



## Isotherms, Kinetics and Break through Curve for Sorptive Removal of Chromium from Wastewater by Activated Sludge

SUNIL KULKARNI<sup>✉</sup>

Department of Chemical Engineering, Datta Meghe College of Engineering, Airoli, Navi Mumbai-400708, India

Corresponding author: E-mail: [suniljayantkulkarni@gmail.com](mailto:suniljayantkulkarni@gmail.com)

Received: 20 February 2019;

Accepted: 14 March 2019;

Published online: 28 June 2019;

AJC-19439

In the present investigations, activated sludge is used for removal of chromium in batch and continuous mode. It was observed that the sorption process followed Langmuir isotherm better than Freundlich isotherm ( $R^2 = 0.95$ ). The Freundlich model with  $R^2$  value above 0.9 suggests that the sorptive removal may involve physical and chemical adsorption with some multilayer sorption. Chromium uptake followed second order kinetics. The maximum adsorption capacity  $q_e$  was observed to be 208.33 mg/g. The breakeven time and exhaustion time were determined for continuous operation. The non-availability of adsorbate at low flow rates play important role in delaying the break point time. Sludge age and initial concentration also affect the removal of chromium. The data follows the Thomas model with  $R^2$  value more than 0.9.

**Keywords:** Adsorption, Kinetics, Isotherms, Chromium, Activated sludge.

### INTRODUCTION

Chromium is used for chrome plating, the manufacture of pigments, metallurgical industries, leather tanning and wood treatment. Exposure to chromium may lead to adverse effects on the respiratory and immune systems [1-3]. Ingestion of chromate leads to gastrointestinal disorders, haemorrhagic diathesis and convulsions. Various physico-chemical, biological and advanced treatment methods are being explored for cost effective treatment of wastewater for chromium removal [4-6].

Adsorption by low cost adsorption is explored for chromium removal by many investigators. Baral *et al.* [7] used adsorption on treated sawdust for chromium removal. Babu and Gupta [8] investigated chromium removal from industrial wastewater by using activated neem leaves. Their investigations indicated that maximum removal efficiency was upto 85 %. Gupta *et al.* [9] reported the adsorption removal of chromium using a low cost fertilizer industry waste material, similarly Talokar [10] used low cost agriculture biomass as adsorbent. Siraj *et al.* [11] successfully removed upto 90 % chromium from tannery effluent using chitosan-charcoal composite.

Chemical methods including chemical precipitation are widely used for the removal of chromium has been cited by

several researchers. Ramakrishnaiah and Prathima [12] successfully remove 99 % chromium from the real samples. Another method *viz.* electrocoagulation for chromium removal is also found to be effective method [13-16].

Activated sludge process is common treatment step in the treatment plants. The activated sludge has the tendency to bioaccumulation of the heavy metals. Many investigations are reported on use of activated sludge for removal of heavy metals [17-20]. Hasani *et al.* [21] applied fixed activated sludge system for removing the heavy metals (Cr, Ni and Pb) from industrial wastewaters. Influence of anoxic selectors on heavy metal removal by activated sludge was investigated by Niec and Cha [22]. They compared an anoxic selector activated sludge system and a conventional activated sludge system for metal removal due to binding. It was observed that the selector sludge had significantly higher sorption capacity than the control sludge.

Studies to explore the potentials for recovery of heavy metals from the wastewaters and sewage sludge were critically reviewed by Saniedanesh *et al.* [23]. This work provided a criteria and selection guideline in selecting the best technology for an industrial or domestic wastewaters. About 94.2 % removal of lead by activated sludge in treatment of 5 mg/L lead solution was investigated Rahmani *et al.* [24]. The usefulness of dried

activated sludge for the removal of copper ions was carried out by Benaissa and Elouchdi [25]. Dried activated sludge was able to remove about 60 % of initial copper at equilibrium. They also observed that the capacity of copper removal at the equilibrium increases with the initial copper concentration.

In the present investigations, wet activated sludge removal in batch and continuous mode is carried out to determine the isotherms and kinetics of the removal and break through curve, respectively.

## EXPERIMENTAL

The total chromium is determined by converting all chromium to chromium(VI) state by oxidation with  $\text{KMnO}_4$  and then chromium(VI) is determined colorimetrically by reaction with diphenyl carbazide in acid solution. The red violet colour of unknown composition is produced. The unknown concentration can be determined by spectrophotometrically.

