

Date seed derived biochar for Ni(II) removal from aqueous solutions

Zainab Mahdi^{1,*}, Ali El Hanandeh¹, and Qiming Yu¹

¹School of Engineering, Griffith University, 170 Kessels Road, Brisbane, Australia

Abstract. The purpose of this study was to investigate the adsorption characteristic of biochars derived from date seed for Ni²⁺ ions removal from aqueous solutions. Two biochars were prepared by slow pyrolysis of date seed for 3 h at 450 °C (DSB450) and 550 °C (DSB550). The adsorption of Ni²⁺ was carried out by batch experiments at room temperature. The effects of pyrolysis temperature, contact time, initial metal concentration, and solution pH were investigated. The results showed that biochar prepared at higher temperature (DSB550) had higher adsorption capacity of Ni²⁺ from aqueous solution than biochar prepared at lower temperature (DSB450). Adsorption efficiency of Ni²⁺ ions was pH dependent and the maximum adsorption was found to occur at pH around 6.0. To describe the equilibrium isotherms, the experimental results were analyzed by the Langmuir, and Freundlich isotherms. The adsorption isotherm for Ni²⁺ by DSB550 was best fit to Langmuir isotherm with ($R^2 = 0.94$). The maximum adsorption capacity of Ni²⁺ of DSB550 biochar was 0.609 mmol g⁻¹. Pseudo-first order, pseudo-second order, and intraparticle diffusion models were used to model the kinetic parameters and mechanism of adsorption process. The results showed that the adsorption kinetics of these biochars are well described by a pseudo-second order kinetic model with correlation coefficient ($R^2 = 0.99$). The results of the study indicated that biochar derived from date seed biomass is a suitable material for adsorption of Ni²⁺ ion from aqueous solution.

1 Introduction

Heavy metal pollution poses significant threat to humans and the environment. Heavy metal can bio-accumulate in living tissues due to their non – biodegradability [1]. The majority of metallic pollutants in aquatic systems are due to the discharge of various untreated industrial effluents such as battery manufacturing, tanneries, electroplating, and chemical manufacturing. Nickel (Ni²⁺) is a highly toxic ion which can induce embryotoxic and nephrotoxic effects, allergic reactions, and contact dermatitis [2].

Therefore, it is important to treat wastewater containing Ni²⁺ to safe levels before it is discharged to the environment. Various treatment methods including chemical precipitation, oxidation/reduction, and electrochemical treatment, ion exchange, and membrane technologies are conventionally used for heavy metal removal. Adsorption using

* Corresponding author: a.elhanandeh@griffith.edu.au

activated carbon (AC) has also proven to be an effective method. However, the high cost of the conventional methods may place a barrier to their utilization on large scale [3].

Biochar has been promoted as a low cost adsorbent for the removal of various contaminants from wastewater. It is a carbon rich solid material created by thermal decomposition of biomass under limited oxygen conditions [5]. Several studies reported that biochar has high adsorption capacity towards heavy metal ion due to the abundance of surface functional groups, and its amorphous structural arrangement [5]. Biochar can be prepared from a variety of organic materials, such as woody biomass and agricultural residue such as date stone. The total world production of date is 7,166,695 tons per year [6]. Date stone represents approximately 10% of the date weight; as a result, large quantities of waste are discarded as unwanted material [7].

Several studies investigated the use of date stones for the preparation of activated carbon either chemical or physical activation. Alhamed & Bamufleh [8] prepared activated carbon from date palm waste using $ZnCl_2$ as activating agent. Girgis and El-Hendawy [9] used date pits for activated carbon production after chemical activation using H_3PO_4 acid. Bouchelta et al. [10] used date seeds for AC preparation using physical activation with water vapor. However, AC is costly material due to high energy and chemicals requirements. Biochar, on the other hand, is cheaper to produce and has shown good heavy metal removal capacity. Therefore, the aim of this work was to investigate the ability of biochar prepared from date stone biomass for Ni^{2+} ion removal from aqueous solution.

