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Biological adsorption of chromium from aqueous solutions using crude meal canola for repeated use as irrigation water for agricultural land

Roya Moradi* and Pegah Dadras Mostafa Khezri
Department of Environmental and Energy,
Azad University, Since and Research Branch (MS) IRAN

(Corresponding author: Roya Moradi)
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ABSTRACT: Bio adsorption, a relatively new process has the ability and potential in the field of removal of pollutants in aquatic environments has been shown in various studies It is highly important to eliminate chromium 6(VI) which is a poisonous metal and potentially harmful for human beings. Considering different physical and chemical methods to eliminate it, adsorption is one of most effective and most prevalent methods in aqueous solutions. Moreover taking advantages of cost-effective bio adsorbents to improve and develop bio adsorption process is so much recommended. Following immerging modern industries, heavy metals are extracted and used as components more than a century. Waste water of Chromium plating industry is one of the most important sources of these heavy metals and leads into its diffusion. Today, bio adsorbents are being studied to resolve this issue. Effective parameters such as pH, contact time of bio adsorbent and initial concentration of metal are consistent variables and final concentration of chromium is considered as inconsistent variable. Findings of this study show that the best bio adsorbing efficiency of crude canola meal is gained at pH equal to 7 the optimized amount is 0/150gr/lit, optimized time is 60 minutes and the maximum bio adsorption occurs at 12/5 mg/lit concentration of the concentration of pollutants in the 98/4 percent.. Based on Frundlich model the Chromium bio adsorption isotherm of crude canola meal as an bio adsorbent regarding to (n) is equal to 2/85 and to k is equal to 167/49 in aqueous solutions and this is where based on Langmuir model the Chromium bio adsorption isotherm of modified canola meal regarding to q is equal to 666/66 and to b is equal to 476/19. With the high values of R2 the bio adsorbent follows and is compatible with the both adsorption isotherm Langmuir and Freundlich adsorption isotherm models.

Keywords: Canola meal, Adsorption, Atomic Absorption, Langmuir, Heavy metals.

INTRUDUCTION

Approximately 60 percent of world water consumption is in agriculture sector mainly on irrigation. 23 percent is consumed by manufacturing sector and not more than 8 percent is consumed by domestic sector. Manufacturing industries and agriculture are demanding main proportion of water and are playing the main role in water pollution. Heavy metals are a group of metallic elements which are highly poisonous and human beings are always exposing to them. Heavy metals are one of the environmental pollution issues and it is increasing. Due to heavy metal pollutions such as Cd, Pb, Cu, Cr, Zn, Hg the quality of surface and underground water is decreased. In response to these pollutants many companies are established and introduced wide range of improved chemical products to remove the heavy metals from surface water and Groundwater (Stratton, 1987). Heavy metals contain two categories of essential and none essential elements which are important in toxicology. These elements have high durability and are potentially toxicant for creatures (Gadd, 1992). Surplus water, Urban Water waste and industrial garbage can be the origin of heavy metal pollution of water. Expanding Urban population and developing industries are one of the main factors of increasing pollutants in drinking water especially heavy metals. There are more than 50 elements which can be categorized in heavy metals category out of which 17 of them are the most prevalent and at the same time the most poisonous ones. The noxious extant of these elements depends on the type of the metal and its biologic role in life cycle. The common heavy metals which are very poisonous for human beings are Pb, Ar, Ag, Cd, Cr other heavy metals like Cu, Zn although are useful for body but they can be poisonous if their amount increases (Gadd, 1992). Heavy metals are one of durable pollutants and are not biodegradable and can penetrate in water and soil then they enter in food chain. Therefore there is a normal level for each heavy metal which if exceeded can be poisonous and harmful (Matlock, *et al.*, 2001, Thompson, 1990, Malik, *et al.*, 1992). Industrial water waste which contains heavy metals is one of main sources of environmental pollutants which are found in many industries such as plating industry.