**Isotherm and kinetics:** Batch experiments were carried out in 250 mL conical flask and 100 mL of synthetic chromium effluent. Net sludge (3 g) was added to the effluent with different initial chromium concentrations (1000, 500 and 250 mg/L) and samples were filtered and collected after every 15 min.

**Freundlich isotherm:** The Freundlich isotherms can be expressed as follows:

$$\frac{X}{M} = KC^{1/n} \quad (1)$$

$$\ln \frac{X}{M} = \ln K + \frac{1}{n} \ln C \quad (2)$$

where X is the amount of adsorbate adsorbed and M is the amount of adsorbent. X/M is the adsorbent loading, C is the equilibrium concentration of solute, K and 1/n are constants. The exponent 1/n is an index of the diversity of free energies associated with the sorption of solute by multiple components of heterogeneous sorbent.

**Langmuir isotherm:** The Langmuir isotherm predicting the monolayer physical adsorption [26-29] is described as follows:

$$q_e = \frac{q_o b C_e}{(1 + b C_e)} \quad (3)$$

$$\frac{1}{q_e} = \frac{1}{q_o b C_e} + \frac{1}{q_o} \quad (4)$$

where  $q_o$  is the maximum capacity for the adsorbents and  $q_e$  is the sorption capacity for equilibrium concentration ( $C_e$ ). This isotherm assumes that a fixed number of accessible sites are available with same energy, adsorption is reversible and monolayer, There are no thermal interactions. Herein,  $q_o$  represents number of surface sites per mass of adsorbent. In ideal case, it would be same for all sorbates.

**Kinetics:** For the adsorption of solute from liquid solutions, pseudo first-order model is most widely used. The model equation [26-29] is expressed as follows:

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

where  $q_e$  is the mass of metal ion adsorbed at equilibrium (mg/g),  $q_t$  is the mass of metal adsorbed at time t (mg/g),  $k_1$  is the first order reaction rate constant, while the pseudo second-order model [26-29] is represented as follows:

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

where  $k_2$  is the second order reaction rate constant.

**Continuous activated sludge method:** Synthetic chromium solution was prepared with addition of potassium dichromate in water. The tank with diameter 20 cm, length 30 cm and cone diameter 20 cm was used in this investigation. The tank was initially filled with required amount of sludge. Then the influent with required chromium concentration was passed through the tank. The effluent was allowed to overflow continuously. Gentle stirring was provided to ensure contact between the metal ions and sludge. Experiments were carried out to study the effect of parameters namely flow rate, initial chromium concentration, sludge age and sludge concentration on chromium removal. Samples were collected for analysis after every 10 min interval. The fractional concentration ( $C/C_o$ ) was noted at various times. Also breakeven time and exhaustion time were determined. Each experiment was repeated with aeration. The sludge from nearby sludge treatment plant was used. The exit chromium concentration was determined by UV spectrophotometric method.

## RESULTS AND DISCUSSION

**Isotherm studies:** It was observed that sorption process follows Langmuir isotherm better than Freundlich isotherm. The investigation carried out by various investigators for activated sludge also indicated that the adsorption of Cu, Cd, Zn, Ni, and Cr followed the Langmuir isotherm and it did not fit well to the Freundlich model [30-32]. Freundlich isotherm was moderately followed with  $R^2$  value of 0.906. Few other investigations have reported that sorptive removal follows Freundlich isotherm [33] only. It can be seen that the sorption isotherms depends on the material used for the biosorption. The result obtained is in agreement with previous studies. The sorption process is mono-molecular since it obeys Langmuir model. This also indicates the high conformity and uniformity of the surface topography. The surface active sites responsible for chromium removal have a similar adsorption energy. The Freundlich model with  $R^2$  value above 0.9 suggested that the sorptive removal may involve physical and chemical adsorption with some multilayer sorption.

The plot of  $x/m$  against C for Freundlich isotherm on logarithmic scale followed following equation:

$$y = 4.4629x + 3.7 \quad (7)$$

The value of 1/n (adsorption intensity) in Freundlich equation was found to be 4.4629. Adsorption capacity (K) was found to be 43.18 mg/g. Investigation by Ong *et al.* [32] indicated K and 1/n value 30.28 and 0.17, respectively for powdered activated carbon.

