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EVALUATING THE PALM LEAVES EFFICIENCY AS A NATURAL ADSORBENT FOR REMOVING CADMIUM FROM AQUEOUS SOLUTIONS: ISOTHERM ADSORPTION STUDY

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Abstract

Recent years, extensive attention to the accumulative toxicity and heavy metal environmental effect resulted in extensive research for the development of alternative technologies in order to remove this potentially dangerous substance from the effluent and wastewater of industries. In line with this study, the researchers pay attention to the use of biological substances as an economic method. In this research the cadmium removal from aqueous solution have evaluated by using palm leaves. In this experimental study, the palm leaves adsorbent efficiency of cadmium removal in batch reactor has evaluated. The effect of various parameters such as the adsorbent amount, balance time, the adsorbate concentration, and pH on the adsorption rate have evaluated. For studying the isotherm adsorption the Langmuir and Freundlich models have used. The tests results showed that the adsorbent optimum concentration was 2.5gr, the balance time 2h, the adsorption optimum concentration 10mg/l, and the pH was 6 and the highest removal efficiency of the optimum concentration have calculated 99.83%. In addition, the Freundlich and Langmuir models fitness on the adsorption data showed that the Freundlich model describe the tests data better. In general, it could have concluded that according to the high adsorption efficiency the palm leaves could have used effectively for cadmium bio adsorption from aqueous solutions. In addition, the cadmium removal efficiency have increased by the increased of the adsorbent germ and contact time and it have reduced by the increased of initial cadmium concentration.

Keywords: Palm Leaves, Cadmium, Isotherm Adsorption, Natural Adsorbent, Aqueous Solution

Introduction

Todays, because of the chemical industry development and entering of various toxic and dangerous chemical substances to the acceptance resources in nature, the environment pollution becomes an important challenge for the human societies in the world. One of the biggest pollutant source of the environment, which caused by industrial activity and have irreversible effect on human health and natural ecosystem, is heavy metals. (1). The heavy metals, because of their accumulative property in living organisms tissues, high toxicity, resistant against biodegradation, high mobility were considered as a priority pollutants (2).

The amount of input metals into the environment is more than the amount, which removed with natural process. Therefore, the heavy metal accumulation in the environment is considerable. Many of these elements not only is not necessary for animals but also is very toxic. Living organism needs a tiny amount of heavy metals for growth and survival. If the amount of these metals increased to a least and necessary amount, caused an impaired in growth. The heavy metals such as cadmium is not vital and don't have beneficial effect on living organisms life in a way that its health adverse effect such as incidence of various cancers, kidney and lung damage, anemia and high blood pressure have approved in humans (3, 4). Therefore, its entrance into the body through water, air and food caused the incidence of disturbances in natural body activity. Therefore, it have high biological and ecological importance (5). Cadmium have used in various industries such as alloying, electroplating, dyeing, plastics, electrical... (6) And its removal from pollutant resource and environment considered as health priority in society (8). The important methods, which used for removal and separation of heavy metals ions such as cadmium from aqueous solutions, are the membrane process, ion exchange, chemical deposition, evaporation, and adsorption (7, 8, and 9). Todays the researches have done in order to find simple and inexpensive methods for using in polluted wastewater treatment particularly in developing countries, which cannot use expensive methods due to their economic problems. In recent years using the natural adsorbent for removing various type of pollution, organic compound pollution which related to oil, textile, pigment removal industry and also heavy metals removal have presented and good results have observed too (10). Some of the important and main effective factors in surface adsorption process include temperature, particle size, the adsorbent amount, the competing ion presence, the initial metals ion concentration and hydrogen ion concentration and contact time (11, 12). Younesi et al. (2012) evaluated the functionality of the palm leaves ash for lead ions removal. The results showed that the best efficiency for removal was 99.72%, which have calculated in the solution with the concentration of 50mg/l

lead ion, adsorbent dose of 5gr/l and pH of 5 (13). Upendra K, Manas (2006) have done a study about the cadmium adsorption with modified bran rice by chlorohydrin, sodium hydroxide, and sodium bicarbonate. Sodium bicarbonate due to its low costs preparation have suggested as the preferred modified solution (14). According to the necessity of applying efficient and economic method with the environment, this study have done with the aim of evaluating palm efficiency in cadmium removal as a heavy metal and evaluating isotherm adsorption models as an important factor in designing adsorption system for determining an adsorbent capacity and optimized the adsorbent consumption.

