Journal of Materials and Environmental Sciences
ISSN : 2028-2508
CODEN : JMESCN

J. Mater. Environ. Sci., 2018, Volume 9, Issue 7, Page 2158-2163

http://www.jmaterenvironsci.com

Kinetic and Thermodynamic Studies on Removal of lead using Tamarind fruit shell powder and Algae

P. Bangaraiah[1*], B. Sarathbabu[2]

1. AMMPC Laboratories ,Chemical Engineering Department, VFSTR University, Guntur-522213, India.*
1,2. Chemical Engineering Department, S.V.University, Tirupati-517502, India.

Received 05 Sep 2017,
Revised 05 Dec 2017,
Accepted 13 Dec 2017

Keywords
- ✓ Tamarind fruit hell,
- ✓ Algae,
- ✓ Biosorption,
- ✓ Lead,
- ✓ Isotherms.

pbangaraiah79@gmail.com;
Phone: +919492730868;

Abstract

The most of heavy metal contaminants come from various manufacturing industries. These heavy metals are toxic to human and aquatic systems even if they were present in low concentrations. Many methods are available for remediation, but those are costly and ineffective. However based on extensive research work, it has found that waste materials like, Tamarind bark, eggshells, agricultural wastes are well suited to remove heavy metals from waste water using biosorption technique.Biosorption is environmentally eco-friendly and alternative method for removal of heavy metals. In this present investigation, Tamarind fruit shell and Algae were used as biosorbents for lead removal. The optimum agitation time,dosage,initial metal ion concentration and pH were studied.The experimental data is fitted to Freundlich and Langmuir isotherm models,but well suited to Freundlich model.The kinetic data followed the pseudo second order kinetics.The maximum lead removal using Tamarind fruit shell is 82.1 % and 73.1 % for Algae biosorbent.

1. Introduction

The major water contamination is considered from heavy metal ions such as lead,zinc and chromium resleasing from various industries like paint,battery and mining.The presence of heavy metal ions in aqueous streams, coming from the discharge of untreated effluents into water bodies, is one of the most important environmental problems. Lead is used as industrial raw material in the manufacture of storage batteries, pigments, leaded glass products. The effluent comes from these industries containing lead discharge into water bodies can damage not only surface water bodies but also underground water. Presence of lead causes several unwanted effects on human body such as kidney damage, disruption of nervous system and brain damage. The permissible limit of lead is concentration is 0.1mg/l as per the environmental standards [1].

The various conventional methods used to remove Lead from effluents is precipitation, extraction, oxidation- reduction process, electro dialysis, reverse osmosis, ion-exchange, evaporation and dilution. Most of these methods are suffer from drawbacks, such as high maintanance cost or the disposal of residual metal sludge, and are not suitable for small-scale industries. These techniques are expensive and hence economically not feasible for the removal of lead and zinc from waste water .The need for an economic and effective method for the removal of heavy metals has resulted in the development of new separation technologies. Biosorption is one of the few alternative techniques available for such a situation. The use of dead biomass for the removal of heavy metals has the advantage of not require the nutrients, often referred to as the biosorption, has attracted much attention in recent time. Biosorbent materials are cheaper, easily available and eco friendly materials [2].

In this present study, biosorbents were prepared from Tamarind tree and Algae.The tamarind fruit shells (TFS) are collected from Jammalamadugu village in Kadapa district, Andra Pradesh,India and algae were collected from natural pond near by vadlamudi village in Guntur district,Andra Pradesh,India.The biosorbent tamarind fruit shell powder (*Tamarindus Indica.L*) and blue green algae were used to carry out experiments for lead removal. Batch experiments are conducted for kinetic, thermodynamic and equilibrium studies for the removal of lead from aqueous solution. The effect of various parameters such as agitation time, biosorbent size, biosorbent dosage, initial ion concentration and pH have been investigated [3-4].

2. Material and Methods

Preparation of biosorbents

Tamarind fruit shell powder

The Tamarind fruit shells are collected from Jammalamadugu in Kadapa district. These shells are washed with distilled water to remove dust and impurities. Then shells are dried in hot air oven for 24 hrs. The dried shells are ground and powdered and the resulting powder is sieved.The required size of biosorbent is stored for further use [5].

