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The Efficiency of Lead Biosorption from Industrial Wastewater by Micro-alga *Spirulina platensis*

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ABSTRACT: Environment contamination by heavy metals is a major issue threatening human health. Adsorption is one of the biological processes for removing toxic metals from wastewater. The aim of this study was to determine the rate of lead biosorption from industrial wastewater by Spirulina platensis. This laboratory scale experimental study was performed during April 2014 to October 2014 in Environmental Health Engineering Research Center, Kerman University of Medical Sciences. In order to determine lead biosorption by Spirulina platensis, different concentrations of biomass (0.1, 0.5, 1, 1.5 and 2 gr) were exposed to different lead concentrations (10, 50, 70, 100 and 150mg/L) under different conditions including pH (3, 4, 5, 6, 7, 8, 9 and 10) and contact time (5, 15, 30, 60, 120 and 180 min). The rate of residual lead was determined using atomic adsorption instrument. Experiments were also performed in real conditions on battery manufacturing industry wastewater sample. Adsorption isotherms and metal ions kinetic modeling onto the adsorbent were determined based on Langmuir, Freundlich and first and second order kinetic models.Lead adsorption onto Spirulina platensis varied based on the conditions. At constant temperature of 25ºC, optimal pH 7, contact time of 60 minutes and adsorbent concentration of 2g/L, lead adsorption efficiency was 84.32% for real sample and92.13% for synthetic sample. Based on the obtained results, lead adsorption followed Langmuir model and second order kinetic equation. Spirulina platensis, due to its high adsorption potential, can be efficiently used for lead removal from industrial wastewater.

Key words: Heavy metals, Spirulina platensis alga, Wastewater treatment, Battery manufacturing industry, Isotherms

INTRODUCTION

Heavy metals contamination is a serious threat to aqueous environments. These metals, through introducing into food chain, cause serious hazards for human being health(Rezaei, 2013). For example, lead has severe toxic effects on liver and the presence of its ions in Wastewater, even in low concentrations, is hazardous for aqueous and human ecosystems (Ferreira, et al., 2011). Disposal of waste matters containing heavy metals by various industries is the major cause of this problem. Industries related to mining, minerals and metals smelting, energy and fuel production, fertilizers, pesticides, electroplating, electrolysis, electro-osmosis, leather, photography, electric appliances manufacturing, aerospace, atomic energy installations, etc are main sources of heavy metal contaminants (Alluri, et al., 2007). There are different methods for removal of heavy metals from polluted water including reverse osmosis, electrophoresis, ion exchange, chemical precipitation and phytoremediation. Each method has its own advantages and disadvantages affecting its efficiency (Al-Homaidan, et al., 2014, Ahalya, et al., 2003). Among these methods, those with less environmental hazards and cost such as using microbial biomass for heavy metals removal have attained more attention. The rate of heavy metal adsorption by biomasses varies based on the metal binding capacity (Al-Homaidan, et al., 2014). Alga biomasses, due to their availability, easily

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cultivating and cost-effectiveness, are very beneficial in heavy metal removal from wastewater(Bayramog?lu and Ar?ca, 2009) .Nilanjana et al (2008) in a study in India showed that the rate of metal removal differs based on adsorption capacity of the applied biomass (alga, fungi, yeast, bacterium,…)(Nilanjana, et al., 2008). According to Cochrane et al study (2006), biosorbents compared to chemical adsorbents are more cost-effective and have higher adsorption capacity (Cochrane. et al., 2006). Al-Homaidan et al. (2014) have studied the efficiency of Spirulina platensis alga in copper removal from aqueous solution (Al-Homaidan, et al., 2014). Rodrigues et al (2012) in a study in Brazil have compared dry biomass of Chlorella vulgaris and Spirulina platensis in removal of heavy metals (Rodrigues, et al., 2012). Abu Al-Rub, et al. (2006) have studied the efficacy of Chlorella vulgaris in copper ion removal from aqueous solutions (Al-Rub, et al., 2006). Ferreiraa et al. (2011) have studied the efficacy of Chlorella vulgaris in heavy metals removal (Ferreira, et al., 2011). Malakootian, et al. (2012) have applied algae Ulothrix Zonata for removal of heavy metals from industrial effluents (Malakootian, et al., 2012). In the present study the efficacy of micro-algae Spirulina platensis in removal of lead from industrial effluents has been studied.

