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RESEARCH ARTICLE

Introduction of Red Soil (Ocher) of Hormoz Island as a Natural Adsorbent to Removal of Cadmium from Aqueous Solutions

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Abstract

Due to teem and low cost ocher red soil in Hormoz Island (south of Iran), this study was conducted to investigate the efficiency of red soil on adsorption of cadmium from aqueous solutions. a series of steps for adsorption of cadmium on ocher were conducted which included the ocher selection/preparation, determination of chemical and physical characteristics of adsorbent, preparation of cadmium stokes, determine the equilibrium time, the effect of cadmium concentration, adsorbent dose, the effect of environmental factors (pH and temperature), and determine the adsorption kinetic and isotherm. raw ocher had better adsorption efficiency than processed type (74.33% vs. 35%), the main component of adsorbent was Fe_2O_3 (59.58%). The optimum conditions as dose, pH and temperature which respectively were as (20 g/L; 10; and 35 ^oC), the adsorption reach to 96%. The study of isotherm and kinetics showed that Cd adsorption on raw Ocher is more fitted to Freundlich isotherm and pseudo second order models. natural ocher of the island of Hormoz would be appropriate to remove the heavy metal, as no need to processing it is economical to use. As temperature has positive effect on Cd adsorption on ocher, this adsorbent can act more effective in hot climate.

Keywords: *Cadmium, Red soil, ocher, adsorption, Hormoz Island, aqueous solutions*

Introduction

Today, due to extensive use of cadmium in the industry for plating, dyeing, plastic processing and metal alloys, ceramics and cadmium batteries, and so on, there has been an increasing concern related to environment by cadmium contamination (1-4). If they enter the environment through industrial effluents, their accumulation in the environment, may create threat to human health.

Cadmium, as a toxic heavy metals, due to its solubility, mobility and biological accumulation (5, 6), from the past have been raised as a health and environmental concern, so in cases of long-term exposure, it could lead to bone and kidney damage (7, 8).

Due to health and environmental problems associated with heavy metals, several methods have been used for their treatment, including: chemical precipitation, ion exchange, adsorption, evaporation, membrane filtration, coagulation and flocculation, flotation, and electrochemical treatment (9-11). Nevertheless, the method has limitations such as these are always very costly or in low concentrations heavy metals (less than 1 mg per liter) are not effective (12, 13).

Among the mentioned methods, adsorption is considered as an effective process to remove heavy metals. Conventional methods to heavy metals removal from aquatic environments Including adsorption, chemical precipitation, coagulation, membrane separation and ion exchange that they often need the high cost or create environmental problems (14).

According to the above, adsorption has higher priority among mentioned methods.

The mechanisms involved in the absorption are including of: complex creating between the adsorbent and adsorbate, ion exchange, chelating, production the micron size sediments, and oxidation-reduction reactions.

In the adsorption process, the most influential factor, is type of adsorbent. Absorbents important characteristics for the application include: capacity, selectivity, reproducibility, kinetics, compatibility and cost (15).

Several adsorbent used for the adsorption process, including inorganic adsorbents, organic and bio-absorbents. Activated carbon is the most commonly used adsorbent, but because of its high cost and decrease rate about 15-10% over the regeneration, low-cost alternatives are considered. Low cost absorbents in compared to commercial activated carbon have good capacity for adsorption of metal ions, for this reason, it has attracted the attention of some investigators.

Thus several studies have been conducted in the field on adsorption of cadmium on an type of soil like sand, coarse silt, fine silt and clay) (16), clay (17, 18), biochar (5, 19), natural Phosphate (20), oyster shell (21), kaolinite (22), and mixtures of soil components (23). Hematite is one of the mineral adsorbent; Hematite (in the mine) with a purity of 40% to 50% and a dark red color is one of the major elements that have the necessary characteristics for an adsorbent. One of the most famous and oldest ocher mine in the world is located on the island of Hormoz in the Persian Gulf Iran that from a long time ago it has been exported to the most parts of the world. It is known and consumed in the world especially in Middle East due to Fe_2O_3 grade and its color coating in surface unit, its unique chemical structure as well. The consumption of this mineral matter is in color and glaze production, plastic production, coloring the concrete and building materials, ceramic, paper milling, cosmetics, fertilizers and glass production.

