC, dosages of DCWT, and temperatures.

Effect of contact time

To study the effect of contact time for adsorption of PC onto DCTW, experimental was carried out using 250 mL of PC at a concentration of 10 mg/L, and 2 g of DCTW at pH of 6.5 for 110 min. As shown in Figure 2, rapid adsorption was observed at the beginning of the experiment until adsorption equilibrium was reached at

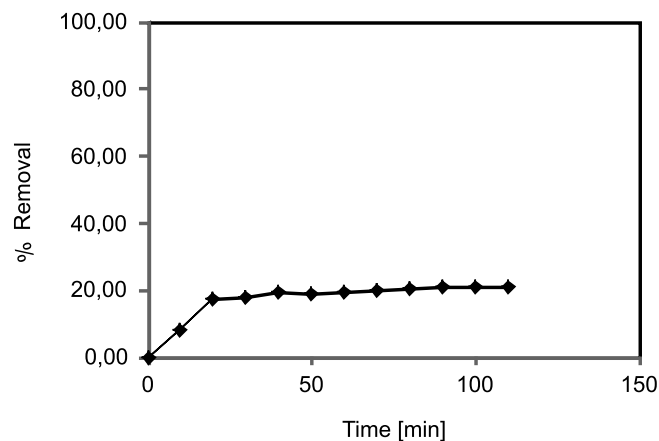


Figure 2. Effect of contact time on removal of PC by DCTW [PC]₀ = 10 mg/L; [DCTW]₀ = 2 g/250 mL; pH = 6.5; T = 25°C

40 min of contact time. Because additional adsorption did not occur after 40 min, all experiments were carried out for 40 min.

DCTW dosage

Figure 3 shows the effect of DCTW dosage on removal of PC at pH of 6.5. Percent removal of PC was increased by increasing the DCTW dosage because higher adsorbent concentration resulted in a greater number of adsorbent particles, surface area of adsorbent and greater availability of adsorption sites¹⁵⁻¹⁶.

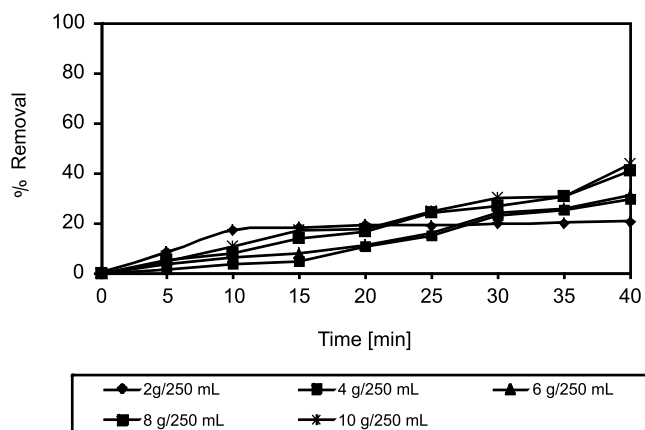


Figure 3. Effect of DCTW dosage on removal of PC by DCTW [PC]₀ = 10 mg/L; pH = 6.5; T = 25°C

pH of solution

One of the main factors affecting the adsorption process is pH; therefore, adsorption studies were done at pH values of 3, 7, and 10 (illustrated in Fig. 4). It is clear that when pH increases from 3 to 10, the % removal decreases from 39.30 to 30.11. Whereas, the pHzpc of tea is around 4.2¹⁷ and the pKa of PC is 2.8, the maximum adsorption of PC was observed at lower pHs. In fact at pH < 4.2, the surface of adsorbent became positive and there were few repulsions between PC and DCTW. By increasing the pH, the surface charge on the adsorbent and PC became negative and repulsion increased. In summary, adsorption decreased by increasing pH.