MATERIAL & METHODS

This laboratory-scale experimental study was performed in Environmental Health Engineering Research Center, Kerman University of Medical Sciences. Algae Spirulina platensis reached to maximum growth in 1L of Zarrouk's medium was purchased from Caspian Sea Ecology Research Center. For more growth, the algae was cultivated in 1L fresh Zarrouk's medium containing 8g NaHCO3, 5g NaCl, 0.2g urea, 2.5g NaNO3, 0.5 g K2SO4, 0.16g MgSO4, 0.05g FeSO4 and 0.052g K2HPO4(Zarrouk, 1966). Then, the medium was kept at 25-30ºC, light intensity of 1500-2000 Lux, 14h light/10h dark cycles and regular air injection.For the separation microalgae from the water, it was centrifuged at 2000 rpm and was dried in the oven at 105oC respectively. Microalgae used as a passive biosorbent. By solving 1.598g Pb(NO3)2(Merck Co., Germany) in 1 L distilled water, 1000ppm lead stock solution was prepared and used for preparing different concentrations of lead solution. In order to prepare solution with required pH for mixing with adsorbent, NaOH and 0.1 N HNO3 were used. All sampling and experiments were performed according to the 20th edition of "Standard Methods for Examination of Water and Wastewater". SPSS18 was used for data analysis.

Adsorption studies: In adsorption studies, the effects of different parameters including pollutant concentration, adsorbent dose, contact time and pH were studied in batch mode. The solution containing pollutant and adsorbent were poured in a 250mL Erlen Mayer Flask and put on shaker at 180rpm in specified intervals. The adsorbent was centrifuged and passed from 0.45µ Whatman filter.

The effect of contact time: In order to determine the effect of contact time on lead adsorbance by biomass, initial dose of lead (50mg/L) was exposed to biomass on shaker and the concentration of residual metal in solution was analyzed for different contact times of 5, 15, 30, 60, 120 and 180 min. while pH and adsorbent concentration were kept constant.

The effect of initial concentration of lead: The effect of initial dose of lead on adsorption by biomass, was determined for different concentration of lead (10, 30, 50, 70, 100 and 150mg/L).While the adsorbent concentration, contact time and pH were kept constant.

The effect of pH: In order to determine the effect of pH on lead adsorbance by biomass, solutions with initial lead concentration of 90ml at pH 3, 4, 5, 6, 7, 8, 9 and 10 were prepared. pH was adjusted using 0.1N nitric acid or NaOH before mixing with adsorbent and determined with pH meter instrument. Equilibrium time, biomass concentration and initial concentration of lead were kept constant during the study.

The effect of biomass dose: The effect of biomass dose on lead adsorption was studied using different concentrations of dry biomass (0.1, 0.5, 1.5, and 2 g dry weight/L). The equilibrium time, pH and initial concentration of lead were kept constant. Before contact, the adsorbent was separated by centrifuging and put in 105ºC oven for one hour to determine the concentration.

Lead ions analysis: After adsorption, solutions were isolated through centrifuging at 1600rpm for 30 minutes. Then, all samples were filtered with 0.45µ Whatman filter for biomass removal. The concentration of residual lead in solutions was analyzed by atomic adsorption spectrophotometer (Youngling AAS8020). Lead concentration was reported as mg/L and the difference between initial and after adsorption doses showed the efficiency of lead removal by Spirulina platensis.

The efficiency of lead removal in real sample: In order to determine the efficiency of lead removal by Spirulina platensis in real conditions, sampling was done from the wastewater balancing tank of Kerman battery manufacturing factory.Then, the quality of sewage in terms of its cations and anions content was determined. Finally, the efficiency of lead removal from real sample exposed to adsorbent was determined in optimal conditions.

Fourier transform infrared spectroscopy (FT-IR):

Infrared imaging spectroscopy of adsorbent was performed through FT-IR prior and after contact with lead in order to identify the functional groups involved in lead adsorption process.