The main consumption of red soil in color production is to prepare and produce rustproof; in the present study, a new consumption for ocher of the Hormoz Island as a natural adsorbent for the adsorption of cadmium was conducted.

Materials and Methods

The site of study was Hormoz Island at the Strait of Hormoz, which is located in the entrance to the Persian Gulf and Oman Sea at 56^{o} 25´ 10˝ to 56^{o} 30´ 08˝ east longitude and 27^{o} 02´ 07˝ to 27^{o} 06´ 25˝ north latitude. Hormoz Island soil due to the high concentration of iron compounds, has a red color. Ocher from the pit of the island were prepared and screened (Fig.1).

Fig 1: Location of Hormoz Island in Iran and picture of soil color

In the present study, a series of steps for adsorption of cadmium on ocher were conducted which included the ocher selection/preparation, determination of chemical and physical characteristics of adsorbent, preparation of cadmium stokes, determine the equilibrium time, the effect of cadmium concentration and adsorbent dose, the effect of environmental factors (pH and temperature), determine the adsorption kinetic and isotherm.

To selection of the best kind of ocher, two type of raw and processed ocher were pretested for adsorption of Cd, then based on the results of pretest, the adsorbent was selected. The process the soil, ocher at first was activated by acid treating (HCl), so; 25 g dry weight of red soil was poured to 1-liter baker containing 50 ml distilled water was poured and then gradually values of 0.5, 1.0, 1.5, 2.0, 4.0, 6.0 and 8.0 ml of HCl (Merck, Germany) was added and the suspension was stirred for 30 minutes.

Then the suspension was rinsed with 100 ml of twice distilled water to acid and soluble substances were removed. After that, the red soil solution was filtered remove the water using Whatman No 1. The cake was dried overnight at a temperature 105° C, after drying of the soil and to re-powdering, it stored until use in experiments in desiccating.

This processed soil was compared to raw soil too. The chemical composition of natural ocher adsorbent was analyzed by X–ray fluorescence (XRF) and loss on ignition (LOI) using XRF Model of XRert and to determine the physical characteristics the analysis of BET-N_2 adsorption was conducted.

Adsorption parameters including determining of optimum (contact time, adsorbent dose, pH and temperature of solution) and the effect of Cd dose, and the isotherm and kinetic of adsorption were carried out by a batch reactor. Cd stoke solution was prepared using distilled water and sodium nitrate, cadmium (Cd $(NO_3)_2$) in concentrations of 3, 5 and 10 mg/L. initial pH were set in values of 3, 4.5,5, 6, 7, 8 and 10 using of 0.1 M sodium hydroxide and hydrochloric acid 0.1 M (Merck).

In order to define the equilibrium time of adsorption, 5 gr of ocher was added to 250 mL solution containing 3 PPM of cadmium. Initial pH adjusted at 7 and samples were taken after (30, 60, 120, 180, 240 and 360 min) contact time, after that, the residual concentration of cadmium in the samples was measured using atomic absorption spectrophotometry model of Thermo, Solar.

To determine the effect of the dosage of red soil on cadmium adsorption process, different doses of 0.1, 0.3, 0.5, 1, and 5 g) of soil, were added to the baker containing 25 ml of water containing 3 mg/L of Cd. The samples were placed in a shaker for 4 hours, were centrifuged and then were measured by atomic absorption spectrometry.

Three concentrations of 3, 5 and 10 mg/L of Cd were prepared and tested to finding the effect of initial Cd concentration on adsorption efficiency. To determine the effect of pH on the red soil adsorbent efficiency, 0.5 gr of adsorbent was added to a baker containing 25 ml of water (3 ppm cadmium).