Algae

The blue green algae (*A. sphaerica*) are collected from ponds in nearby Jagarlamudi village in Guntur district. The algal biomass was washed with distilled water for six times to remove any impurities. After this, algae are dried in a Hot air oven. Then, the dried biomass was ground and sieved. After this alga biosorbent was stored in bottles for further use[6-7].

Preparation of stock solution

The known quantity of $Pb(NO_3)_2$ is dissolved in one litre of distilled water to prepare 1000 mg/l of standard solution.Samples of different metal concentrations such as 5 mg/l, 10 mg/l, 15 mg/l, 20 mg/l, 25 mg/l, 30 mg/l, 40 mg/l,50 mg/l and 60 mg/l are prepared by appropriate dilutions. The pHof the solution is adjusted using 0.1N sodium hydroxide or Hydrochloric acid[6-7].

Method

Batch biosorption method is used.In this method, known amount of sample is taken in a conical flask to this add 0.5 g of biosorbent and kept for agitation for a period of one minute,after this sample is filtered , dried and analysed by using spectrophotometer.The same procedure is followed for remaining experiments[8].

3. Results and discussion

Effect of agitation time on % removal of lead

The process conditions of Initial concentration of lead (C_0) 20 mg/l, biosorbent size (dp) 82.5μm, biosorbent dosage (w) 1 g,volume of aqueous solution, 30 ml are maintained to find the optimum agitation time.

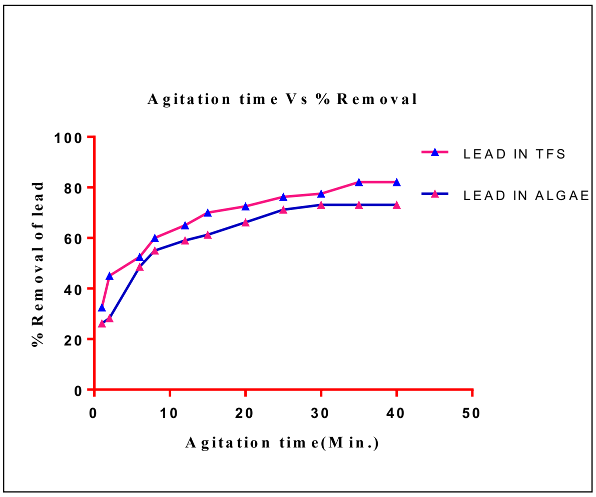

Figure 1: Effect of agitation time on lead removal

The optimum agitation time is estimated by plotting the percentage removal of lead against agitation time in Figure 1 using Table 1 at the interaction time of 1 minute to 40 minutes. The % removal is found to increase up to 35 miutes and 30 minutes for TFS and Algae biosorbents respectively, thereafter, no change in % removal is noticed with agitation time. It is noticed that the rate of biosorption is faster in the initial stages because adequate surface area of the biosorbent is available for the adsorption of lead [8].So the optimum agitation time is 35 minutes and 30 minutes for TFS and Algae biosorbents respectively[9-10].

Effect of biosorbent dosage on % removal of lead

The percentage removal of lead is drawn against biosorbent dosage in Figure 2. It is evident from the plot that the percentage removal of lead increases with increase in biosorbent dosage from 0.1gm to 1.0.gm. The removal of lead at 1.0 gm dosage is 82.1 %and 73.6 % for TFS and Algae biosorbents respectively. Such behavior is obvious because the number of active sites available for metal removal would be more as amount of the biosorbent increases [11-12].The optimum dosage is 1.0 g for both TFS and Algae bioosrbents. (Table 2)