2 Materials and methods

Biochars were prepared in the lab from date stones using slow pyrolysis process at terminal temperatures of 450 and 550 °C for 3 h. Detailed description of biochar preparation can be found in our previous works [11, 12]. Adsorption studies were carried out using batch adsorption experiments at room temperature. The effects of pH solution, contact time, and initial metal ion concentration on Ni^{2+} removal efficiency were studied. The kinetic and equilibrium batch experiments were carried out to study the adsorption mechanism of the Ni^{2+} from aqueous solution.

2.1 Chemicals

All the chemicals used in the experiments were of analytical reagent grade. Deionized water was used in preparing the solutions throughout this study. Stock solution of 5.0 mM of metal ion was prepared by dissolving 1.454 g $Ni(NO_3)_2 \cdot 6H_2O$ supplied by (Scharlau Chemical) in 1 L of deionized water. Then dilute solutions of different concentrations ranging from 1.0 to 4.0 mM were prepared by successive dilutions to the required working concentrations. The standard solutions for atomic absorption spectroscopy analysis were freshly prepared before use. The initial pH of the solutions was adjusted from 2.0 to 6.0 using 0.1M NaOH and 0.1M HCl.

2.2 Batch adsorption experiment

Batch adsorption studies for Ni^{2+} removal was carried out by mixing 0.1 g of the biochar with 10 mL of Ni^{2+} solution (initial Ni^{2+} concentration 1.0 mM) the solution was kept at pH = 6. All the experiments were carried out at room temperature using 50 ml glass container (Hybex) soaked with 0.1 M HCl and washed with deionized water before use. The mixture was agitated for 24 h using rotary shaker. After 24 h, the mixture of biochar and metal solution was separated using Millex[®] syringe filter pore size 0.45 μm connected to a glass

syringe (10 mL). The final concentration of Ni^{2+} ion was determined using atomic absorption spectrophotometer (Avanta, GBC-SDS) and the amount of Ni^{2+} ions adsorbed on the biochar q_e (mmol g^{-1}) and removal efficiency (R) were calculated using mass balance equation:

$$q_e = \frac{(C_o - C_e) V}{W} \quad (1)$$

$$R = \frac{(C_o - C_e)}{C_o} \times 100 \quad (2)$$

where, q_e is the quantity of metal ion adsorbed onto the biochar (mmol g^{-1}), C_o is the initial metal ion concentration (mM), C_e is the final concentration of metal ion at equilibrium (mM), V is the solution volume (L) and W is the biochar dosage (g).

Blank run adsorption experiments (without biochar) were carried out in identical manner to find the effect of glassware on Ni^{2+} ion removal. The investigations showed that the quantity of metal ions adhering on the container walls were negligible (2.36 ± 0.65 %). Adsorption performance of date seed biomass in their native form was also investigated and compared to the biochar. The effect of pH of the solution was investigated over pH range from 2 to 6 by mixing 0.1 g of biochar with 10 mL of Ni^{2+} solution at initial metal concentration of 1.0 mM. The pH of the solution was adjusted by using 0.1 M NaOH or HCl as required. The adsorption experiments were conducted in triplicate under similar conditions and the average value was reported.

2.3 Adsorption isotherms studies

The equilibrium isotherm is used to describe adsorption performance relation between adsorbate phase (metal solution, C_e mM) and adsorbent phase (biochar, q_e mmol g^{-1}) at equilibrium [13]. The isotherms experiment was conducted at room temperature (23 ± 2 °C) by mixing 0.1 g of the biochar with 10 mL of Ni^{2+} solution with initial Ni^{2+} concentrations range of (1.0-4.0 mM). The solution was kept at pH 6.0. The experimental results were fitted to Langmuir and Freundlich isotherm models.