At first the pH of the samples (containing 3 ppm cadmium) were set at (3, 4, 5, 6, 7, 8 and 10), so they were placed in a shaker for equilibrium time and then centrifuged and finally were measured by atomic absorption spectrometry. The effect of temperature on adsorption was evaluated by addition of 0.5 gr ocher adsorbent to 25 ml of water containing 3 ppm cadmium. The solution temperature was set at 15, 25, 35°C using shaking incubator device model of TS606-G / 2-VAR for equilibrium contact time and then the samples were centrifuged and Cd concentration was measured by atomic absorption spectrometry.

The isotherm of Cd adsorption on ocher was described using Freundlich and Langmuir models; and the adsorption kinetics was analyzed by the most common models (pseudo-first and second order) kinetics models were used. Statistical Data analysis was done using one-way ANOVA test and LSD post hoc analysis using SPSS version 20 for Windows.

Results and Discussion

Retest results showed that raw ocher has better efficiency in removal of Cd than the processed soil; the Cd adsorption percentage were 77.49 and 28.91 percent respectively for raw and processed adsorbents. T-test statistical analysis confirmed the significant difference between two mean of values for two types of adsorbents efficiency ($p<0.000$).

The results of BET analysis is presented in Table.1 that shows the physical properties of the ocher-adsorbent and in table. 2 the absorbent soil constituents are presented. According to table 1, the some of the physical of raw and processed ocher are different; so particle size in processed is finer than the raw soil and units of pore volume and surface area values are higher in the processed kind.

Table 1: physical properties of the raw and processed ocher-adsorbent

Parameter	Unit	Value	
		Raw ocher	Processed ocher
density	g/Cm³	5.12	5.44
Particle size	µm	85-115	67-93
Micro-pore volume	m³/g	0.006	0.011
BET Surface Area	m²/g	5.27	8.06
Solubility @(20°C)	%	63	27

Table 2: XRF results for constituents of the raw ocher-adsorbent

composition	% weight	composition	% weight
Fe_2O_3	59.58	MgO	0.91
SiO_2	9.74	ZrO_2	0.01
Na_2O	1.01	MnO_3	0.02
$CaCO_3$	5.25	ZnO	0.06
K_2O	0.81	CuO	0.09
Al_2O_3	6.23	CaO	11.09
CO_2	2.73	TiO_2	1.33
Na_2O	1.14	LOI	43.24

As it is clear from the tables, the adsorbent physical characteristics are less than conventional adsorbents namely activated carbon, while due to presence of ferric oxide, it has good chemical specific for an effective adsorbent. The results of the tests to determine the equilibrium time is provided in Figure 1.

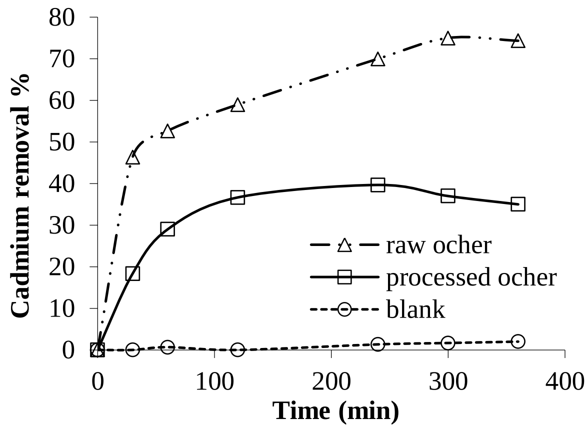


Fig 2: comparison of raw and processed ocher in adsorption of Cd and determining the equilibrium time (pH = 7, C_0 = 3 mg/L, ocher dose = 5 g/L)

Based on presented results in fig.2, the raw ocher had the better efficiency in Cd adsorption; so after the equilibrium time, the removal percent of Cd were as 74.33 and 35 percent for raw and processed ocher respectively.