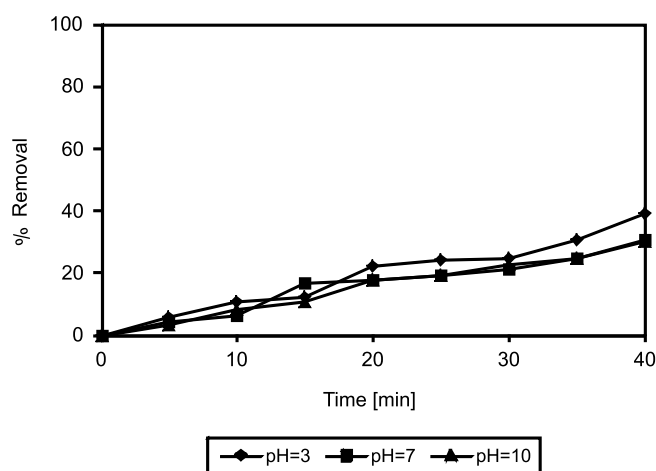


Figure 4. Effect of pH on removal of PC by DCTW [PC]₀ = 10 mg/L; [DCTW]₀ = 2 g/250 mL; T = 25°C

PC concentration

Figure 5 shows the effect of PC concentration, whereby, increases in the PC concentration are due to decreases of PC adsorption onto DCTW. However, by increasing the adsorbate, available sites for adsorption become fewer, hence, the adsorption decreased¹⁸.

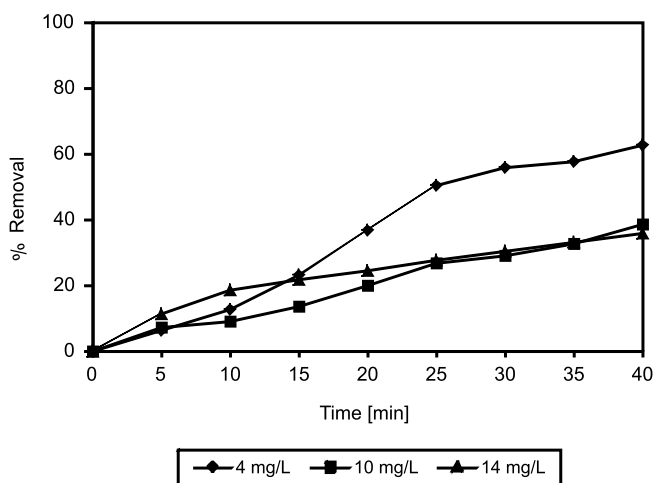


Figure 5. Effect of PC concentration on removal of PC by DCTW [DCTW]₀ = 2 g/250 mL; pH = 6.5; T = 25°C

Temperature

Adsorption of PC onto DCTW was investigated at various temperatures to study the effect of temperature. The efficiency of adsorption decreased with temperature (Fig. 6), because at higher temperatures, the mobility of molecules increased and desorption was occurred¹⁹⁻²⁰.

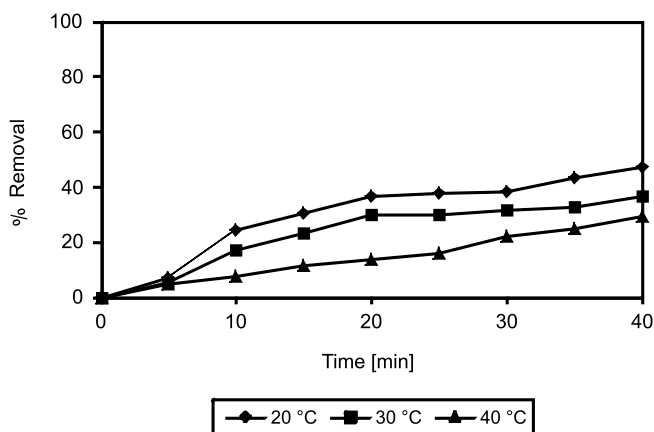


Figure 6. Effect of temperature on removal of PC by DCTW [PC]₀ = 10 mg/L ; [DCTW]₀ = 2 g/250 mL; pH = 6.5

Isotherms equations

A variety of isotherm equations can be used to explain experimental sorption data. In this paper, Langmuir, Freundlich, and Temkin models were used to depict the relation of adsorbed PC and the corresponding equilibrium concentration.