Equilibrium isotherms: For isotherm studies, the solution with initial concentration of 10-150mg/L was exposed to the adsorbent at optimal pH for ion (180 cycle/min, 25ºC) and contact time of 60 minutes. The residual ions in filtered solution were analyzed. The adsorption equilibrium capacity for each sample in terms of mass balance in mentioned ions was calculated by the (1) equation (Rahmati, et al., 2011):

$$q_e = (C_0 - C_e)V/W \qquad (1)$$

where q_e is equilibrium capacity of adsorbed metal by biomass (mg/g), C_0 is initial concentration of metal (mg/L), C_e is metal concentration in equilibrium (mg/L), V is initial volume of metal solution (L) and W is algae cell mass (g).

The efficiency of metal removal is calculated by the (2) formula (Ferreira, et al., 2011):

$$YR = (C_0 - C_e/C_0) \times 100 \qquad (2)$$

Linear Langmuir isotherm is in equation (3) (Mousavi, et al., 2011):

$$C_e/q_e = 1/(q_m k) + (1/q_m)C_e \qquad (3)$$

Where q_e is adsorption capacity of metal ion at equilibrium (mg/g), C_e is metal ion solution equilibrium concentration (mg/L), q_m is adsorption capacity and K is Langmuir constant that is obtained through plotting Ce graph against Ce/qe.

Freundlich adsorption isotherm equation is as follows (Aksu and Do¨nmez, 2006, Nabizadeh and Naddafi, 2005):

$$q_{eq} = K_f C_{eq}^{1/n} \qquad (4)$$

And its linear is the equation (5) (SarI and Tuzen, 2009):

$$\text{Log } q_e = \text{Log}K + 1/n \log C_e \qquad (5)$$

Where C_e is equilibrium concentration (mg/L), q_e is adsorption capacity at equilibrium (mg/g) and n and k are Freundlich constants obtained through plotting logqe graph against log Ce.

Kinetics modeling: Adsorption kinetic was calculated through analyzing pseudo-first-order and pseudo-second- order kinetic models. Pseudo-first-order kinetic equation Eq. (6) is offered as a general (Shokohi et al., 2011):

$$Dq_t/dt = K_1 (q_e - q_t) \qquad (6)$$

The (7) equation can be obtained through calculating the integral of the previous equation:

$$\text{Ln}(1 - q_t/q_e) = -Kt \qquad (7)$$

q_e and q_t are adsorption capacity at equilibrium and time t. K is constant coefficient and through plotting graph of Log (qe-qt) versus t, the amounts of K1 and qe can be obtained. Pseudo-second kinetic is expressed in equation (8):

$$dq_t/dt = k_2 (q_e - q_t)^2 \qquad (8)$$

Through calculating the integral of the previous equation the (9) equation is obtained (CL and XK, 2006, VK and A, 2008):

$$t/q_t = 1/(k_2 q_e^2) = (1/q_e)t \qquad (9)$$

where K2 is the rate constant of pseudo-second order (g/mg per min). T/qe graph against t is a straight line. The amounts of qe and K2 can be obtained from the graph slop and intercept.

RESULTS & DISCUSSION

FT-IR spectrum: The results of Spirulina platensis FT-IR analysis prior and after lead adsorption have been shown in figs 1 and 2.