2.4 Adsorption kinetics studies

The kinetics experiments were carried out by conducting 1.0 g of the biochar with 100 mL of Ni^{2+} solution at initial Ni^{2+} concentration of 1.5 mM. The pH of the solution was kept constant at 6.0. The content in the container was shaken using rotary shaker for the duration of the experiment. Samples were withdrawn at time intervals and analyzed to find the amount of Ni^{2+} adsorbed at time as shown below:

$$q_t = \frac{(C_o - C_t) V}{W} \quad (3)$$

where, q_t is the quantity of Ni^{2+} adsorbed onto the biochar (mmol g^{-1}) at given time, C_o is the initial Ni^{2+} concentration (mM), C_t is the Ni^{2+} concentration at given time (mM), V is the solution volume (L) and W is the biochar dosage (g).

3 Results and discussion

3.1 Effect of pyrolysis temperature on Ni²⁺ adsorption

Adsorption equilibrium uptake is the main parameter used to compare adsorption performance of different adsorbents towards adsorbate. Adsorption performance of date seed biomass in their native form as well as biochars was investigated and compared as shown in Figure 1. It can be seen from Figure 1 that DSB550 biochar had higher adsorption capacity for Ni²⁺ ions than the original biomass. This can be attributed to the influence of pyrolysis on the chemical and physical biochar characteristics. DSB450 biochar had marginally lower adsorption capacity than DS550. However, successful implementation of heavy metal ion adsorption from aqueous solution depends largely on the total cost of adsorption process including cost of original biomass, energy, handling, transportation, drying, disposal, ...etc. [14]. After adsorption, laden biochar can be classified as hazardous material which can be expensive to transport, handle, treat and dispose of due to the high degree of caution requirement and environmental regulations. Therefore, DSB550 was chosen for further investigation in this study.

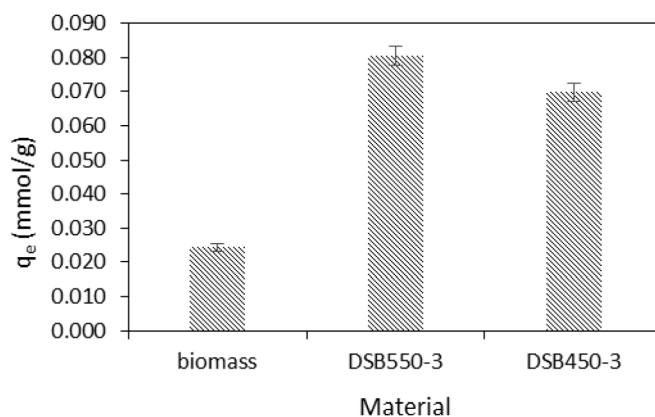


Fig. 1. Adsorption performance of biochar as well as original biomass for Ni²⁺ ion removal.

3.2 Effect of Solution pH on Ni²⁺ Adsorption

The effect of solution pH on Ni²⁺ adsorption was investigated over the pH range 2 to 6 and keeping all other parameters constant as shown in Figure 2. It can be seen from Figure 2 that the adsorption amount of Ni²⁺ increased as pH increased from 2 to 6. This can be attributed to the effect of pH on affinity between adsorbent (biochar) and adsorbate (metal ion solution) and the speciation of metals and dissociation of active functional sites on the adsorbent [15]. At low pH, the surface functional groups (mainly oxygen-containing groups) linked to the H⁺ ion making competition between Ni²⁺ ions and H⁺ ions which resulted in a lower electrostatic repulsion [16]. Similar findings were observed Kılıç et al. [17] for almond shell biochar who reported that maximum adsorption of Ni²⁺ occurred around pH 7. In this study, pH values higher than 6 were not used to avoid the precipitation of nickel ion in the form of Ni(OH)₂.