Materials and Methods

The chemical and reagents materials:

In this study, all the chemical substances and reagents with the purity of 99.99% have purchased from Merk Company of Germany. The two times distilled water, which required for preparing stock solution have made in laboratory.

Adsorbent preparation

The required palm leaves have prepared from Ahwaz palm trees. The leaves have washed and then dried. For increasing the contact level of leaves with the adsorbate metal, after crushing it have screened with 30 mesh sieve with the pore size of 0.5mm and then for removing dust and other particles it have washed with distilled water and dried by the laboratory's Feb in the 100°c until it reached to a constant weight. The leaves for the subsequent use have stored in the plastic container, which have first washed with distilled water and dried.

Adsorbate preparation

The cadmium stock solution (1000mg/l) has prepared by solving cadmium in two time-distilled water and then the cadmium solution with various concentrations have prepared (10, 30, 60, 90 mg/l).

Adsorption process

In the present study, the effect of pH (3, 6, 9), the adsorbate concentration (10, 30, 60, 90mg/l), adsorbent dose (1, 1.5, 2, 2.5 gr/l) and contact time (0, 2, 4, 4h) through batch adsorption process have tested. In different contact time sampling, the residual cadmium concentration have evaluated.

Regulation of samples pH have done by using 1N acid nitric and sodium hydroxide solution with the pH meter Mil51 model. For mixing and proper contact of adsorbent and cadmium, the orbital mixer with the intensity of 200 rpm and 25°c have used.

For separating the adsorbent particles from aqueous solution, the samples have filtered in different time of reaction with the 0.2µ filter. In this study the cadmium residue in samples have evaluated by atomic adsorption spectroscopy

with the atomic adsorption device, which made in Germany with the 288.8nm wavelength of the standard atomic adsorption condition. The cadmium efficiency removal have evaluated by using the bellow equation:

$$Removal,\% = \frac{(C0 - Cf)}{C0} \times 100 \qquad (1)$$

In this equation, C_0 and C_f were the initial and final cadmium concentration respectively (based on mg/l). All the analysis has done based on the standard method book (15) with three time repeating and the results have presented based on the average.

Adsorption isotherm

Langmuir isotherm

Langmuir isotherm is valid for single-layer surface adsorption. In this model, it have assumed that the surface adsorption energy was constant and the material, which have adsorbed in surface adsorption have no migration (7) and its equation have presented as bellows:

$$\frac{Ce}{qe} = \frac{1}{Kl\ qmax} + \frac{Ce}{qmax} \qquad \textbf{(2)}$$

The main property of Langmuir isotherm with a constant and without dimension number have presented as a separation factor in equation (3) R_L:

$$R_L = \frac{1}{1 + K_L C_0} \qquad \textbf{(3)}$$

Ferundlich isotherm

Freundlich isotherm have used for describing multi-layer adsorption in heterogeneous surface with the interaction between the surface adsorbent molecules. Freundlich model suggested that the surface adsorption energy have reduced exponentially by the increased of surface coverage level (16). This equation has represented as the equation 4 and 5:

$$q_e = KCe^{1/n} \qquad (4)$$

$$Ln\ q_e = LnK_f + \frac{1}{n} LnCe \qquad (5)$$

Results

- **Evaluating the effect of various adsorbent on the adsorption level:** Based on the figure 1, by the increased of adsorbent level from 1 to 2.5 mg/l the adsorption percentage have increased from 68.3% to 79% by the palm leave.