The plot of 1/x/m against 1/C for Langmuir isotherm indicated much better fit than Freundlich. The plot followed following equation:

$$y = 0.0741x + 0.0039 \quad (8)$$

The value of  $q_o$  in Langmuir isotherm was 256 mg/g and b was found to be 0.052 L/mg. The value of maximum adsorption capacity is high indicated tendency of heavy metal to

accumulate in the activated sludge. The maximum adsorption capacity by Langmuir model, 256.4 mg/g is better than the adsorption capacities obtained in earlier research by various investigators. Similar results were obtained for the Langmuir isotherm. Djafer *et al.* [34] reported value of maximum adsorption capacity 47.61 mg/g for granular pozzolana. Maximum capacity for heavy metal in Langmuir equation was reported as 192 mg/g and Langmuir constant 0.16 by Mousavi and Seyedi [35].

**Kinetic studies:** The first order model for sorption kinetics was not followed for chromium uptake ( $R^2 = 0.7484$ ). The value of constant  $k_1$  in first order model was observed to be 4.4629. The sorptive removal followed second order. Many investigations revealed that the sorptive removal of heavy metals by dried activated sludge follows second order kinetic model [25]. Some investigations indicated first order kinetic model for activated sludge [36]. The maximum adsorption capacity  $q_e$  was observed to be 208.33 mg/g. The values of the parameters obtained are in agreement with earlier results. The adsorption capacity of the activated sludge was higher than many other biosorbents. Pseudo-second order equation for metal was followed with  $q_0$  value in the range of 20 to 36 mg/g as reported by Benaissa and Elouchdi [25].

**Continuous activated sludge process:** The effect of flow rate, initial concentration ( $C_0$ ), sludge age, sludge concentration on the chromium removal is studied. It was observed that in the experiments with aeration, the removal was 5-10 % more than its counterpart in experiments without aeration. This indicates that 5 to 10 % removal was due to aerobic process, while most of the chromium removal was due to sorption process.

**Effect of flow rate:** As shown in Fig. 1, it was observed that the break point was 12 min with aeration and 15 min without aeration. The experiments were carried out for flow rates of 200, 150 and 100 mL/min and constant initial chromium concentration (1000 mg/L). With decrease in the flow rate to 150 mL/min from 200 mL/min, time required for reaching the break point is increased by 22 min. Further decrease to 100 mL/min indicates decrease in the time by 10 min. The non-availability of adsorbate at low flow rates play important role in delaying the break point time. The experiments with aeration yielded 5-7 % more removal than experiments with aeration. The maximum removal of 95.5 % was observed in first 10 min. The packed bed sorption has shown similar results for various heavy metals [37,38]. The exhaustion time required was observed to be 120, 150 and 210 min for 200, 150 and 100 mL/min.

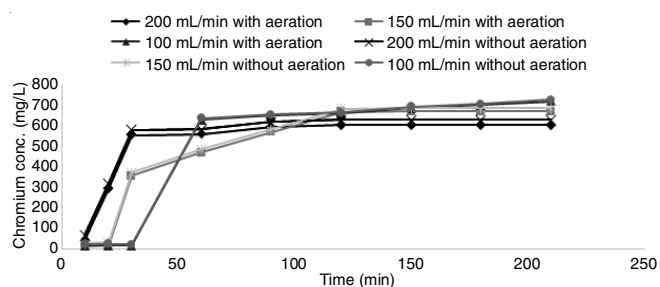


Fig. 1. Effect of flow rate on chromium removal

**Effect of initial concentration on removal of chromium:** As shown in Fig. 2, a decrease in concentration delays the

break-through time. Experiments were carried out at constant flow rate, 200 mL/min with initial concentrations (1000, 500 and 250 mg/L) to assess the effect of initial concentration on the chromium removal. Several investigations [37-39] revealed that with decrease in initial concentration, the breakthrough time delays. However, the present results differ from other literatures. The investigations also indicated that the trend of delay in the break point time is followed for change in the concentrations. This becomes insignificant at higher concentrations. With decrease in initial concentration from 1000 mg/L to 500 mg/L, the breakthrough time decreased from 11 min to 5 min. Further decrease in the initial concentration was characterized by increase in the time required for breakthrough. The exhaustion time required was observed to be 90, 240 and 300 s respectively with exhaustion concentrations 610, 590 and 601 mg/L. The maximum fractional removal 0.95 was observed at 1000 mg/L. The reason may be attributed due to the rapid availability of adsorbate and the next maximum fractional removal was 0.82 at 250 mg/L. At 500 mg/L, the removal was least which may be due to the slow availability of chromium ions coupled with congestion of active sites.