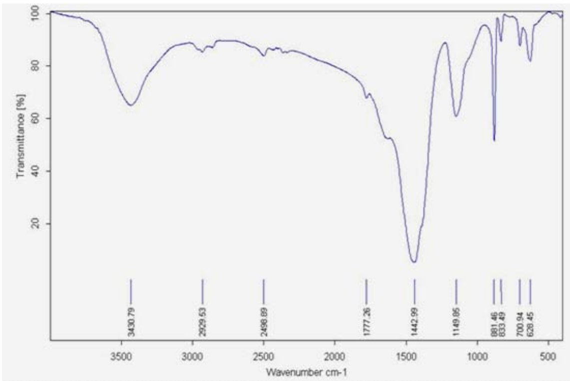

Fig. 1. FTIR spectra of algae spirulina platensis before of adsorbed

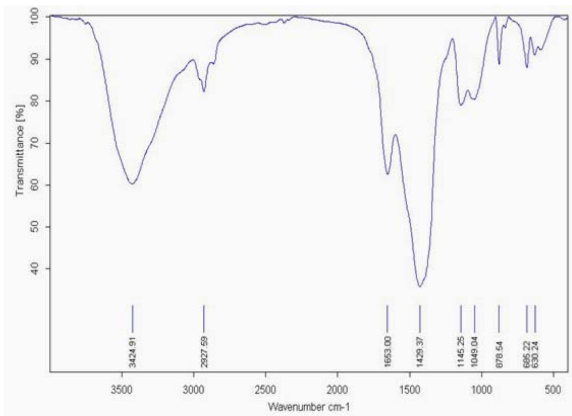

Fig. 2. FTIR spectra of algae spirulina platensis after of adsorbed

The present picks at wave length of 3430 cm-1 show the presence of OH-stretching vibration group which is a type of hydroxyl group. The present picks at wave length of 2984-2780 cm-1 show CH-stretching vibration group. Strong bands at wave lengths of 1651.92 and 1545.25 cm-1 can be attributed to types I and II vibrating amid. In 1455.82 cm-1, COO- group, at wave length of 1820-1660 cm-1 carbonyl group, at pick of 2600-1800 cm-1 C=N and C=O groups, at pick of 1250-1050 cm-1 C-C and C-O groups and at picks lower than 1000 cm-1 phosphate, -PO, O-P-O and C-X groups are active (Pistorius et al., 2009, Ferreira et al., 2011, Gagrai et al., 2013). In the present study, after adsorption the wave length of hydroxyl decreased and that of carboxyl group increased and amid and phosphate groups were created. The presence of these functional groups and their chemical substances content caused electron cloud with negative bar that was of a great importance in adsorbing lead positive ion. The present study and other studies related to adsorption of metal ions by micro-alga Spirulina platensis and other alga in aqueous solutions show that adsorption of lead ions onto adsorbent is mainly dependent on the presence of OH-, COO-, amide, phosphate and amine functional groups (Gagrai et al., 2013, Ferreira et al., 2011).

The effect of contact time on lead absorption: The effect of contact time, removal of metal ions the optimum pH, adsorbent dosage 2gr/L, at 25 ° C and the initial concentration of metal ions 50 mg/Lis shown in Figure 3. In the first 5 minutes, 60% of the metal ions removed with increasing contact time, removal of lead, 64.26 percent increased. Maximum removal of lead exposure time is 60 minutes. In the present study, contact time increase led to increase of adsorption efficiency. This was due to the increase of contact between the adsorbent and metal and caused removal of 60% of metal ions during the first 5 minutes of contact. Maximum adsorption occurred at contact time of 60 minutes and there was no significant change in adsorption after 60 minutes. In Malakootian and Khazaei study, maximum adsorption of cadmium ion onto Fe nano-particle and manganese compounds occurred at contact times of 60 and 10 minutes respectively(Malakootian, M and Khazaei.A, 2014).

The effect of pH on lead adsorption: Effect of pH on Pb uptake capacity by algae Spirulina Platensis, at a concentration of 50 mg/L, 25 ° C, 60 minutes contact time and concentration 2gr/L adsorbents were studied. The effect of pH on the absorption shown in Figure 4 and as it is seen at pH 7 the efficiency of lead removal is optimal. According to the previous studies, pH is one of the important factors in adsorption of metal ions through its direct effect on metal solubility or on the dissociation degree of groups located on the adsorbent surface (Al-Homaidan, et al., 2014). Accordingly, in the present study, lead adsorption by Spirulina platensis occurred as a function of pH. In another study, optimal pH for lead absorbance was 7 in a way that metal adsorption by biomass increased with pH increase from 3 to 7 and decreased with pH increase from 7 to 10 (Aksu and Akpinar, 2001). In alkaline conditions (pH 10) the adsorption efficiency declines. In general, at pH> 6.0-7.0, metal adsorption rate decreases in a great extent (Vannela and Verma, 2006). In this relation, pH increase means lower amount of protons that reduces the competition between proton ion and heavy metals. Elevated pH increases the available ligands for metal ion binding and consequently increases the absorbance efficiency (Al-Homaidan, et al., 2014). At pH<3 , hydrogen ions compete with metal ions for adsorption sites in the same adsorbent and decrease metal ion adsorption; therefore, optimal pH for the absorbance of each metal is approximately in the range of 4-6 in which competition of hydrogen ions reaches to minimum and consequently metal adsorption increases. In spite of different results about the effect of pH on adsorption, it has been seen that pH affects adsorption of metal ions on cell surface and this effect depends on the type of adsorbents (cells) and metal ion (Gholizadeh, et al., 2012).