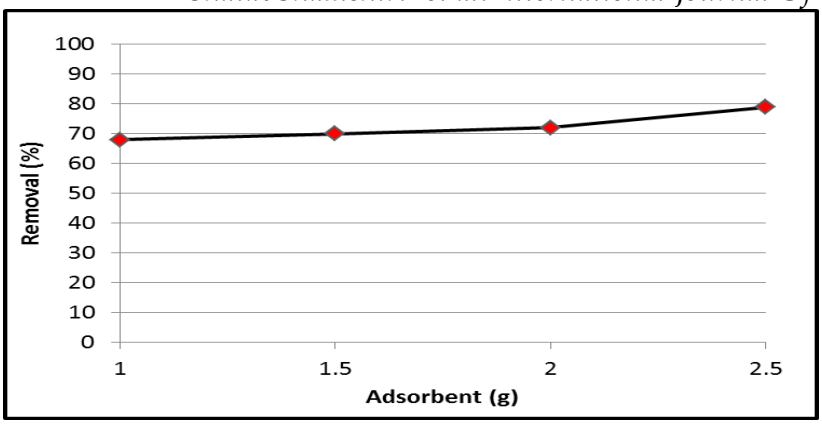

Figure-1. The removal efficiency based on the various adsorbent amounts.

Evaluating the contact time effect on the adsorption level in constant adsorbent and adsorbate concentration

As the figure 2 showed in initial contact time, the adsorption rate is high but after 2 hours the cadmium adsorption level have reduced and it is possible that the desorption phenomenon have occurred after 2 hours.

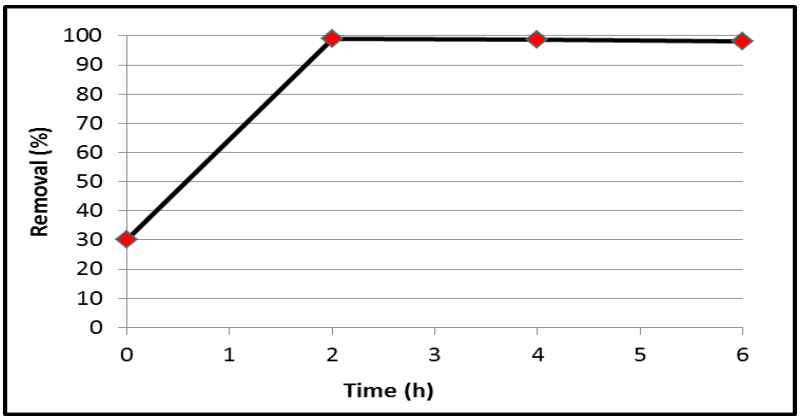

Figure-2. The removal efficiency in various time of initial concentration (30mg/l).

Evaluating the effect of various adsorbate concentrations on adsorption level

The results showed that the cadmium ion adsorption percentage have reduced by the increased of initial ion concentration and the removal percent have reduced from 84.92% to 55.64% (figure3).

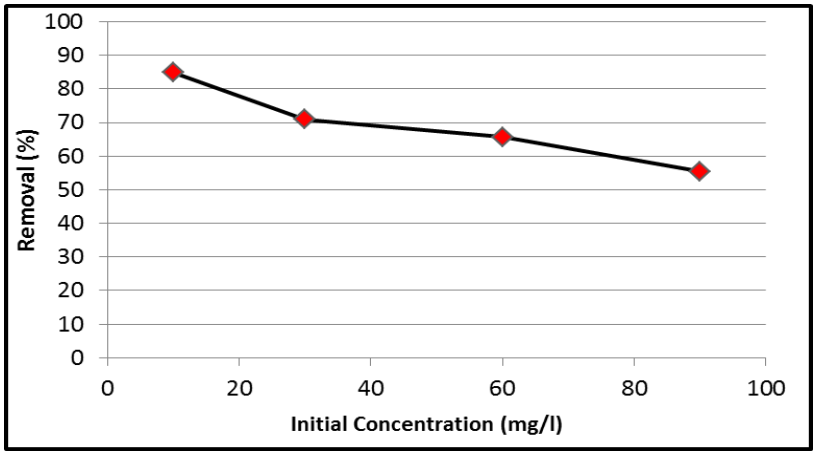

Figure-3. Removal efficiency in various cadmium concentration (the optimum adsorbent amount of 2.5 gr and balance time of 2hours).