The effect of the raw ocher dose is shown in Figure 3. As it can be seen from the figure, by increasing of adsorbent dose, the removal of cadmium is increased; while in dose of 1g/50cc, the removal rate is about 92 percent while when the dose increases to 5 time, just less than 4.5 percent adsorption increase has been shown; so the dose of 1g/50 cc which is equal to (20g/L) has been defined as the optimum raw ocher dose.

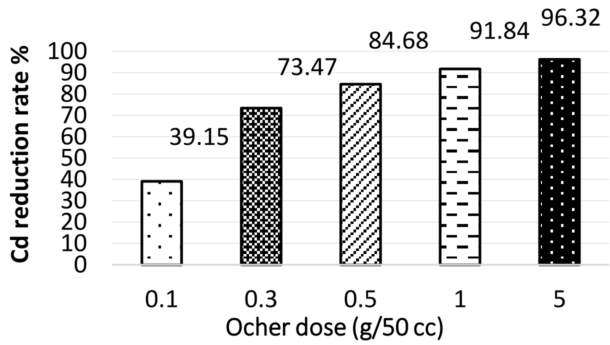


Fig 3: the effect of Ocher dose on removal of Cd during the adsorption (pH = 7, C_0 =3 mg/L, t = 240 min)

The effect of initial concentration of cadmium has been shown in fig.4, and to present the effect of pH and temperature of solution of cadmium removal efficiency, fig.5 is prepared so as A and B are for pH and temperature respectively

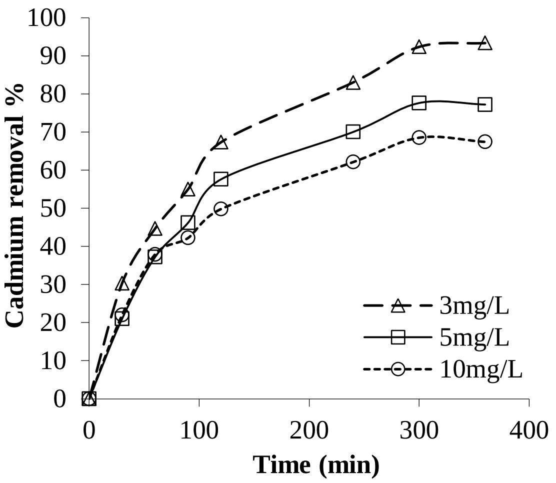
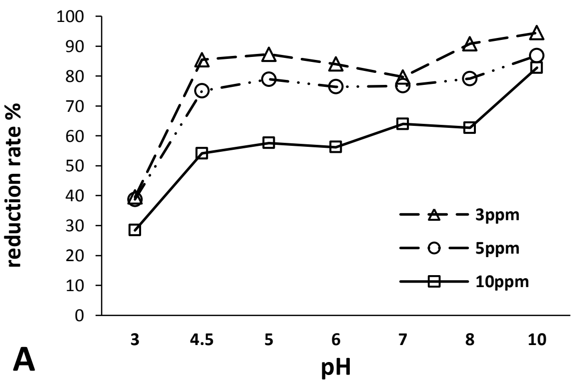


Fig 4: The effect of initial concentration of cadmium on efficiency of raw Ocher to removal of cadmium

By increasing the concentration of Cd, the adsorption efficiency showed a reduction trend, so Cd removal percent in concentration of 3mg/L and 10 mg/L were 93.3 and 67.4 percent.



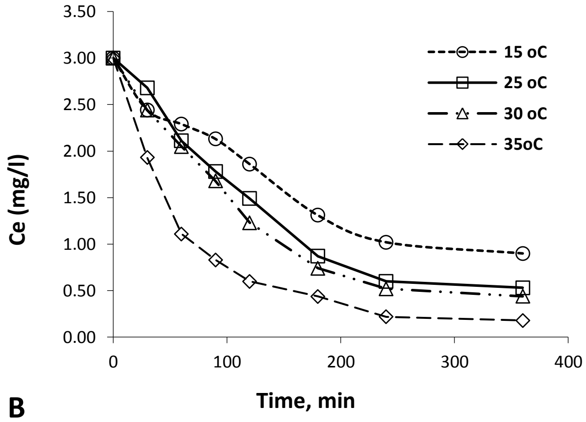


Fig 5: The effect of solution pH (A) and temperature (B) on efficiency of raw Ocher to removal of cadmium