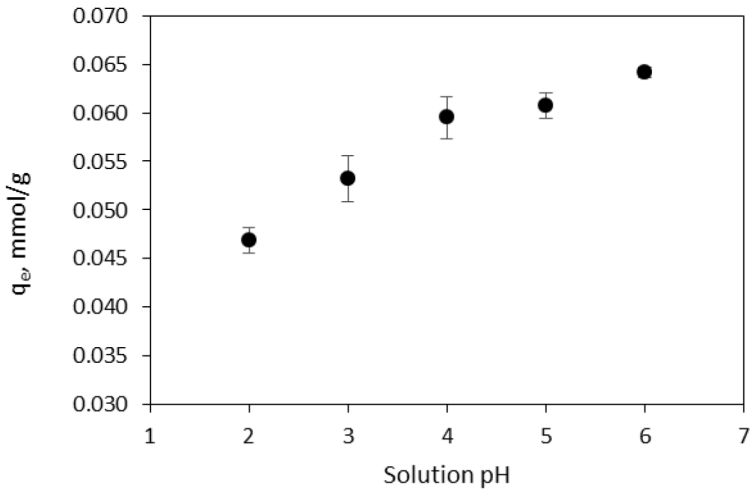


Fig. 2. The effect of pH solution on Ni²⁺ ion removal onto DSB550 biochar .

3.3 Kinetics of Ni²⁺ adsorption

Figure 3 shows the influence of contact time on Ni²⁺ adsorption onto DSB550 biochar. A two stage adsorption mechanism was observed: the first was rapid adsorption and occurred within the first hour followed by slower stage until the reaction reached equilibrium. This can be explained by the availability of a large number of vacant sites on the adsorbent surface at the beginning, as time passed the remaining vacant sites were difficult to access [18]. Adsorption kinetics of Ni²⁺ onto the biochar DSB550 was fitted using pseudo-first order, pseudo second-order models, and intraparticle diffusion model. The Pseudo first-order rate of Lagergren (1898) is expressed as follows:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (4)$$

The linear form of the above equation can be written as below:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (5)$$

where, q_e and q_t are the amount of Ni²⁺ adsorbed per unit mass (mmol g⁻¹) at equilibrium and at time, t respectively. k_1 (min⁻¹) is the pseudo first order adsorption rate constant.

A linear form of the Pseudo second order kinetic model is expressed as following equation:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_t} \quad (6)$$

The second-order rate constant k_2 and q_e are obtained from the intercept and the slope of the plot obtained by plotting t/q against time t .

The Weber–Morris intraparticle diffusion model is described as follows [19]:

$$q_t = k_p t^{0.5} + C \quad (7)$$

where k_p is the intraparticle diffusion rate constant ($\text{mmol g}^{-1} \text{min}^{-0.5}$), t is the time (min), and C is the intercept (mmol g^{-1}), which represents the thickness of the boundary layer effects.

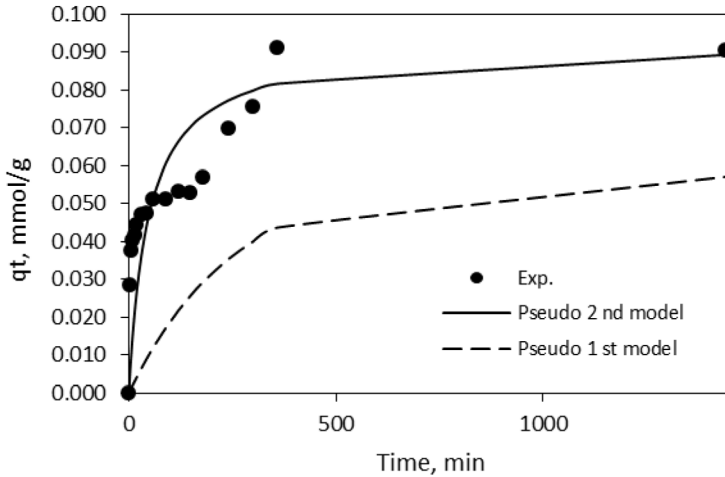


Fig. 3. Effect of contact time on Ni^{2+} adsorption.