In case these metals enter the body of human beings will cause many kinds of diseases such as cancer and also they pollute the water sources and the soil which leads to death of aquatic creatures. As a result the standard level of chromium in latest announcements of world health organization is defined less than 0.05 mg/lit (Zazouli, 2009). Considering the huge amount of heavy metals in water waste of plating industry it is one of the most dangerous chemical industries. Water waste of these industries which includes heavy metals such as Cr, Cd, Cu, Ni, Zn tends to aggregate in food chain. Due to their high dissolubility in aquatic environment the heavy metals can be adsorbed by living organisms. If these metals are absorbed more than permitted amount can a serious health problem. So this is why treatment of water waste polluted with heavy metals before discharging in environment is necessary (Agustionokurniawan *et al.,* 2006).

MATERIALSAND METHODALOGY

A. Specifications and Absorbent

Crude canola meal is applied in this study which is obtained from an oil extracting plant of Golestan a province of Iran. Canola is one of the most important seeds in cooking oils in the world and stands next to soybean. In order to purify the canola out of any external dust and dirt it was mixed with twice distilled water with mass ratio of 1/10 then stirred for 1 hour. After filtering and rinsing it was exposing to 80 centigrade degree temperature in an oven for 24 hours to make it dry. Then it was milled and sifted with a 1 millimeter sieve which is equal to 12 mesh. The size of canola particles were adjusted to at most 1 millimeter and kept in a container with closed door for further uses. This was based on 3500-cr standard Measurement of chromium (Goudarzi *et al.,* 1390). To make Chromium solution, 0.282 gr $Cr_2O_7K_2$ powders in 1 liter of twice distilled water was dissolved and the 100 mg/l solution of chromium is obtained Stock solution. Using NaOH the pH of solution adjusted and the HCL provided based on 0.1 Molar concentrations. This solution is used to conduct absorbent experiments and provide standard solutions.

B. Method of sampling and measurement

To determine the pH of solution pH meter (H q 40d (HACH) model) is used. Atomic absorption (Perkin Elmer model) is applied to measure the chromium 6(VI). Therefore some standard solutions of Cr2o7k2are obtained to calibrate the device. Effective parameters such as absorbent dose, pH, and contact time of bio adsorbent and initial concentration of metal are consistent variables and final concentration of chromium 6(VI) is considered as inconsistent variable. Each phase of the experiment is an input for the next phase. The number of samples is defined based on Full Factorial. To examine each variable 6 samples and for time parameter 8 samples were prepared. As there were 4 consistent variables then 26 samples prepared the experiments were repeated twice which adding up 2 control solutions the final number of samples reached to 54. 0.60 gr of crude canola mixed with in 100 ml chromium 6(VI) in a 250 ml container. Then it was shaken with a shaker on 200 rpm for 120 minutes in lab temperature. After spending the contact time the solid particles were extracted by suction and ash less filter paper then by the aid of atomic absorption device the remaining chromium 6(VI) were measured. 0.60 gr of adsorbent added to 6 100 ml samples of chromium 6(VI) solution with different values of pH (2, 3, 4,5,6,7 and 8) then they were shaken in 200 rpm for 2 hours in lab temperature then samples refined with suction and ash less filter paper. To determine the optimum contact time 8 samples 0.60 gr absorbent mixed with 100ml of chromium 6(VI) solution with 100mlg/l concentration. PH of solution was adjusted on the basis of optimum pH found in first experiment. The solution was shaken in 8 different times (0:00, 00:15, 00:30, 00:45, 01:00, 01:30, 02:00 , 04:00). Then samples refined with suction and ash less filter paper. To determine the optimum dose of absorbent first the pH of 100ml of chromium 6(VI) solution was adjusted according to the optimum pH. Then different amount of absorbent (0.200gr, 0.150gr. 0.100gr, 0.075gr, 0.050gr, 0.025gr) was added to 6 samples of 100ml chromium 6(VI) solution with 100mlg/l concentration. Again the solution shaken in 200 rpm. Then samples refined with suction and ash less filter paper. To determine the optimum concentration of the chromium 6(VI) solution. Firstly the pH is adjusted at its optimum level than 7 samples of different concentrations (12.5, 25, 50, 75, 100, and 150) in mg/l were mixed with optimum amount of absorbent in lab temperature. Then they were shaken in 200 rpm and refined with suction and ash less filter paper. All the samples were examined with atomic absorption device to find the remaining chromium 6(VI) in solutions.