In the pH of 3, reduction rate of Cd was between 30-40 % for Cd concentration of 3 and 10mg/L respectively, while for mentioned concentrations, the removal percent of Cd were between 80-90% in pH of 10, it presents that the removal rate of adsorption is low in acidic pH, so the optimum pH was selected as 10. In the warmer solutions, adsorption efficiency showed an increasing trend; (63% adsorption in temperature of 15°C and 93.5% in 35°C).

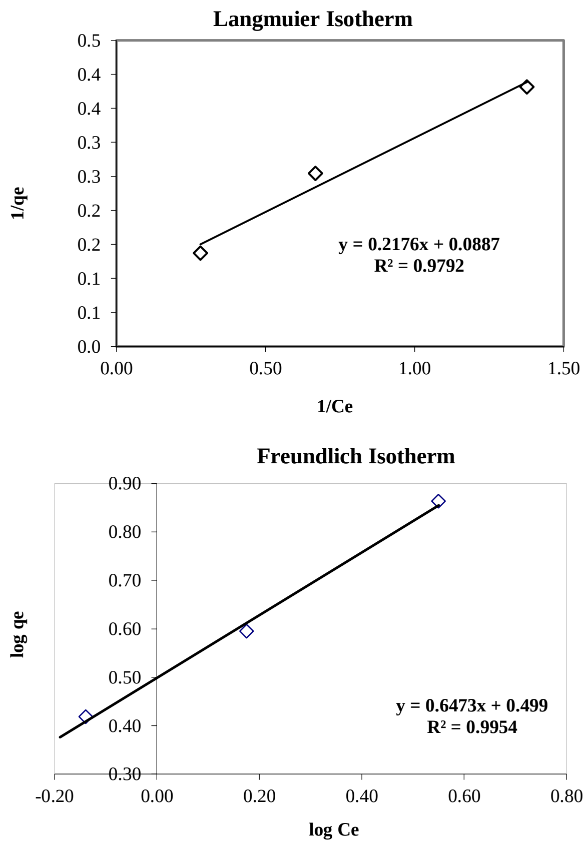
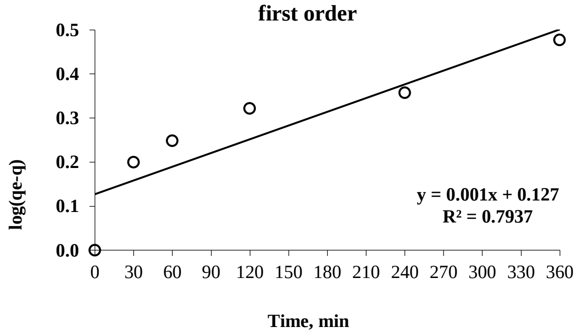


Fig 6: The studied isotherms for cadmium adsorption on raw Ocher



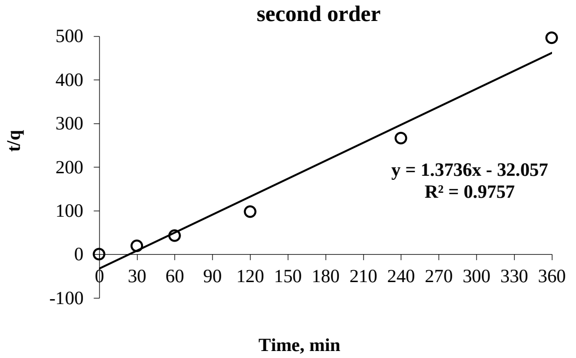


Fig 7: The studied kinetic for cadmium adsorption on raw Ocher

The study of isotherm and kinetics showed that Cd adsorption on raw Ocher is more fitted to Freundlich isotherm and pseudo second order models; fig6 and 7 and tables of 3 and 4.