The kinetics parameters of adsorption kinetics models were presented in Table 1. The $q_{e,calc}$ from the pseudo second order model showed good agreement with the experimental values with $q_{e,exp}$ with correlation coefficient (R^2) of 0.92.

Table 1. Adsorption kinetics parameters of DSB550 biochar.

| Pseudo first order model | | Pseudo second order model | | Intraparticle diffusion model | |
|----------------------------|-------|----------------------------|-------|-------------------------------|-------|
| k_1 | 0.004 | k_2 | 0.234 | k_p | 0.003 |
| $q_{exp, \text{ mmol/g}}$ | 0.090 | $q_{exp, \text{ mmol/g}}$ | 0.090 | C | 0.03 |
| $q_{calc, \text{ mmol/g}}$ | 0.057 | $q_{calc, \text{ mmol/g}}$ | 0.089 | $q_{calc, \text{ mmol/g}}$ | 0.087 |
| R^2 | 0.84 | R^2 | 0.99 | R^2 | 0.87 |

3.4 Equilibrium isotherms for Ni^{2+} adsorption

The adsorption performance of an adsorbent is a function of the initial metal ion concentration [17]. The amount of Ni^{2+} adsorbed onto DSB550 biochar increased with increasing initial Ni^{2+} concentrations and finally reached to an upper adsorption limit as shown in Figure 4. This can be attributed to the availability of vacant sorption sites on the surfaces of the biochar [17]. With increasing metal concentration, the adsorption of Ni^{2+} decreased because of the saturation of the sites.

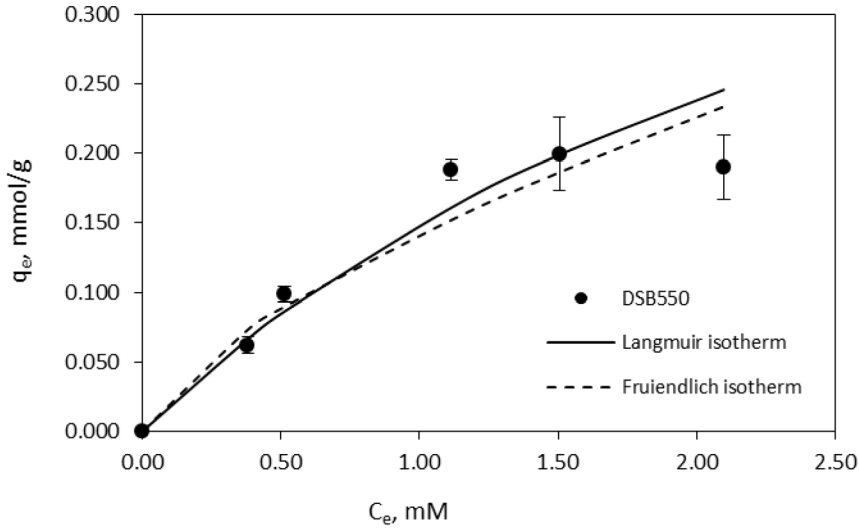


Fig. 4. Equilibrium isotherms of Ni^{2+} adsorption onto DSB550 biochar

The adsorption isotherms were characterized using Langmuir and Freundlich isotherms models. Langmuir isotherm (1918) model assumes that the surface of the adsorbent is homogeneous with monolayer sorption onto surface and has finite number of identical sites. Langmuir isotherm is given by equation [20]:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (8)$$

This can be arranged to the linear form as shown below:

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{K_L q_m C_e} \quad (9)$$

where, q_e is the amount of Ni^{2+} adsorbed (mmol g^{-1}), C_e is the equilibrium concentration of the adsorbate (mM), q_m is the maximum adsorption capacity (mmol g^{-1}), and K_L is the adsorption equilibrium constant (L mmol^{-1}). The empirical Freundlich isotherm model (1906) assumes the surface of adsorbent is heterogeneous with multilayers and it is expressed as shown in equation below:

$$q_e = K_F C_e^{\frac{1}{n}} \quad (10)$$

A linear form of the Freundlich model is given as:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (11)$$

where, K_F (mmol g^{-1}) and n (g L^{-1}) are the Freundlich constants related to adsorption capacity and adsorption intensity, respectively. The adsorption isotherm parameters of Langmuir and Freundlich isotherms are given in Table 2. The dimensionless separation factor (R_L) of Langmuir is used to predict the affinity between the metal ion solution and the biochar. R_L can be calculated by the following equation:

$$R_L = \frac{1}{1 + K_L C_o} \quad (12)$$

where, C_o is the highest initial metal concentration in the solution (mM). This is often used to judge whether a sorption process is a thermodynamically favorable process or not: $R_L > 1$ it is an unfavorable adsorption; $R_L = 1$, indicates a linear adsorption; when $0 < R_L < 1$, adsorption is favorable; when $R_L = 0$, it is an irreversible adsorption [21]. As shown in Table 2 the value of R_L for this study was 0.437 which indicates a favorable adsorption. The adsorption isotherm of Ni^{2+} was adequately fitted to Langmuir isotherm with R^2 equal to 0.94. According to Freundlich model, the value of adsorption intensity ($1/n = 1.47$) which was higher than 1.0 thus confirming a favorable adsorption and Ni^{2+} adsorption is more of chemisorption than physical adsorption [22].

Table 2. Calculated parameters of the adsorption isotherms models

| Langmuir isotherm model | | Freundlich isotherm model | |
|----------------------------|-------|----------------------------|-------|
| k_L L mmol ⁻¹ | 0.322 | k_F mmol g ⁻¹ | 0.141 |
| R^2 | 0.94 | R^2 | 0.88 |
| q_{max} , mmol/g | 0.609 | 1/n | 1.47 |

The adsorption uptake capacities for Ni^{2+} ions on various adsorbent were shown in Table 3. The adsorption capacity of biochar derived from date stone was higher than that reported by Kılıç et al., [17] and Vijayaraghavan et al., [23]. However, the comparison with other reported adsorbent is difficult due to the varying experimental conditions employed in those studies such as initial concentrations and the adsorbent doses.

Table 3. Adsorption capacity toward Ni^{2+} from aqueous solution

| Adsorbent | pH | q_{max} mg g ⁻¹ q_{max} (mmol g ⁻¹) | References |
|-------------------------------|-------|---|------------|
| Seaweeds | 4.5-4 | 20.63 (0.351) | [23] |
| Waste apricot | 5 | 101.01 (1.72) | [24] |
| Almond shell biochar | 7 | 22.22 (0.378) | [17] |
| Hickory wood biochar | - | 0.24 (0.004) | [25] |
| Modified hickory wood biochar | | 0.89 (0.015) | |
| Date seed biochar | 6.0 | 35.74 (0.609) | This study |

4 Conclusion

In this study, biochar prepared from date seed biomass was used for Ni^{2+} adsorption from aqueous solutions. Biochar prepared at higher pyrolysis temperatures (DSB550) showed higher adsorption capacity for Ni^{2+} . The amount of Ni^{2+} ion adsorbed was found to vary significantly with process parameters such as initial Ni^{2+} concentration, solution pH, and contact time. The maximum adsorption capacity was 0.609 mmol/g. The Langmuir isotherm model showed a good fit ($R^2 = 0.94$). Adsorption kinetics showed good agreement of the experimental data with the pseudo-second order kinetic reaction model ($R^2 = 0.99$)

indicating a favorable adsorption and that Ni²⁺ adsorption is more of chemisorption than physical adsorption. The high adsorption capacity of biochar towards Ni²⁺ ions suggest that biochar has the potential to be an economical and efficient sorbent for treatment of wastewaters contaminated with Ni²⁺ ion.