The isotherm parameters were evaluated by non-linear trial-and-error method using polymath 6.10 software with results shown in Table 1. All models were assumed to be non-linear to minimize the error of variance. The parameters of models (R^2 , R^2_{adj} , S^2 , R_{msd}), were shown at 95% of confidence interval in Table 1. If the correlation coefficient value was close to 1 and R^2_{adj} , the regression model was considered correct. The results of Langmuir, Freundlich, and Temkin models are shown in Figure 7.

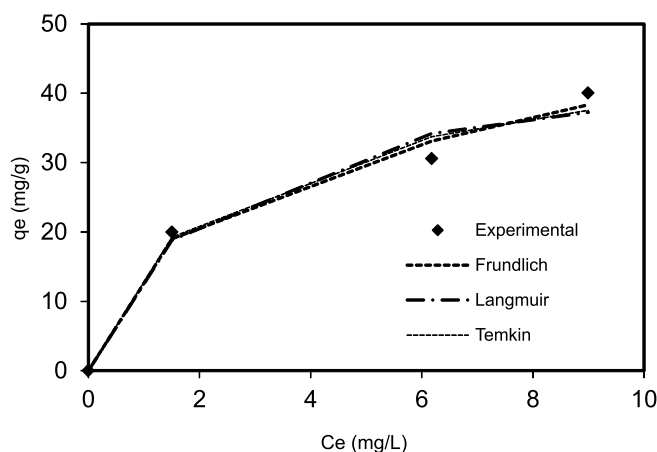


Figure 7. Comparison of Langmuir, Freundlich and Temkin isotherm models for removal of PC by DCTW

The Langmuir isotherm

One of the simplest and most widely used isotherms is the Langmuir isotherm. This isotherm assumes that the surface of the sorbent is completely uniform. The Langmuir equation can be described as follows:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (4)$$

Here, q_e is the amount of adsorbate at equilibrium (mg/g), C_e is equilibrium concentration of solute (mg/L), q_m is the maximum adsorption capacity (mg/g) and K_L is the Langmuir adsorption constant (L/mg). Affinity between PC and DCTW was obtained using a dimensionless separation factor, R_L [21] which indicates the nature of adsorption, such that unfavorable adsorption is when $R_L > 1$, linear adsorption is when $R_L = 1$, and favorable adsorption is when $0 < R_L < 1$, and irreversible adsorption is when $R_L = 0$.

It can be seen from Table 1, that the R^2 value ($R^2 = 0.9750$) is not enough close to 1 and, therefore, the Langmuir isotherm model is not able to fit the sorption data.

Table 1. Isotherm parameters and error deviation data for PC adsorption onto DCTW

Model	R^2	R^2_{adj}	R_{ms}	s^2	Parameters	Values
Langmuir	0.975	0.962	11.174	11.042	q_m (mg/g)	46.3565(±0.0038)
					K_L (L/mg)	0.4552(±0.0001)
Freundlich	0.988	0.982	0.793	5.042	$K_F [(mg/g)(L/mg)^{1/n}]$	16.2122(±0.0289)
					n	2.5535(±0.0060)
Temkin	0.981	0.972	1.015	8.247	B_T	10.2185(±9.2734)
					K_T (L/g)	4.3847(±12.1461)

The Freundlich isotherm

The Freundlich isotherm model can be applied to describe nonideal sorption on heterogeneous surfaces²². Freundlich isotherms are represented by equation 5:

$$q_e = K_F C_e^{\frac{1}{n}} \quad (5)$$

Where, C_e (mg/L) is the concentration of solute at equilibrium, q_e (mg/g) is the amount of equilibrium adsorbed of solute, K_F [L/g] and n are the Freundlich constants indicating adsorption capacity and intensity, respectively, and $1/n$ is a constant (dimensionless) that refers to the adsorption intensity or the factors that describes reversible adsorption²³. If $n = 1$, this indicates that the partition of two phases are independent of concentration and the adsorption isotherm can be reduced to a linear form. If $1 < n < 10$, this indicates a favorable sorption process²⁴.