The effect of lead initial concentration on adsorption: In order to determine maximum capacity of lead adsorption by Spirulina platensis, it is necessary that adsorption equilibrium data were studied in different concentrations of metal. For this purpose, the exposure conditions were initial metal concentrations= 10-150mg/L, optimal pH, contact time= 60 min., temperature= 25ºC and adsorbent concentration =2gr/L. The rate of lead removal was decreased by 42.85% with increase of metal initial concentration from 10 to 150mg/L (fig. 5). In the present study, adsorption decreased with increase of lead initial concentration and any increase of metal ion initial concentration led to increase of the residual ion in solution. It is probable that along with increase of surface load (adsorbed substances) on the adsorbent, upper surface adsorption sites on adsorbent are saturated and the efficiency of removal decreases rapidly (Banat, et al., 2000). Rezaei (2013) has reported that with increase of metal ion initial concentration, adsorption decreases (Rezaei, 2013).

The effect of adsorbent concentration on metal removal: The effect of adsorbent concentration on lead removal was studied under conditions of 50mg/L concentration, temperature = 25ºC, contact time = 60min and optimal pH. As it is seen in fig.6, the rate of lead removal has increased by 36.01% with increase of adsorbent concentration from 0.1 to 2g. In the present study, removal efficiency and adsorption capacity in-

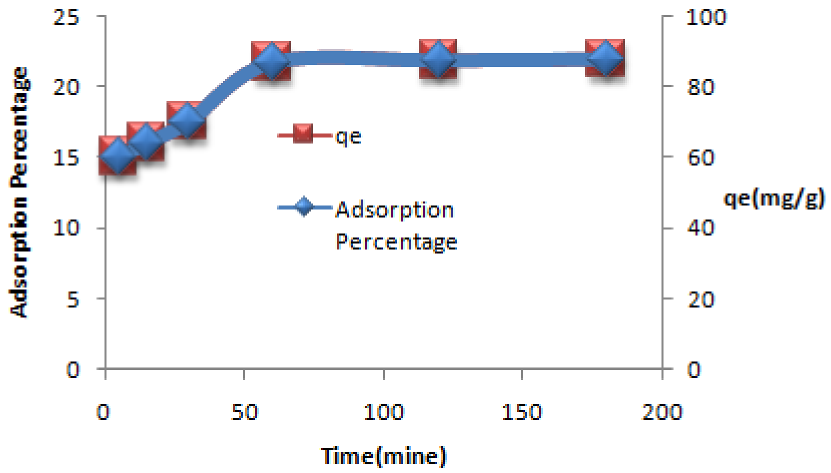

Fig. 3. The effect of contact time on the removal of lead ions in the optimum pH, adsorbent dose, 2gr/L and initial concentration of metal ions 50 mg / L

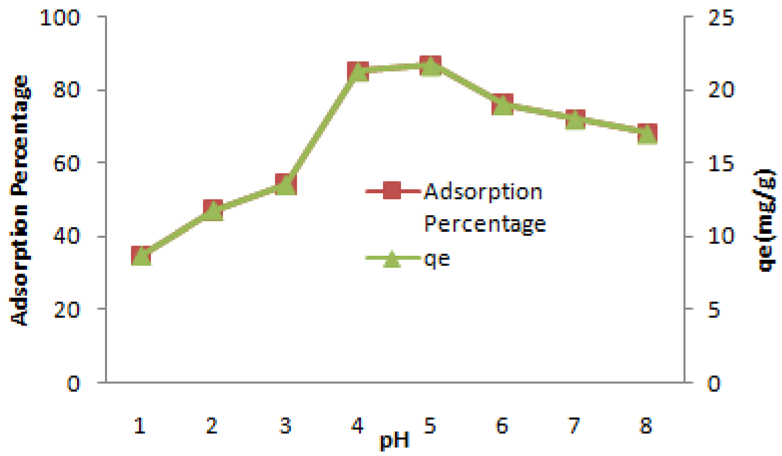

Fig. 4. The effect of pH on the removal of lead ions in the contact time 60 minutes, adsorbent dose, 2 gr / L and initial concentration of metal ions 50 mg / L