The authors would like to thank Miss Jasmine Rossler for her assistance in conducting the experiments.

References

1. L. Järup, Br Med Bull, **68**,167-182, (2003)
2. Y.C. Sharma, *A guide to the economic removal of metals from aqueous solutions* (John Wiley & Sons, 2012)
3. D. Mohan, A. Sarswat, Y.S. Ok, C.U. Pittman, Bioresource Technol., **160**, 191-202, (2014)
4. J. Lehmann, M.C. Rillig, J. Thies, C.A. Masiello, W.C. Hockaday, D. Crowley, Soil Biol Biochem., **43**, 1812-1836, (2011)
5. X. Chen, G. Chen, L. Chen, Y. Chen, J. Lehmann, M.B. McBride, A.G. Hay, Bioresource Technol, **102**, 8877-8884, (2011)
6. Food and Agriculture Organization of the United Nations, <http://www.fao.org/statistics/en/> (2012)
7. T. Ahmad, M. Danish, M. Rafatullah, A. Ghazali, O. Sulaiman, R. Hashim, M.N.M. Ibrahim, Environ. Sci. Pollut. Res., **19**, 1464-1484, (2012)
8. Y.A. Alhamed, H.S. Bamufleh, Fuel, **88**, 87-94, (2009)
9. B.S. Girgis, A.N.A. El-Hendawy, Microporous Mesoporous Mater, **52**, 105-117, (2002)
10. C. Bouchelta, M.S. Medjram, O. Bertrand, J.P. Bellat, J Anal. Appl. Pyrol., **82**, 70-77, (2008)
11. Z. Mahdi, A. El Hanandeh, J.Y. Qiming, *EPPM2015*, (2015)
12. Z. Mahdi, A. El Hanandeh, J.Y. Qiming, Waste Biomass Valor, 1-13, (2016)
13. S. Wang, (Doctoral dissertation, UNIVERSITY OF FLORIDA, 2014)
14. R. M. Ali, H.A. Hamad, M.M. Hussein, G.F. Malash, Ecol. Eng., **91**, 317-332, (2016)
15. F.M. Pellera, A. Giannis, D. Kalderis, K. Anastasiadou, R. Stegmann, J.Y. Wang, E. Gidarakos, J. Environ. Manage, **96**, 35-42, (2012)
16. N.T. Abdel-Ghani, M. Hefny, G.A. El-Chaghaby, Int. J. Environ Sci. & Tech., **4**, 67-73, (2007)
17. M. Kılıç, Ç. Kırbıyık, Ö. Çepelioğullar, A.E. Pütün, Appl. Sur. Sci., **283**, 856-862, (2013)
18. Q. Cheng, Q. Huang, S. Khan, Y. Liu, Z. Liao, G. Li, Y.S. Ok, Ecol. Eng., **87**, 240-245, (2016)
19. L. Sun, D. Chen, S. Wan, Z. Yu, Bioresource Technol., **198**, 300-308, (2015)
20. M. Zhang, Chem. Eng. J, **172**, 361-368, (2011)
21. F.C. Wu, R.L. Tseng, R.S. Juang, J. of hazard. Mater., **69**, 287-302, (1999)
22. A. El Hanandeh, R.A. Abu-Zuryk, I. Hamadneh, A.H. Al-Dujaili, Water Sci. Technol. **74**, 1899-1910, (2016)
23. K. Vijayaraghavan, J. Jegan, K. Palanivelu, M. Velan, Sep. Purif. Technol., **44**, 53-59, (2005)
24. S. Erdoğan, Y. Önal, C. Akmil-Başar, S. Bilmez-Erdemoğlu, Ç. Sarıcı-Özdemir, E. Köseoğlu, G. Icduygu, Appl. Surf. Sci., **252**, 1324-1331, (2005)
25. Z. Ding, X. Hu, Y. Wan, S. Wang, B. Gao, J. Ind. Eng. Chem., **33**, 239-245, (2016)