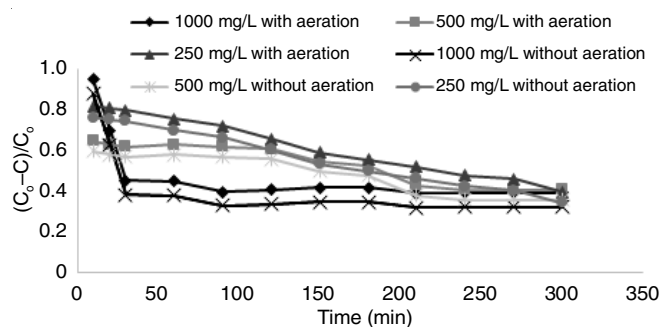


Fig. 2. Effect of initial concentration on chromium removal

**Effect of sludge age on removal of chromium:** Effect of sludge age on chromium removal is shown in Fig. 3. It can be seen that the percentage removal was maximum for sludge age of 8 days. Time required for break point decreased for increase in sludge age from 4 to 8 days. Further increase in sludge age has negative effect and increase in break through time. These experiments were carried out for initial concentration 1000 mg/L and flow rate 200 mL/min.

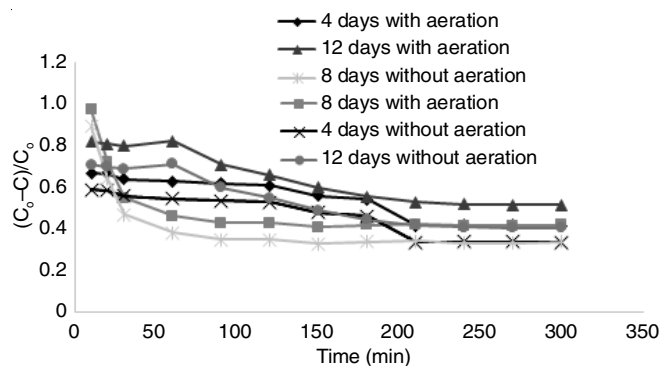


Fig. 3. Effect of sludge age on chromium removal

**Effect of sludge concentration on removal of chromium:** Fig. 4 shows the effect of sludge concentration on chromium

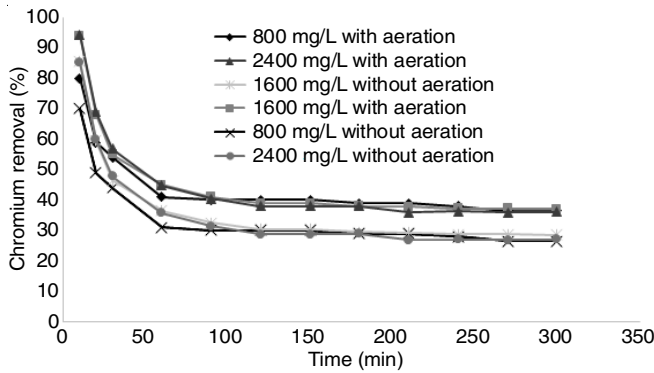


Fig. 4. Effect of sludge concentration on chromium removal

removal. It can be observed that fractional removal is maximum for the sludge concentration of 2400 mg/L. The experiments with aeration yielded 10 % additional chromium removal. The sludge concentration of 1600 mg/L was optimum as further increase to 2400 mg/L resulted in only 0.3 % increase in the removal. Thus for 200 mL/min, 1000 mg/L effluent and sludge age 8 days, sludge concentration 1600 mg/L was optimum. The breakthrough time delayed with increase in adsorbent mass (Table-1).