C. Adsorption Isotherm Tests

To determine the adsorption isotherm first of all, the pH of chromium (VI) was set on optimal to determine adsorption isotherm. In the next stage, adsorbent with optimal value was added to the each seven containers, including 100 ml of chrome's solution with different concentrations12.5, 25, 50, 75, 100, 150, 200 mg/L in the laboratory temperature. The solution was placed in the shaker with a speed of 200 rpm and solid materials were removed by the use of suction device and filter paper to implement the filtration process. Then, the remaining amount of chromium (VI) was measured by atomic absorption. Adsorption isotherms were created and displayed by Microsoft Excel.

FINDINGS

A. Adsorbing Potential Parameters pH and Time in the Absorption of Chromium

To evaluate the efficiency of absorption in the two parameters pH and time absorbing raw rapeseed meal with the conditions listed in each section. The results showed that the absorption rate of pollutants by crude rapeseed meal in seven different pH's (2, 3, 4, 5, 6, 7, and 8) with equal amount of raw adsorbent, 0.6 mg in 100 ml of dissolved contaminants and 120 minutes varied. The maximum adsorption was observed at pH 7. It is necessary to define the optimal PH due to the fact that the optimal pH has a major role in the adsorption process. When the optimal pH was clarified, 0.6 mg of the adsorbent was added to each of the eight containers with pH 7 and tested in 8 different times (0, 15, 30, 60, 45, 90, 120, and 240). Consequently, it was observed that the maximum absorption happened at 60 minutes and the maximum contact time was achieved. The results of heavy metal bio sorption in various pH and time contacts have been presented in Fig. 1 and 2.

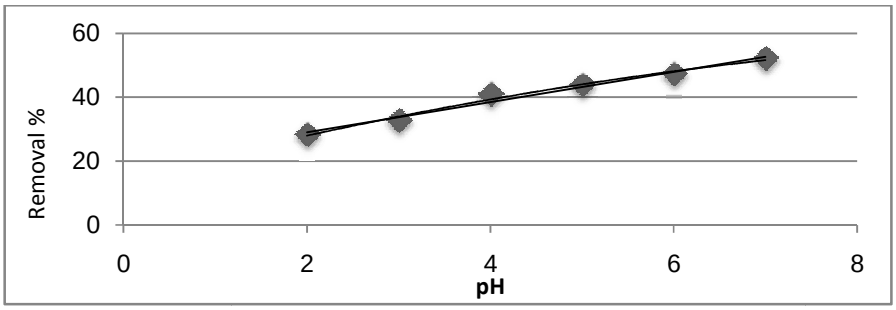

Fig. 1. Adsorption potential for Cr removal in different pH.

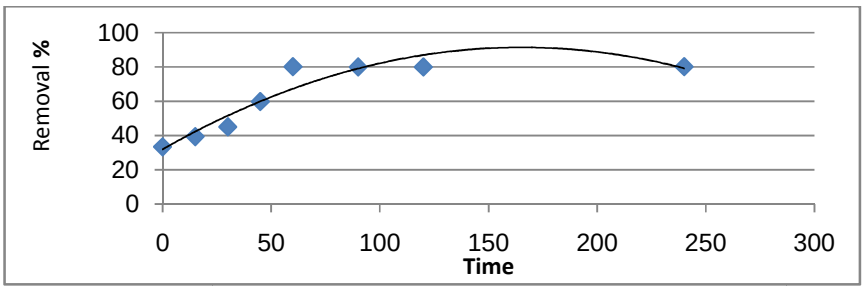

Fig. 2. Adsorption potential for Cr removal in different Time.