Evaluating the effect of pH on the adsorption level

The results showed that by the increased of solutions pH, the cadmium adsorption percentage have increased too and in fact reach its maximum level pH=60 (figure4).

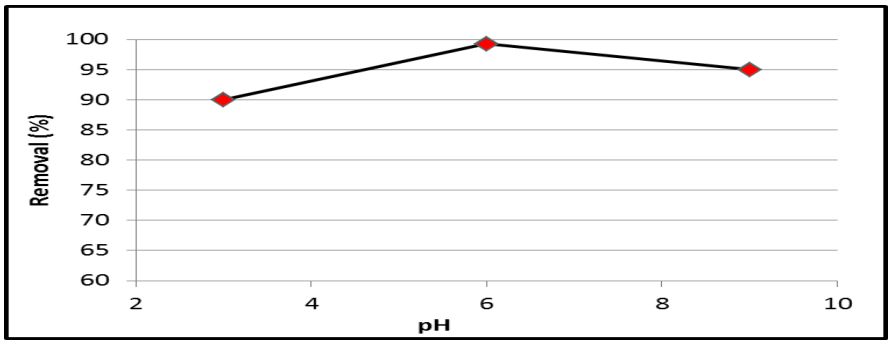

Figure-4. The removal efficiency changes based on the pH (the optimum adsorbent level 2.5 gr and balance time of 2h and optimum adsorbate concentration of 10mg/l).

Evaluating isotherm adsorption

Based on the reported results in table1 the R_l level in Langmuir model is in the range of 0-1, which showed that the adsorption process is desirable on the adsorbent.

The n amount in the Freundlich isotherm of 1-10 represent that the adsorption process is desirable. The results of isotherm model constant have presented in table1. Evaluation of linear isotherm and R^2correlation coefficient figures showed a good adaption of experimental results with Freundlich adsorption model in comparison with Langmuir model.

Table-1: Constant of synthetic cadmium adsorption model by adsorbent.

Langmuir adsorption isotherm	Freundlich adsorption isotherm
q_{max}= 0.027 mg/g	n=1.79 g/lit
K_L=0.067 l/mg	K_f = 0.0027mg/g
R^2 = 0.9544	R^2 = 0.9937
R_L=0.599	-

Discussion

Based on the results it have revealed that the palm could have used as an effective adsorbent for removing cadmium from aqueous solutions. According to the obtained results in this research it have revealed that the increase of the adsorbent amount from 1 to 205gr/l caused the increased of removal efficiency from 68-79%. It was obvious that reaching this high efficiency without changing or providing a particular environmental condition and lack of

environmental adverse effect is very desirable. As the results showed, there was a significant relation between adsorbent concentration and removal efficiency in a way that by increasing the adsorbent dose, the efficiency has increased. Garg et al. (2008) in a study which have done about cadmium removal by biomass of agricultural waste in the concentration of 2.5, 5, 10, 15, 20 showed that the metal adsorption have increased by the increased of the adsorbent concentration (17). It should have noted that by the increased of the adsorbent dose, the possibility of adsorbent encounter with metal cation has increased and the pollutants adsorption has increased too, because by the increased of the adsorbent dosage the exchange sites and the adsorbent particular surface have increased. Ding et al. (2012) in a study, which have done about cadmium bio adsorption by unmodified straw rice showed that by the increase of the adsorbent germ the cadmium removal efficiency have increased (18) which is consistent with the results of this study. Also Atar et al. (2012) in a study about cadmium adsorption by the waste of Bohr enrichment process reach the same results as this study (19). One of the effective factors for the adsorption process of pH is the aqueous environment. Because by changing the environments pH, the ion form of the metal is change too. In addition, the pH changes caused the pollutants ionization and the surface adsorbent load, which these changes have; affected the reactions between adsorbent and adsorbate substances (20). Therefore, for the palm it has observed that the adsorption efficiency in acidic pH is proper and the maximum removal have occurred in the pH of 6. In the acidic pH, the H_3O^+ ion amount is competed with the metal ions for the adsorption on the adsorbent in a way that in the pH of more than 6 the metal ions have precipitated and the metal ion separation from the solutions prevented its removal by the adsorbent. The result of this research is in contrast with the Gupta et al. (2008) study (21). Elouear et al. (2008) in their study estimated the pH=6 as the optimum level for cadmium removal by the olive waste ash (22). While in a study which have done by Kumar et al. (2008) about three type of modified padding rice for removing cadmium, they reported the pH=9 as the best for the three adsorbent. In this situation the highest level of removal by the modified adsorbate with bicarbonate have estimated 97% (23). The contact time and initial concentration of pollutants are among the evaluated parameters in this study, which have interfered in the adsorption process. The increased of cadmium initial concentration from 10-90 mg/l caused the reduction of removal efficiency from 84.92% to 55.4%.the removal efficiency reduction in the high concentrations is related to the saturation of the active adsorption sites on the adsorbent surface by the pollutants. By the reduction of cadmium initial concentration the amount of metal ions in solutions have reduced. Therefore high percentage of ions have adsorbed to the adsorbent. In low concentration of cadmium the particular surface and adsorbent exchange sites was higher and the cadmium ions interact with the