Table 1 shows that the value of $1/n = 0.392$ ($n = 2.553$), which indicates that adsorption of PC onto DCTW is favorable. The higher R^2 value ($R^2 = 0.9886$) for this isotherm also confirms that the adsorption of PC onto DCTW is fit well with the Freundlich isotherm model.

The Temkin isotherm

The Temkin isotherm assumes that the adsorption heat of all molecules in the layer would decrease linearly rather than logarithmically with coverage²⁴. The model is expressed by the following equation²⁵:

$$q_e = \frac{RT}{b_T} \ln(K_T C_e) \quad (6)$$

$$B = \frac{RT}{b_T}$$

Where, K_T is the Temkin equilibrium binding constant (L/g), b is Temkin constant, R is the ideal gas constant (8.314J/mol/K), T is temperature in Kelvin (298K) and B is a constant related to heat of sorption (J/mol). Temkin parameters were estimated as $K_T = 4.3847$ L/g, $B = 10.2185$ J/mol, with an $R^2 = 0.9813$. The estimated value for B confirms that there is a physical adsorption process²⁴.

Adsorption kinetic

In this study, two kinetic models were examined to determine the kinetic adsorption of PC onto DCTW, pseudo- first- and -second-order kinetic models¹⁷.

Forms of these two models are present in following equations, respectively;

$$q_t = q_e (1 - e^{-k_1 t}) \quad (7)$$

$$q_t = \frac{q_e^2 k_2 t}{1 + k_2 q_e t} \quad (8)$$

Here, q_t is amount of adsorbed PC onto DCTW (mg/g) at contact time t and q_e is amount of adsorbed PC onto DCTW (mg/g) at equilibrium time and k_1 (min^{-1}) and

k_2 (g/mg min) are the pseudo-first- and -second-order constants, respectively. All parameters of the models were obtained at 95% confidence using polymath 6.10 software and results are shown in Table 2. Figure 8 shows the experimental data and results of the two kinetic models.

It can be concluded that the pseudo-first order model, with an R^2 of 0.9916, provided a better fit with to the data than the pseudo-second order model.

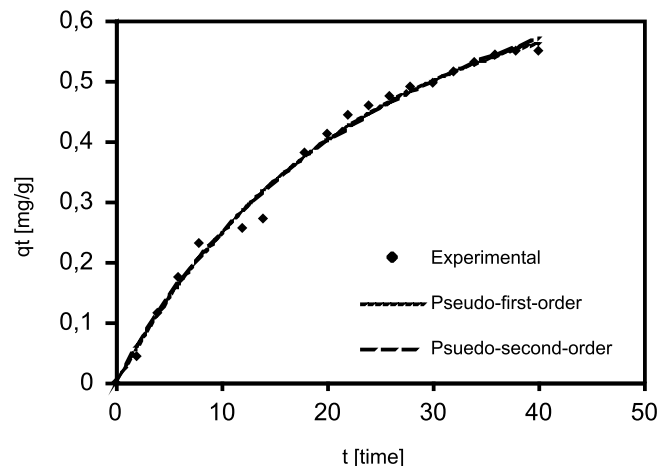


Figure 8. Comparison of kinetic models for removal of PC by DCTW

CONCLUSION

Green tea is largely consumed around the globe and is considered the second most popular beverage in the world after water. Hence, the utilization of such waste is most desirable. Therefore, the use of spent tea waste an abundantly available solid waste be economically and technically feasible. In this paper, removal of PC onto DCTW from aqueous solutions was studied. Based on the results obtained, DCTW appears to be an effective bioadsorbent for removal of PC from aqueous solutions. Adsorption of DCTW onto PC was fitted using a Freundlich isotherm and followed by a pseudo-first-order kinetic model. The amount of PC adsorbed varied with contact time, pH, and concentration of PC, temperature, and DCTW dosage. The maximum adsorption of PC by DCTW occurred at a pH of 3 and adsorption reached equilibrium after 40 min of contact time. So, it is recommended to use of tea waste as a cheap and environmentally friendly adsorbent in removal of organic pollutants from aqueous solutions.