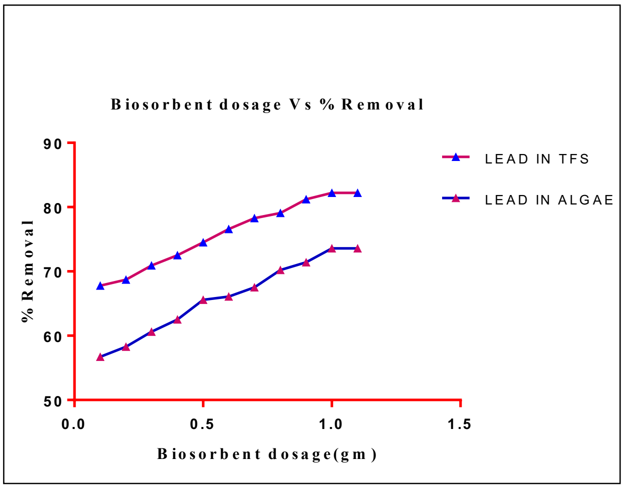

Figure 2: Effect of biosorbent dosage lead removal

Effect of initial metal ion concentration on % removal of lead

The percentage removal of lead is plotted against initial metal ion concentration to study the variation in percentage removal in Figure 3.The percentage removal of lead is decreased from 81.8 to 46.6 and 75.2 to 42.6 for TFS and Algae biosorbents respectively with increase of initial concentration of lead from 5 mg/l to 60 mg/l. Such behavior can be attributed to the increase in the amount of adsorbate to the unchanging number of available active sites on the biosorbents (since the amount of biosorbent is kept constant)[13]. (Table 3)

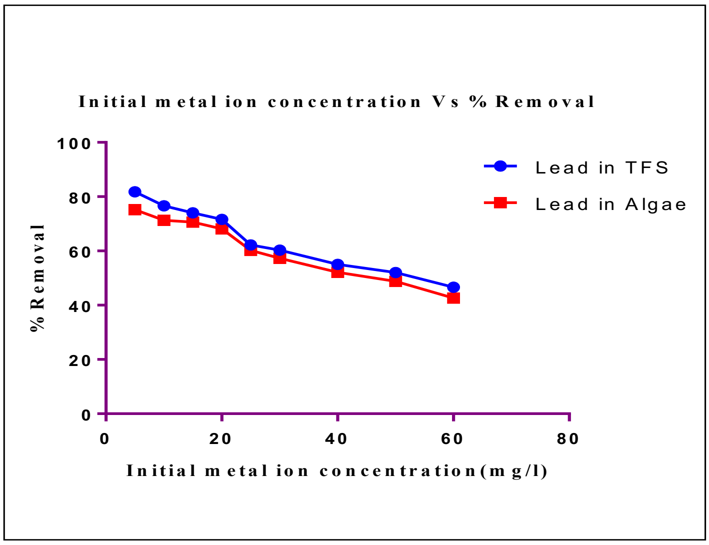

Figure 3: Effect of initial metal ion concentration on lead removal

Effect of pH on % removal of lead

The effect of P^H of the aqueous solution on % removal of lead is studied by plotting percentage removal of lead against pH in Figures 4. The % removal of lead is increased from 65% to 82% as p^H is increased from 1 to 5 and for TFS and Algae biosorbents respectively. At higher p^H value, the capacity of the biosorbent recessed [14-15]. (Table 4).pH influence the sorption capacity significantly.The optimum pH is 5 for both TFS and Algae biosorbents.

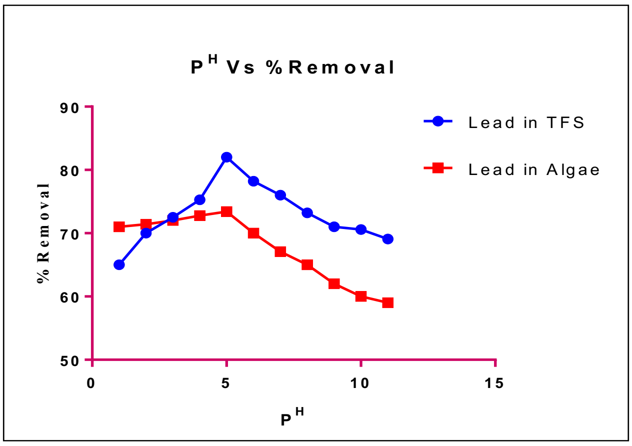

Figure 4: Effect of pH on lead removal

Biosorption isotherms

The modeling of the process was done by using two different isotherm models Freundlich and Langmuir isotherms.The Freundlich equation is given by :

Log q_e = Log k +1/n Log c_e ,where qe is qmount of metal ion on to the biosorbent in mg/g at equilibrium,c_e metal ion concentration,mg/l in solution and k and n are freundlich constants. .(Figure 5) (Figure 6)