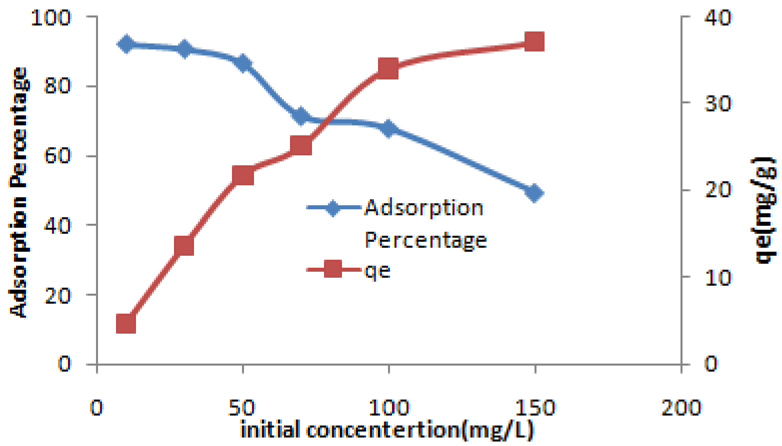

Fig. 5. Effect of initial concentration of metal ions on the adsorbent at 60 minutes contact time, adsorbent dose, 2 gr / L and the optimum pH

creased with increasing adsorbent dose. In adsorbent concentration of 0.1g, the rate of adsorption was very low and equilibrium was obtained faster. In lower doses, adsorption deceases due to less adsorption sites (Mahvi, et al., 2004). Moreover, maximum adsorption occurred at adsorbent dose of 2 g. Similar results have been reported in Rezaei et al study (Rezaei, 2013). In Mahesh Kumar Gagrai et al study in 2013, Chrome ion (VI) removal increased along with increase of Sprulina biomass concentration from 1 to 4g (Gagrai, et al., 2013).

The removal of lead in the real sample: The results of studying the chemical composition of wastewater of Kerman battery making factory in regard to anions and cations have been presented in Table 1. Adsorption percentage of lead in battery factory wastewater Kerman in optimal conditions (pH = 7, 60 minutes contact time and adsorbent dose of 2 g/ L) is the 84.32 percent which is lower than that of synthetic sample. This can be attributed to the competition of metal ions for adsorption sites on the adsorbent (Malakootian and Khazaei, 2014).

Equilibrium and kinetic studies: The results of isotherm studies have been shown in figs 7 and 8 and Table 2 shows isotherm models parameters. As it is seen in figs 10 and 11, lead absorbance by micro-alga Spirulina platensis follows pseudo second order equilibriums. Table 3 shows parameters of kinetic reactions. The obtained equilibrium data of lead adsorption onto Spirulina showed that lead adsorption process follows Langmuir model. The qm obtained from Langmuir model shows sufficient metal ions for monolayer adsorption. In the process of adsorption, of other adsorbents for the removal of lead is used as a sorbent have different absorption capacities in this area, Fig. 9 is a comparison of some of the adsorbent (Romera, et al., 2006, Rincon, et al., 2005).In this model, 1/n indicates the rate of surface adsorption intensity. The value of 1/n=0 shows that the adsorption is irreversible, being between 0-1 is favorable and 1/n>1 is unfavorable. In the present study, this value was less than 1 that shows favorable adsorption (Mesdaghinia. et al., 2013). According to the results, adsorption kinetics intended to follow pseudo second order kinetic equilibrium. K1 and the value of qe were obtained through plotting log (qe-qt) graph versus t and the correlation coefficient (R2) was obtained too (table 3) K2, the value of qe and correlation coefficient were obtained through plotting t/qt graph against t and it has been presented in Table 3