ACKNOWLEDGEMENTS

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Table 2. Kinetic parameters and error deviation data for PC adsorption onto DCTW

Model	R^2	R_{adj}^2	Rms	s^2	Parameters	Values
Pseudo-first order	0.991	0.990	0.003	0.003	$q_{e,cal}$ (mg/g)	0.6719(± 0.0004)
					k_1 (min^{-1})	0.0624($\pm 8.20 \cdot 10^{-5}$)
Pseudo-second order	0.990	0.989	0.0039	0.0003	$q_{e,cal}$ (mg/g)	1.002(± 0.1306)
					k_2 (g/mg.min)	0.032(± 0.0122)

LITERATURE CITED

1. Ania, C.O., Pelayo, J.G. & Bandosz, T. J. (2011). Reactive adsorption of penicillin on activated carbons. *Adsorption* 17, 421–429. DOI: 10.1007/s10450-010-9271-9.
2. Choi, K.J., Kim, S.G. & Kim, S.H. (2008). Removal of antibiotics by coagulation and granular activated carbon Filtration. *J. Hazard. Mater.* 151, 38–43. DOI: 10.1016/j.jhazmat.2007.05.059.
3. Al-Ahmad, A., Daschner, F.D. & Kummerer, K. (1999). Biodegradability of cefotiam, ciprofloxacin, meropenem, penicillin G, and sulfamethoxazole and inhibition of waste water bacteria. *Arch. Environ. Contam. Toxicol.* 37, 158–163. DOI: 10.1007/s002449900501.
4. Zümriye, A. & Özlem, T. (2005). Application of biosorption for penicillin G removal: comparison with activated carbon. *Process Biochem.* 40, 831–847. DOI: 10.1016/j.procbio.2004.02.014.
5. Chaubal, M.V., Payne, G.F., Reynolds, C.H. & Albright, R.L. (1995). Equilibria for the adsorption of antibiotics onto neutral polymeric sorbents: Experimental and modeling studies. *Biotechnol. Bioeng.* 47, 215–226. DOI: 10.1002/bit.260470213.
6. Zhang, H., Yu, X., Chen, L., Jing, Y. & Ge, Z. (2010). Study of Ni-63 adsorption on NKF-6 zeolite. *J. Environ. Radioact.* 101, 1061–1069. DOI: 10.1016/j.jenvrad.2010.08.009.
7. Zuorro, A. & Lavecchia, R. (2010). Adsorption of Pb(II) on Spent Leaves of Green and Black Tea. *Am. J. Appl. Sci.* 7, 153–159. DOI: 10.1016/j.procbio.2005.02.004.
8. Chen, C. & Wang, J. (2009). Biosorbents for heavy metals removal and their future. *Biotechnol. Adv.* 27, 195–226. DOI: 10.1016/j.biotechadv.2008.11.002.
9. Arshad Khosa, M., Wua, J. & Ullah, A. (2013). Chemical modification, characterization, and application of chicken feathers as novel biosorbents. *RSC Adv.* 3, 20800–20810. DOI: 10.1039/C3RA43787F.
10. Srinivasan, A. & Viraraghavan, T. (2010). Decolorization of dye wastewaters by biosorbents: A review. *J. Environ. Manage.* 91, 1915–1929. DOI: 10.1016/j.jenvman.2010.05.003.
11. Hameed, B.H. (2009). Spent tea leaves: A new non-conventional and low-cost adsorbent for removal of basic dye from aqueous solutions. *J. Hazard. Mater.* 161, 753–759. DOI: 10.1016/j.jhazmat.2008.04.019.
12. Uddin, M.T., Islam, M.A., Mahmud, S. & Rukanuzzaman, M. (2009). Adsorptive removal of methylene blue by tea waste. *J. Hazard. Mater.* 164, 53–60. DOI: 10.1016/j.jhazmat.2008.07.131.