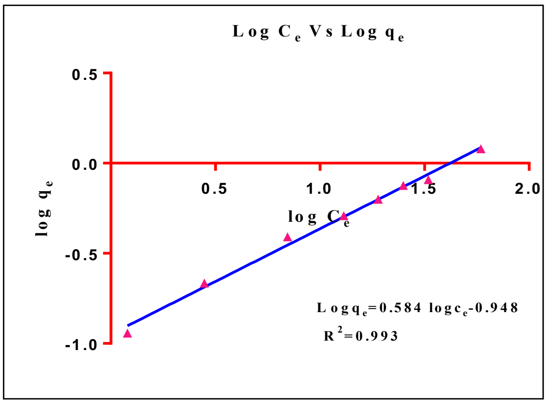

Figure 5: Freundlich isotherm using TFS

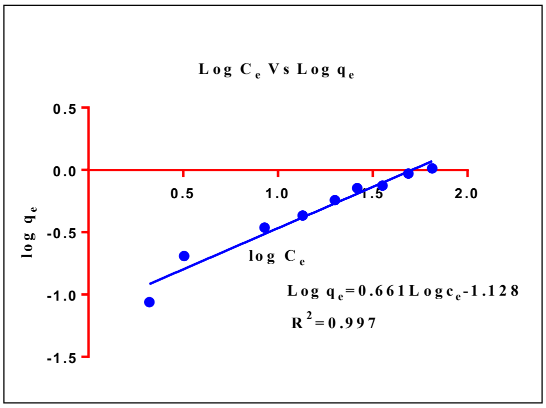

Figure 6: Freundlich isotherm using algae

Langmuir equation is given by

$C_e/q_e = 1/q_m\, k + c_e/_{qm}$ where qm is biosorbent capacity,mg/g

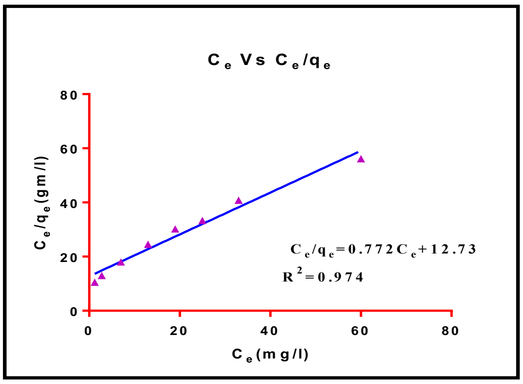

Figure 7: Langmuir Isotherms using TFS

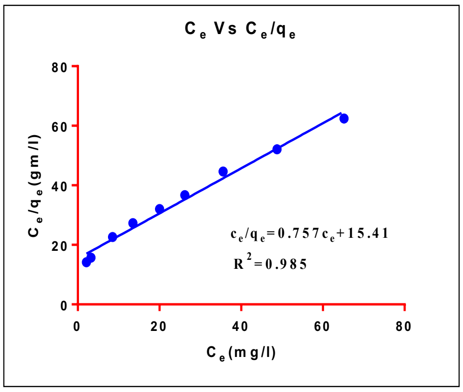

Figure 8: Langmuir Isotherms using algae

The slope n value satisfies the condition 0<n<1 and R^2 values are 0.993 and 0.997 for TFS and Algae in Freundlich model. The freundlich isotherm is more linear than Langmuir isotherm.This indicates Freundlich model is well fitted than Langmuir isotherm model[16]. (Figure 7) (Figure 8)

Kinetics

Pseudo first order kinetic equation is given by $Log(q_e\text{-}q_t) = Log\ q_e\text{-}k_1t/2.303$,where k_1 is rate constant , q_e and q_t are amount of metal ion on to the biosorbent at equilibrium and time t respectively.The correlation coefficient R^2 is less than 0.99.It shows that it not best fit for the calculated experimental data. (Figure 9) (Figure 10)

Pseudo second order equation is given by $t/q_t=1/k_2\ q_e^2 + t/q_e$,where k_2 is rate constant.The correlation coefficient for this model is more than 0.99. It was observed that the linearity of the plots (R^2 = 0.99) confirms the suitability of pseudo second order kinetics than first order kinetics[17].(Figure 11) (Figure 12)