**Modeling:** The continuous mode data with optimum parameter values was tested for two models namely Thomas-BDST (Bed Depth Service Time) model and Yoon Nelson model

Thomas-BDST model is expressed [40] as follows:

$$\frac{C}{C_o} = \frac{1}{1 + \exp\left(\frac{K_T}{Q}(q_m - C_o)V\right)} \quad (9)$$

$$\ln\left(\frac{C}{C_o} - 1\right) = \frac{K_T q_o M}{Q} - \frac{K_T C_o V}{Q} \quad (10)$$

where  $C$  and  $C_o$  are the effluent and inlet solute concentrations (mg/L),  $q_o$  is the maximum adsorption capacity (mg/g),  $M$  is the total mass of adsorbent (g),  $Q$  is the volumetric flow rate (mL/min),  $V$  is the throughput volume (mL) and  $K_T$  is the Thomas rate constant (mL/min/mg).

Yoon Nelson model is expressed [41,42] as follows:

$$\frac{C}{C_o} = \frac{1}{1 + \exp(K(\tau - t))} \quad (11)$$

$$\ln\left(\frac{C}{C_o - C}\right) = kt - \tau k \quad (12)$$

where,  $k$  is the rate constant,  $\tau$  is time required for 50 % adsorbate break through and  $t$  is sampling time.

Figs. 5 and 6 depicted the Thomas model and Yoon Nelson model, respectively. It can be seen that the data follows the Thomas model with  $R^2$  value more than 0.9, however the data

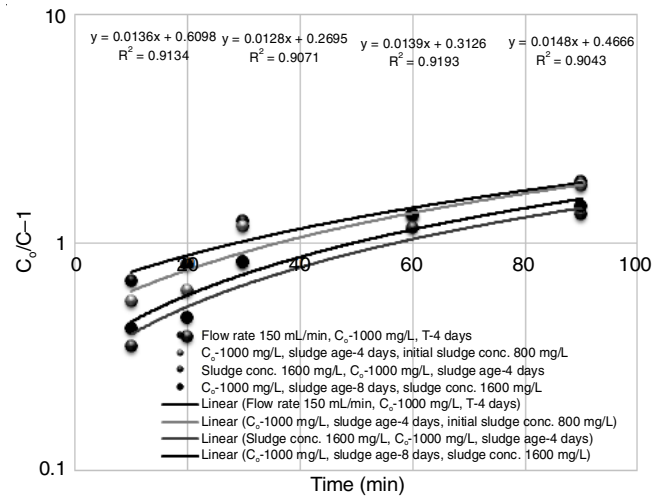


Fig. 5. Thomas model

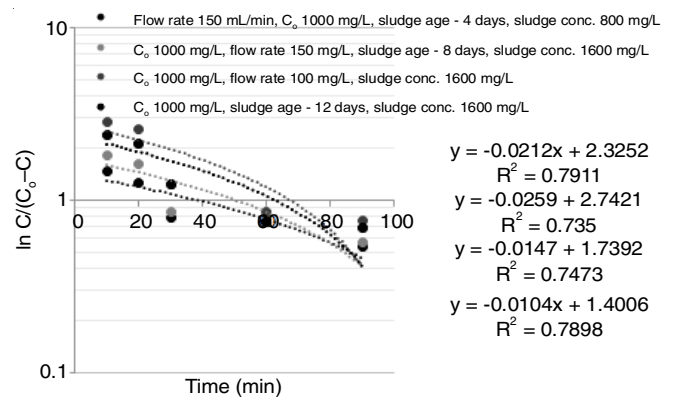


Fig. 6. Yoon Nelson model

shows poor fit for the Yoon Nelson model. The values of model parameters ( $K_T C_o = 0.0136, 0.0128, 0.0139, 0.0148$ ) in Thomas model are in agreement with similar work carried out for various heavy metal ions and adsorbents [37,40].

**Conclusion**

The results revealed that the aeration doesn't have significant effect on chromium removal using activated sludge. In various experiments, only 3 to 10 % increase in chromium removal was observed. Considering cost of aeration, the bio-sorption without aeration is cost effective. The sorption process followed Langmuir isotherm better than Freundlich isotherm. The sorption process is monomolecular since it obeys Langmuir model. This also indicates the high conformity and uniformity of the surface topography. The surface active sites responsible for chromium removal have a similar adsorption energy. The Freundlich model with  $R^2$  value above 0.9 suggests that the sorptive removal may involve physical and chemical adsorption with some multilayer sorption. The chromium uptake followed