13. Yang, X. & Cui, X. (2013). Adsorption characteristics of Pb (II) on alkali treated tea residue. *Water Resour. Ind.* 3, 1–10. DOI: 10.1016/j.wri.2013.05.003.
14. Amarasinghe, B.M.W.P.K. & Williams, R.A. (2007). Tea waste as a low cost adsorbent for the removal of Cu and Pb from wastewater. *Chem. Eng. J.* 132, 299–309. DOI: 10.1016/j.cej.2007.01.016.
15. Cay, S., Uyanik, A. & Ozasik, A. (2004). Single and binary component adsorption on copper (II) and cadmium (II) from aqueous solution using tea industry waste. *Sep. Purif. Technol.* 38, 273–280. DOI: 10.1016/j.seppur.2003.12.003.
16. Wasewar, K.L., Atif, M., Prasad, B. & Mishra, I.M. (2009). Batch adsorption of Zn on tea factory waste. *Desalination* 244, 66–71. DOI: 10.1016/j.desal.2008.04.036.
17. Mohammad, A.H. & Md, S.A. (2012). Adsorption kinetics of Rhodamine-B on used black tea leaves. *Iranian J. Environ. Health Sci. Eng.* 9, 1–7. DOI: 10.1186/1735-2746-9-2.
18. Jeyakumar, R.P.S. & Chandrasekaran, V. (2014). Adsorption of lead(II) ions by activated carbons prepared from marine green algae: Equilibrium and kinetics studies. *Inter. J. Indu. Chem.* 5, 1–10. DOI:10.1186/2228-5547-5-2.
19. Chen, D.Z., Zhang, J.X. & Chen, J.M. (2010). Adsorption of methyl tert-butyl ether using granular activated carbon: Equilibrium and kinetic analysis. *Int. J. Environ. Sci. Tech.* 7, 235–242. DOI: 10.1007/BF03326133.
20. Pandey, P.K., Sharma, S.K. & Sambhi, S.S. (2010). Kinetics and equilibrium study of chromium adsorption on zeolite NaX. *Int. J. Environ. Sci. Tech.* 7, 395–404. DOI: 10.1007/BF03326149.
21. Tseng, R.L. & Wu, F.C. (2009). Analyzing concurrent multi-stage adsorption process of activated carbon with a favorable parameter of Langmuir equation. *J. Taiwan Inst. Chem. E.* 40, 197–204. DOI: 10.1016/j.jtice.2008.09.002.
22. Ho, Y.S., Porter, J.F. & Mckay, G. (2002). Equilibrium isotherm studies for the sorption of divalent metal ions onto peat: copper, nickel and lead single component systems. *Water Air Soil Poll.* 141, 1–33. DOI: 10.1023/A:1021304828010.
23. Ahmed Dhahir, S. & AL-Saade, K.A. (2013). Adsorption study of rhodamin b dye on iraqi bentonite and modified bentonite by nanocompounds TiO ZnO, Al₂O₃, sodium dodecyl sulfate. *Am. J. Environ. Sci.* 9, 269–279. DOI: 10.3844/ajessp.2013.269.279.
24. Zheng, H., Liu, D., Zheng, Y., Liang, S. & Liu, Z. (2009). Sorption isotherm and kinetic modeling of aniline on Cr-bentonite. *J. Hazard. Mater.* 167, 141–147. DOI: 10.1016/j.jhazmat.2008.12.093.
25. Tosun, I. (2012). Ammonium Removal from Aqueous Solutions by Clinoptilolite: Determination of Isotherm and Thermodynamic Parameters and Comparison of Kinetics by the Double Exponential Model and Conventional Kinetic Models. *Int. J. Environ. Res. Pub. Health.* 9, 970–984. DOI: 10.3390/ijerph9030970.