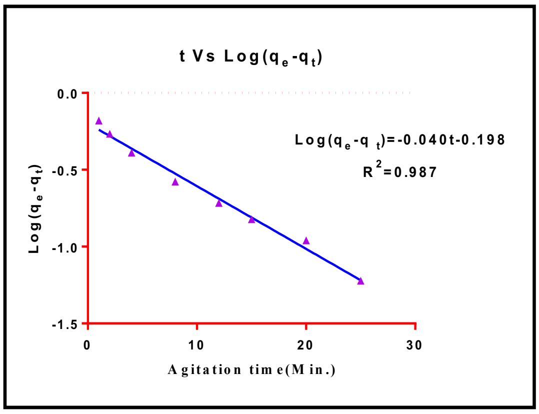

Figure 9: First order kinetics using TFS

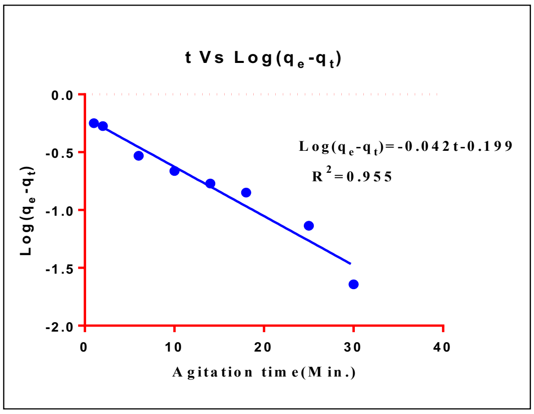

Figure 10: First order kinetics using algae

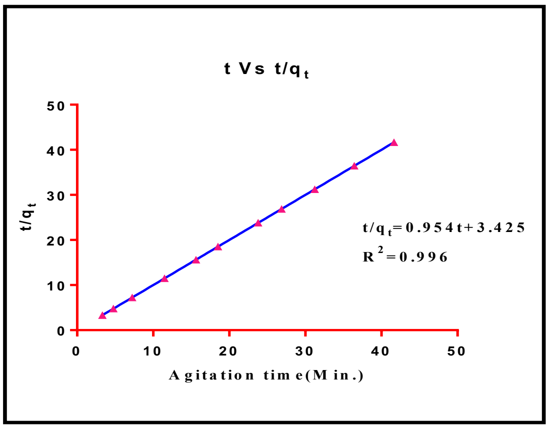

Figure 11: Second order kinetics using TFS

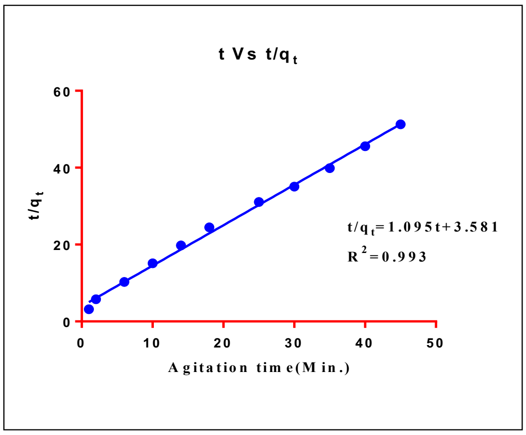

Figure 12: Second order kinetics using algae

Thermodynamic study

From Table 5 it was observed that, the +ve values of Enthalpy indicates biosorption is endothermic and the value of entropy above zero said the biosorption process is irreversible. The –ve values of ΔG show the reaction is spontaneous[17].

Table 5: Thermodynamics of lead

S.No	Initial Conc., C_0, mg/l	ΔH, J/mol-K	ΔS J/mol	ΔG at different temperatures J/mol				
				293 K	303 K	313 K	323 K	333 K
1	20	21.195	45.570	-13330.8	-13786.5	-14242.2	-14697.9	-15153.6
2	40	21.176	41.434	-12119	-12533.3	-12947.7	-13362	-13776.3
3	60	23.225	46.910	-13721.4	-14190.5	-14659.6	-15128.7	-15597.8
4	80	19.549	32.416	-9478.34	-9802.5	-10126.7	-10450.8	-10775
5	100	15.241	17.060	-4983.34	-5153.94	-5324.54	-5495.14	-5665.74