adsorption situation of the adsorbent surface. Therefore, the adsorption efficiency is more. By the increased of the initial concentration, the adsorbent to solution ratio is constant due to the exchange sites saturation with the adsorbent metal in high concentration, so by the increased of the adsorption weight its efficiency have reduced. This is because of the fact that at first the exchange sites is more and caused the increased of cadmium adsorption and by reducing the exchange site of adsorbent the adsorption efficiency have reduced. Also the results showed the increased of cadmium removal efficiency by the increased of time which is because of the fact that by increasing the time the cadmium ion have more chance for contact to the adsorbent surface. First by passing time the adsorption level have increased but after some time the adsorption level have not a noticeable change, which showed that the reaction reached the balance and after that the removal efficiency reduced. According to the presented results in table1, the more cadmium adsorption process is consistent with Langmuir and freundlich model. In a study, which has done by Min et al. (2004) on the sawdust of juniper for removing cadmium from aqueous solutions, they declared the consistency of the Langmuir model with cadmium surface adsorption (24). Mohan et al. (2006) in a study, which have done on the cadmium adsorption by the activated carbon, which derived from bagass concluded that the adsorption data have more consistency with the Freundlich isotherm and is consistent with the results of this study (25). According to the results of batch test, the Freundlich and Langmuir model described the laboratory data and Freundlich model is more consistent. The estimated q_{max} amount from Langmuir model showed the required ion metal for forming the single-layer, which this amount is low and showed that a low amount of this metal is need for formation of single-layer. The n and k_f parameters in Freundlich model and k_1 in Langmuir model showed the adsorption energy, which its amount in Langmuir model is more than Freundlich model. In Das et al. (2013) study, which have done about cadmium removal by synthetic zeolite with volatile ash, and Asman et al. study about cadmium removal by refined old newspaper the adsorption data is consistent with both Langmuir and Freundlich isotherm (26). This fact showed that the adsorption on the heterogeneous sites have occurred on the adsorbent. Therefore, in this evaluation palm as a natural, abundant and inexpensive adsorbent have high adsorption capability for cadmium heavy metal removal from synthetic effluent.

Conclusion

Based on the results of this study it could have concluded that the palm is a good adsorbent for cadmium removal from aqueous solutions even in high concentrations. Based on the results of the present study the cadmium removal efficiency have increased by the increased of the adsorbent germ and contact time and reduced by the increased of the

cadmium initial concentration. According to the frequency of palm forest in the west and south of the country the palm could have used as an inexpensive adsorbent in treatment of wastewater which contain cadmium. However, the performance of this adsorbent in real wastewater is different with the synthetic wastewater and depend on the ions of sewage and other metals interfere. The strength point of this research include the use of inexpensive adsorbent, evaluating cadmium as an important and abundant metal pollutant in the environment specially in Ahwaz metropolis (the Khuzestan steel industry's sewage) in addition to evaluation of the palm, Gold as an inorganic adsorbent after the adsorption process is not a threat for the environment and is abundant in Iran and consider as the strength point of the project.

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