Table 3: linear formula and R^2 for pseudo first and second order kinetic models

C_0	Pseudo first order		Pseudo second order	
	Line equation	R^2	Line equation	R^2
3	y = 0.001x + 0.127	0.7937	y = 1.3736x - 32.057	0.9757
5	y = -6E-06x2 + 0.0032x + 0.1983	0.6582	y = 0.6553x - 9.9645	0.9835
10	y = -1E-05x2 + 0.0053x + 0.2822	0.5912	y = 0.2786x - 3.7429	0.989

Table 4: linear formula and R^2 for pseudo first and second order kinetic models

Freundlich isotherm			Langmuier isotherm		
n	Kf	R2	a	b	R2
-	(mg Cd/g Ocher) (L water/mg Cd)1/n	-	mmol/g	Dm3/ mmol	
0.016	0.013	0.99	4.59	0.1	0.97

Despite increase cadmium removal per adsorbents dose, a reduction in adsorption capacity was observed that this could be the use of available surface in the form of unsaturated attributed absorbent. Ionic bonding between the adsorbent and Cd is one of the main reasons for good adsorption.

The correlation coefficient (R^2) for the pseudo-first-order adsorption kinetics for Cd concentrations of 3, 5 and 10 mg/L were 0.59, 0.65, and 0.79 respectively and for pseudo-second order in the same Cd concentrations were as 0.98, 0.98 and 0.97, respectively. So it found a good correlation coefficient between cadmium adsorption kinetics and pseudo second model on studied adsorbent red soil. For increasing the Cd concentration from 3 to 10 mg/L, 11.5 percent reduction was observed in its adsorption efficiency. The reason for this is that by increase the Cd concentration, more ionized molecules will have adsorbed on the adsorbent surface.

With increasing concentrations of cadmium, the driving force for mass transfer and therefore the transmission velocity of Cd molecules from solution to the liquid layer surrounding absorbent and finally to the surface of the particles adsorbents increases.

Efficiency reduction caused by increasing of Cd concentrations, may be due to reduction of active surfaces with a positive charge on the absorbent surface; because in high concentrations of Cd to there are lesser available active bands for contaminants, so the mass transfer rate in this concentration is reduced. Active sites of adsorbent will have saturated at high concentrations of contaminant ions. pH effects on the ionization degree and the allocation of various pollutants that lead to changes in the kinetics and equilibrium characteristics of the absorption process. Evaluation of the effect of initial pH solution showed that the maximum removal rates was observed in pH of 10 for all Initial Cd concentrations. Cd removal rate increased with increasing temperature, so increasing the temperature from 25 degrees to 35 degrees, leading to improve the cadmium adsorption about 10%.

An increase in temperature increases the volume of the absorbent structure and provide conditions for greater penetration of cadmium. In addition, increase in temperature causing more molecular diffusion of cadmium in the boundary layer of external and internal pore that lead to more adsorption. According to the results, it seems that the natural ocher of Hormoz Island would be appropriate for the removal of cadmium and because it requires little preparation, so the use of this adsorbent is affordable.

Even in cases of the cadmium concentration to 10 ppm, according to the studied conditions, the ocher can easily reduce it up to 65 percent. The optimal parameters for cadmium removal by ocher were including: contact time 240 (min), adsorbent dose of 0.5 (g/L), pH equal to 8, and temperature of 35 °C.

Conclusion

This study was conducted to investigate the efficiency of red soil on adsorption of cadmium from aqueous solutions. According to the results, natural ocher of the island of Hormoz would be appropriate to remove the heavy metal, as no need to processing it is economical to use. The ability of the sorbent to remove heavy metals from industrial wastewaters can be used. The concentrations up to 10 ppm of cadmium can be the adsorbed by ocher easily, by addition a low cost alkaline agent such as lime, it can be improve the adsorption condition. As temperature has positive effect on Cd adsorption on ocher, this adsorbent can act more effective in hot climate.

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