Conclusion

Investigations are carried out to find out the effect of kinetic and thermodynamic parameters for biosorption of lead using Tamarind tree fruit shell powder and algae, easily available and low cost biosorbents[18]. The analyses of the experimental data stated that the optimum agitation time for lead biosorption is 35 minutes for TFS and 30 minutes for Algae respectively.The percentage removal of lead is increased with increase in amount of the biosorbent from 0.1g to 1g respectively. The optimum biosorbent dosage is 1g. Higher the initial metal ion concentration of lead in the solution, the percentage removal of lead is decreased. The removal of lead in the solution is increased with increase in pH value from 1 to 5.The maximum percentage removal of lead is 82.1 and 73.1 for TFS and algae biosorbents respectively.The data is well represented by Freundlich isotherm.The kinetic studies stated that the biosorption of lead is better described by pseudo-second order kinetics.The experimental data indicate that sorption process is endothermic.The sorption process is found to be irreversible and spontaneous[19-20]. Biosorbents can be also used for the purification of ionic pharmaceuticals like proteins, antibodies, and peptides[21].

References

1. Yen Ling Sharain-Liew, Collin G. Joseph, Siew-Eng How, *J. Serb. Chem. Soc.* 76 (2011) 1037–1047.
2. C. N. Deepa, S. Suresha, *J. Environ. Sci. Toxicol. Food Technol.*8 (2014) 69-79.
3. M.Azza, Abdel .Aty, S.Nabila, Ammar, H.Hany, Abdel Ghafar, K.Rizka Ali, *J. Adv. Res.* 4 (2013) 367–374.
4. M. Malakootian, A. Toolabi, S. Gh. Moussavi, M. Ahmadian, , *Aust. J. Basic Appl. Sci.* 5 (2011) 1030-1037.
5. H. Naeema, Yarkandi *, Int. J. Curr. Microbiol. Appl. Sci.* 3 (2014) 207-228.
6. M.Salem, Hamza, F.Hanan, A. M.Ahmed Ehab, F. M.Mohammad, *J. Am. Sci.*6 (2010) 597-604.
7. M. A. O. Badmus, T. O. K. Audu, B. U. Anyata, *Turkish J. Eng. Environ. Sci.* 31 (2007) 251 – 263.
8. Alaa Kareem Mohammed , Safaa Abdalrasool Ali , Ali Muayyed Najem, Kais Kassim Ghaima, *Int. J. Pure Appl. Sci. Technol.* 17 (2013)72-78.
9. F. Chigondo , B.C. Nyamunda , S.C. Sithole , L. Gwatidzo, *J. Appl. Chem*. 5 (2013) 43-50.
10. Naima Azouaoua , Mohamed Belmedanib , Hassiba Mokaddema , Zahra Sadaoui, *Chem. Eng. Trans*. 32 (2013)55-60.
11. Ozdemir Guven, Ozturk Tansel, *Bioresour. Technol.* 90 (2003) 71-74.
12. Sushil Bachale, Dr. Sarita Sharma, Dr. Ashok Sharma ,Dr. Sanjay Verma, *Int. J. Appl. Res.* 2 (2016) 523-527.
13. S.Klimmek, H. J.Stan, A.Wilke, G.Bunke, R.Buchholz, *Environ. Sci. Technol*. 35 (2001) 4283–4288.
14. Mohammed Abdulsalam, *Aust. J. Basic Appl. Sci.* 4 (2010) 3591-3601.
15. H.Ouasif, S.Yousfi, M.L.Bouamrani, M.El Kouali, S.Benmokhtar, M.Talbi, *J. Mater. Environ. Sci*.4 (2013) 1-10.
16. W.Slawomir, *Pol. J. Chem. Technol.* 17 (2015) 79 - 87.
17. Senol Alpat, Sibel Kilinç Alpat, Bilge Hilal Çadirci, Özge Özbayrak, Ihsan Yasa, *Electron. J. Biotechnol.,*13 (2010) 1-19.
18. P. Muthusamy, S. Murugan, *Int. J. Eng. Res. Appl*. 6 (2016) 05-10.
19. Handojo Djati Utomo, Keng Xuan Donovan Tan, Zhi Yi Danie Choong, Jia Jia Yu, Jie Jun Ong, Zheng Bang Lim, *J. Environ. Prot.,*7 (2016) 1547-1560.
20. N.Gupta , J.K.Shrivastava, A.Shriwastava, A.K.Gupta, *Res. J. Chem. Environ. Sci.,*4 (2016) 58-61.
21. Omran Abdia , Mosstafa Kazemia, *J. Mater. Environ. Sci.* 6 (2015) 1386-1399.

(2018) ; http://www.jmaterenvironsci.com