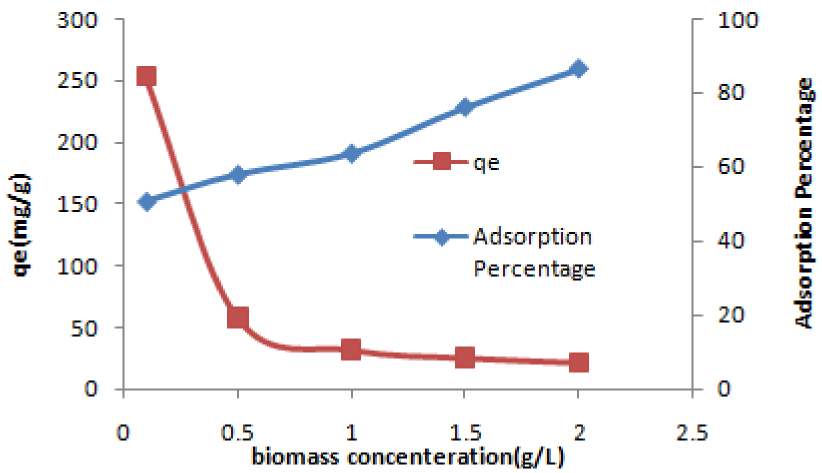

Fig. 6 . Effect on the concentration of the adsorbent to adsorb the contact time of 60 minutes, initial metal concentration 50 mg / L and the optimum pH

Table 1. The chemical composition of wastewater of Kerman battery making factory in regard to anions and cations have been presented

chemical composition wastewater / Type wastewater	Pb^{+2} (mg/L)	Cd^{+2} (mg/L)	Cu^{+2} (mg/L)	Temperature (^{0}C)	pH	BOD (mg/L)	COD (mg/L)	TDS (mg/L)
battery factory	52	20.32	2.8	22	5.5	180	350	1100

(Malakootian, et al., 2012). In a study performed by Malakootian et al., adsorption of heavy metals in aqueous solutions followed second order kinetic equation (Malakootian, et al., 2012).

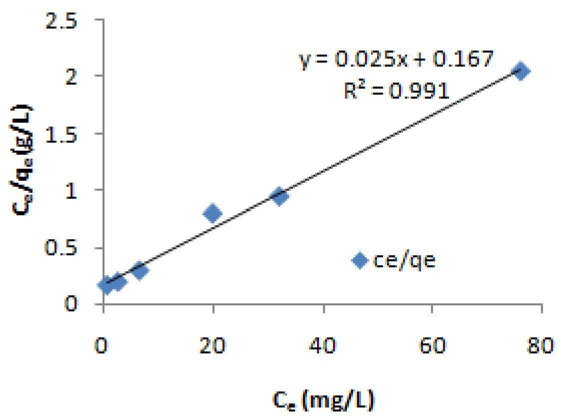

Fig. 7. Langmuir model for efficient removal lead by algae Spirulina platensis

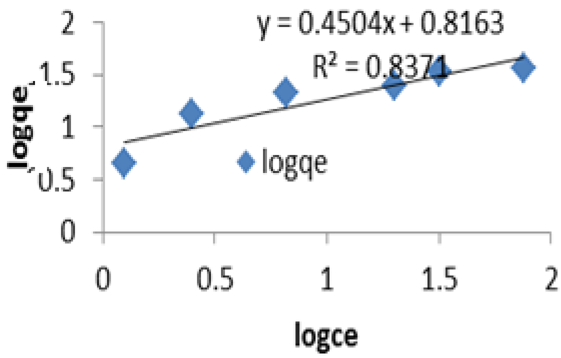

Fig .8. Freundlich model for efficient removal of lead-algae Spirulina platensis

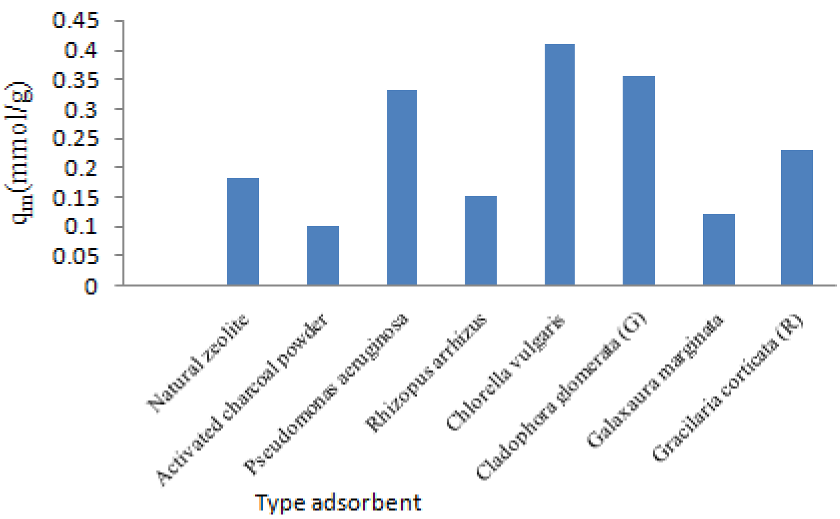

Fig. 9. Comparison of some of the adsorbent to Spirulina platensis

Table 2. Freundlich and Langmuir isotherm constant coefficients and correlation coefficients of adsorption of lead