B. Adsorbing potential in Parameters of adsorbent dose and concentration of the contaminant in the adsorption of chromium

To evaluate the effect of different ratios of the adsorbent in the adsorption of solution chromium with optimal adsorbent dose, 0/6 containers with different amount of crude rapeseed meal (0.025, 50, 0.75, 100, 150, and 200) gr, Ph 7 and a contact time of 60 minutes were examined which consequently the optimum adsorbent dose estimated at 0.150 In determining the optimal concentration of pollutants, the absorption of chromium in pH 7, contact time of 60 minutes, 0.150 gr adsorbent dose and Different concentrations of 25.5, 12, 50, 75, 100, and 150, 200 mg /Lit tested. The maximum absorption was found at a concentration of 12.5 mg/L. it became clear that by reducing the concentration of pollutants the absorption process is approximately complete.

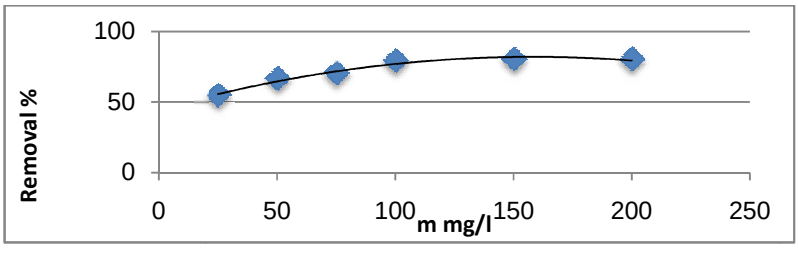

Fig. 3. Adsorbent potential in Cr removal with different Concentration of adsorbent.

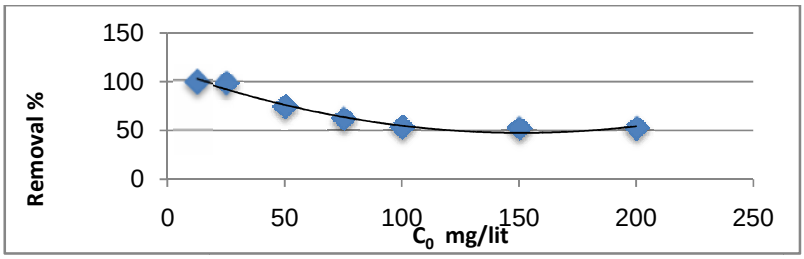

Fig. 4. Adsorbent potential in Cr removal with different Concentration of Cr.

DISCUSSION

Biological treatment with adsorption by biological mass (fungi, yeast, bacteria, algae) do have the mechanisms of absorption, the cell surface is complex and has many advantages such as lower operating costs, reduced biological and chemical sludge disposal efficiency high potential biological mass reduction and recycling heavy metals.

Plants Float. And Marginal rooted plants that grow naturally in water resources, the creation of artificial wetlands flora of vascular macrofite can be practical, effective and cost-effective water treatment (Msafrkhvrjstan *et al.,* (1387). Possibility remove the metal chromium enriched possible level of concentration of 150 mg GE sludge by three species of aquatic bamboo reed mat Louis and the highest uptake was observed after 60 days in organs underground plant bamboo reed with 378/6 mg kg of dry matter and thereafter Louis and mat highest concentrations of 212/3 and 98/8 have gathered. Undoubtedly waste as a source domestic of environmental pollution is, because it wastes human potential and actual own set of physical, chemical and biological environment, mostly aquatic environment cause. The lack of water resources and the high cost in the region of the need for and use of wastewater is necessary for different purposes (Goudarzi, *et al.*, 1390, Begum and Sediq 1387).