TABLE-1  
PARAMETERS IN CONTINUOUS ACTIVATED SLUDGE PROCESS

Parameter	Effect of flow rate (mL/min)			Effect of initial concentration (mg/L)			Sludge age (days)			Sludge concentration (mg/L)		
	150	100	50	1000	500	250	4	8	12	800	1600	2400
Break point time (min)	12	24	14	11	5	17	3	8	5	7	10	11
Exhaustion time (min)	120	150	210	90	240	300	210	150	240	270	240	210

second order kinetics. The maximum adsorption capacity  $q_e$  was observed to be 208.33 mg/g. In continuous experiments, for 200 mL/min flow rate, 1000 mg/L effluent concentration and sludge age 8 days, sludge concentration 1600 mg/L was optimum. The non-availability of the adsorbate at low flow rates play important role in delaying the break point time. The investigations indicated that the trend of delay in the break point time is followed for initial rise in the concentrations and becomes insignificant at higher concentrations. Sludge age and initial concentration also affect the removal of chromium. The continuous data followed the Thomas model with  $R^2$  value more than 0.9.

### CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

### REFERENCES

1. S. Mishra and R.N. Bharagava, *J. Environ. Sci. Health, Part C: Environ. Carcinog. Ecotoxicol. Rev.*, **34**, 1 (2016); <https://doi.org/10.1080/10590501.2015.1096883>.
2. S. Jeyamala, A.K. Kumaraguru and N. Nagarani, *Toxicol. Environ. Chem.*, **94**, 1583 (2012); <https://doi.org/10.1080/02772248.2012.715382>.
3. R. Shrivastava, R.K. Upreti, P.K. Seth and U.C. Chaturvedi, *FEMS Immunol. Med. Microbiol.*, **34**, 1 (2002); <https://doi.org/10.1111/j.1574-695X.2002.tb00596.x>.
4. P. Rajasulochana and V. Preethy, *Resour.-Efficient Technol.*, **2**, 175 (2016); <https://doi.org/10.1016/j.refit.2016.09.004>.
5. A. Demir and M. Arisoy, *J. Hazard. Mater.*, **147**, 275 (2007); <https://doi.org/10.1016/j.jhazmat.2006.12.076>.
6. T.A. Kurniawan, G.Y.S. Chan, W.-H. Lo and S. Babel, *Chem. Eng. J.*, **118**, 83 (2006); <https://doi.org/10.1016/j.cej.2006.01.015>.
7. S.S. Baral, S.N. Das and P. Rath, *Biochem. Eng. J.*, **31**, 216 (2006); <https://doi.org/10.1016/j.bej.2006.08.003>.
8. B.V. Babu and S. Gupta, *Adsorption*, **14**, 85 (2008); <https://doi.org/10.1007/s10450-007-9057-x>.
9. V.K. Gupta, A. Rastogi and A. Nayaka, *J. Colloid Interface Sci.*, **342**, 135 (2010); <https://doi.org/10.1016/j.jcis.2009.09.065>.
10. A. Talokar, *Int. J. Adv. Biotechnol. Res.*, **2**, 452 (2011).
11. S. Siraj, M.M. Islam, P.C. Das, S.M. Masum, I.A. Jahan, M.A. Ahsan and M. Shajahan, *J. Bangladesh Chem. Soc.*, **25**, 53 (2012); <https://doi.org/10.3329/jbcs.v25i1.11774>.
12. Ramakrishnaiah and B. Prathima, *Int. J. Eng. Res. Appl.*, **2**, 599 (2012).
13. A.M. Khalaf, A.A. Mubarak and S.A. Nosier, *Int. J. Electrochem. Sci.*, **11**, 1601 (2016).
14. S.U. Khan, D.T. Islam, I.H. Farooqi, S. Ayub and F. Basheer, *Process Safety Environ. Prot.*, **122**, 118 (2019); <https://doi.org/10.1016/j.psep.2018.11.024>.
15. Y.A. El-Taweel, E.M. Nassef, I. Elkheriany and D. Sayed, *Egypt. J. Petrol.*, **24**, 183 (2015); <https://doi.org/10.1016/j.ejpe.2015.05.011>.