Freundlich isotherm			Langmuir isotherm		
1/n	k_f (mg1- 1/n L1/n g- 1)	R_2	q_m(mg/g)	k(L/mg)	R2
0.4504	6.55	0.8371	40	0.149	0.9918

Table 3. The correlation coefficients of static and kinetic model pseudo-class and pseudo-second adsorb lead

kinetic model pseudo-class			kinetic model pseudo- second		
k_1(1/hr)	q_e(mg/g)	R^2	k_2(g/mg min)	q_e(mg/g)	R^2
0.12	1.32	0.7068	0.545	22.57	0.9988

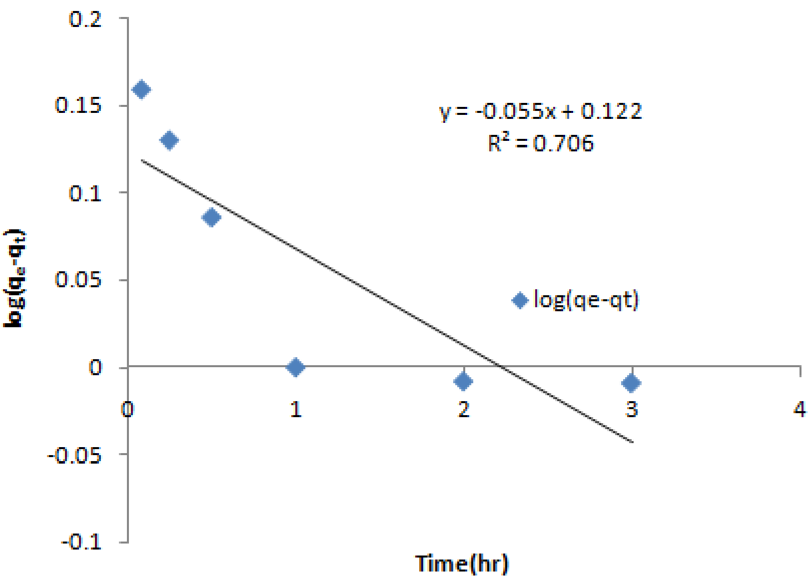

Fig. 10. Reaction kinetic model pseudo-class remove the lead with algae spirulina platensis

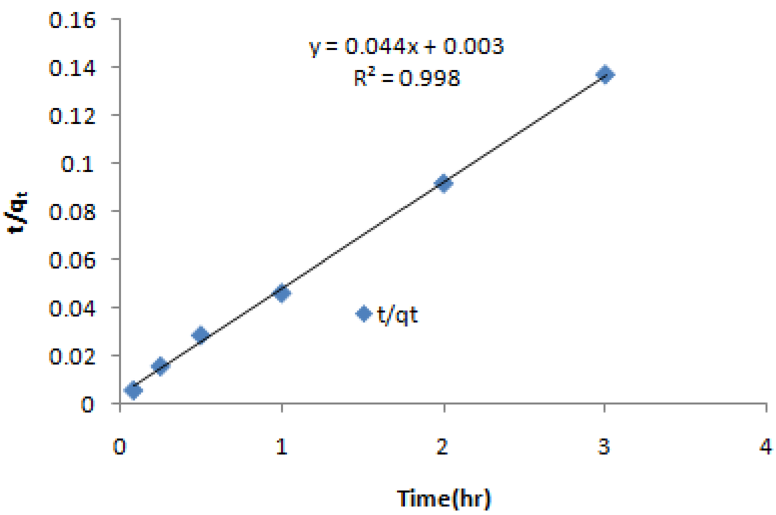

Fig. 11. Reaction kinetic model pseudo- second remove the lead with algae spirulina platensis

CONCLUSION

According to the obtained results, Spirulina platensis algae has desirable efficiency in removing lead from effluents and the adsorption follows Langmuir and second order kinetic equation. In real wastewater sample compared to the synthetic sample, lead removal efficiency is lower due to the competitive effect of metal ions for appropriate sites on the adsorbent.

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