There are number of different methods to use the purified water waste indirectly in developed countries whereas implementation of those methods is not applicable in developing countries. Hence cost effective methods to purify water waste are highly recommended to take advantages in agriculture, gardening, artificial lakes, Artificial Nutrition and enhance the capacity of the aquifer groundwater. This article attempted to introduce a cost effective and applicable method of purifying water waste through crude canola meal which is a bio adsorbent with no harmful effect on environment. Table 1 shows the previous researches on different adsorbents and their corresponding adsorption percentage findings in Iran and the world.

CONCLUSION

The result of isotherm equations shows that the crude canola meal is highly absorptive for chromium 6(VI). Findings clearly show that the crude canola sample had 54 percent of adsorption where the pH was 7 the contact time was 60 minutes and the solution concentration was 100mlg/l. this natural product is potentially high adsorptive. Referring to adsorption isotherm of chromium 6(VI) fig. 5 and based on Longmire model in aquatic solutions with concentrations of chromium 6(VI) between 12.5 gr/l to 200 gr/l , pH 7, contact time 60 minutes and 0.150 mass the value of q is equal to 0.0256 and b is equal 20 2000.Based on frundlich model Fig. 6 the adsorption of chromium 6(VI) isotherm by using the crude canola meal in aquatic solutions with concentrations of chromium 6(VI) between 12.5 gr/l to 200 gr/l , pH 7, contact time 60 minutes and 0.150 mass the value of n was equal to 2.89 and the value of K was 1166.66 these show a good capacity of adsorption which is expected to have much more adsorption results when the modifiers such as HCl, HNO_3, NaOH, $CaCl_2$, SDS that can be recommended for further researches Dhananjay and Gaur 2011, Toabina *et al.*, 2010).

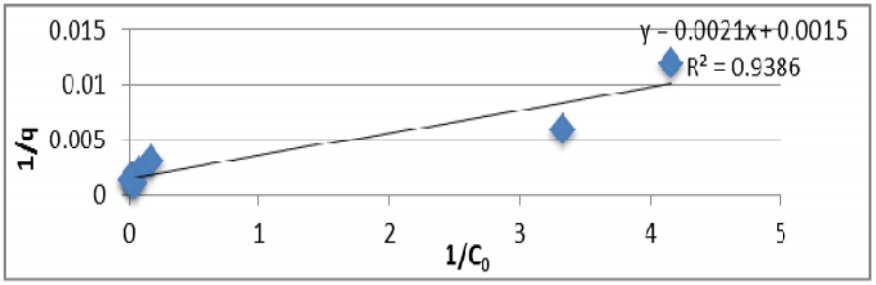

Fig. 5. Adsorption Isotherms applying Langmuir Isotherms model.

Table 1: A summary of the results of research previous on chromium removal from waste products agriculture.