16. K. Thirugnanasambandham and K. Shine, *Int. J. Chem. React. Eng.*, **16**, (2018); <https://doi.org/10.1515/ijcre-2017-0155>.
17. M.A. Barakat, *Arab. J. Chem.*, **4**, 361 (2011); <https://doi.org/10.1016/j.arabjc.2010.07.019>.
18. A.J. Hargreaves, C. Constantino, G. Dotro, E. Cartmell and P. Campo, *Environ. Technol. Rev.*, **7**, 1 (2018); <https://doi.org/10.1080/21622515.2017.1423398>.
19. S. Azizi, I. Kamika and M. Tekere, *PLoS One*, **11**, e0155462 (2016); <https://doi.org/10.1371/journal.pone.0155462>.
20. X. Zhang, X.-Q. Wang and D.-F. Wang, *Sustainability*, **9**, 2020 (2017); <https://doi.org/10.3390/su9112020>.
21. A.H. Hassani, I. Hossenzadeh and B. Torabifar, *J. Environ. Studies*, **36**, 71 (2010).
22. J. Niec and D. Cha, *Bioprocess Eng.*, **5**, 431 (2000); <https://doi.org/10.1007/BF02931943>.
23. M. Saniedanesh, S. Alwi and Z.Z. Abdul Manan, Proceedings of the 6th International Conference on Process Systems Engineering (PSE ASIA) 25 - 27 June 2013, Kuala Lumpur, Malaysia (2013).
24. K. Rahmani, A. Mahvi and F. Vaezi, *Int. J. Environ. Res.*, **3**, 471 (2009).
25. H. Benaissa and M.A. Elouchdi, Ninth International Water Technology Conference, IWTC9 2005, Sharm El-Sheikh, Egypt, pp. 69-83 (2005).
26. R.D. Tyagi and Y.G. Du, *Environ. Technol.*, **13**, 883 (1992); <https://doi.org/10.1080/09593339209385223>.
27. P. Miretzky, A. Saralegui and A. Fernandez-Cirelli, *Chemosphere*, **62**, 247 (2006); <https://doi.org/10.1016/j.chemosphere.2005.05.010>.
28. J.C. Igwe and A.A. Abia, *Afr. J. Biotechnol.*, **5**, 1167 (2006).
29. Y.-S. Ho and A.E. Ofomaja, *J. Hazard. Mater.*, **137**, 1796 (2006); <https://doi.org/10.1016/j.jhazmat.2006.05.023>.
30. Y. Liu, M.C. Lam and H.H.P. Fang, *Water Sci. Technol.*, **43**, 59 (2001); <https://doi.org/10.2166/wst.2001.0340>.
31. W. Hai-suo, Z. Ai-qiang and W. Lian-sheng, *J. Environ. Sci. (China)*, **16**, 640 (2004).
32. S.-A. Ong, E. Toorisaka, M. Hirata and T. Hano, *Sci. Asia*, **36**, 204 (2010); <https://doi.org/10.2306/scienceasia1513-1874.2010.36.204>.
33. P. Muthusamy, S. Murugan and M. Smitha, *J. Biol. Sci.*, **1**, 7 (2012).
34. A. Djafer, S.K. Moustefai, A. Idou, M. Douani, *Int. J. Environ. Ecol. Eng.*, **7**, 665 (2013).
35. H.Z. Mousavi and S.R. Seyedi, *Int. J. Environ. Sci. Technol.*, **8**, 665 (2013).
36. M. Singanan, *Sci. Asia*, **37**, 115 (2011); <https://doi.org/10.2306/scienceasia1513-1874.2011.37.115>.
37. Z. Saadi, R. Saadi and R. Fazaeli, *J. Nanostruct. Chem.*, **3**, 48 (2013); <https://doi.org/10.1186/2193-8865-3-48>.
38. S. Kulkarni and J. Kaware, *Int. J. Thermal Environ. Eng.*, **9**, 75 (2015).
39. S. Gupta and B.V. Babu, *J. Water Resource Prot.*, **2**, 706 (2010); <https://doi.org/10.4236/jwarp.2010.28081>.
40. D. Kavak and N. Ozturk, *Illustrararasi. Bor. Sempozyumu*, **23-25**, 495 (2004).
41. J.T. Nwabanne and P.K. Igbokwe, *Int. J. Appl. Sci. Technol.*, **2**, 106 (2012).
42. Z. Aksu and F. Gönen, *Process Biochem.*, **39**, 599 (2004); [https://doi.org/10.1016/S0032-9592\(03\)00132-8](https://doi.org/10.1016/S0032-9592(03)00132-8).