Agricultural waste material	Metal Ions	Range pH	Results		Model Adsorption	
			Removal (%)	Capacity Adsorption (mg/g)		
Sawdust modified tree raji	(Cr)	12-2	99/67-29/87	-	Langmuir	Samarghandi *et al.,* (2009).
Ash active bark Hazelnut	(Cr)	3	82	-	Freundlich	Bayrak *et al.,* (2006).
Ash bark rice	(Cr)	6/2-3/2	91/42 - 66	240/2-16/1	-	Wang and Lin (2008).
Sawdust modified with Acacia Formaldehyde	(Cr)	3-10	62/2-10	-	-	Garg *et al.,* (2004).
Carbon active Sawdust modified with *Acacia*	(Cr)	3-10	86/6-10	-	-	Garg *et al.,* (2004).
Carbon active rice bran	(Cr)	2-12	88/88-40	-	Freundlich	Bishnoi *et al.,* (2004).
Carbon active put on rice bran	(Cr)	1-10	-	3-38	-	Guo *et al.,* (2002).
Iron modified With tears in wheat straw	(Cr)	1-11	96/8-30	-	Langmuir	Chun *et al.,* (2004).
Walnut bark	(Cr)	3/5	85/43	8/01	Langmuir	Witek-Krowiak *et al.,* (2010).
Hazelnut bark	(Cr)	3/5	88/46	8/28	Langmuir	Pehlivan and Tu (2008).
Almond bark	(Cr)	3/2	55	3/40	Langmuir	Pehlivan and Tu (2008).
Peanut bark	(Cr)	2-5	-	27/86	Langmuir	Pehlivan and Tu (2008).
Oat biomass	(Cr)	2-6	80	-	-	Gardea-Torresdey *et al.,* (2000)
Flower stalk waste *Helianthus annuus*	(Cr)	2-7	17-32	4/9	-	Jain *et al.,* (2009).
Sugar beetScumFe_2OH	(Cr)	4/4	83/1	-	Langmuir	Bayrak *et al.,* (2006).
rice bran crude	(Cr)	2-8	40-50	0/2	Freundlich	Oliveira *et al.,* (2005).
Extract Oak Fruit	(Cr)	5-11	80	-	-	Masoudnejad and Yazdanbakhsh (2003).
Biomass Alfalfa	(Cr)	2-6	13/9	7/7	-	Gardea-Torresdey *et al.,* (2000).
Alfalfa biomass	(Cr)	2-6	0/0	0/0	-	Gardea-Torresdey *et al.,* (2000).
bark Pomegranate Activated carbon	(Cr)	1-10	20-92	35/5	Langmuir	Nemr AE. (2009).
Tea factory waste	(Cr)	5-2	37-99	54-65	Langmuir	Malkoc and Nuhoglu (2007).
Modified Scum Sugarcane with NaOH & CH_3COOH	(Cr)	2-12	96/2-56/2	-	Langmuir	Rao *et al.,* (2002).
Wheat barn	(Cr)	2	-	310-58	Langmuir	Kobya M (2004).
Activated Carbon bark Hazelnut	(Cr)	1-8	92	170	Langmuir	Hasan *et al.,* (2008).
Corn bran	(Cr)	8/5-1/4	-	312/5	Langmuir	Hasan *et al.,* (2008).
Rice bark	(Cr)	2-7	20-39/6	8/5	Freundlich	Bansala *et al.,* (2009).
Rice bran	(Cr)	1/4-7/8	12/5-97/2	10	Langmuir	Singh *et al.,* (2005).
Ash Scum Sugarcane	(Cr)	2-9	96-98	3/7	Both models	Gupta and Ali (2004).
Tree bark *Eucalyptus*	(Cr)	2-11	100	-	Freundlich	Sarin and Pant (2006).
Crude canola meal	(Cr)	2-8	52	34/6	Both models	

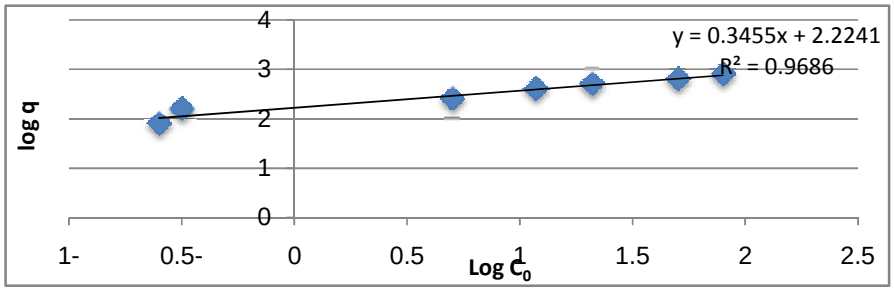

Fig. 6. Adsorption Isotherms applying Froundlich Isotherms model.

The reason of selecting the canola meal as an adsorption is its properties of low protein and high fiber and amino acid. Rape seed meal contains large amounts of non- starch polysaccharide and is 2.5 percent more sugar, including raffinose and stachyose the canola meal containing 15% sugar free and non- starch polysaccharides is solved and in general, the amount of fiber in canola meal (12 %) and higher than soybean meal (7%). Thus able to absorb increases Remove heavy metals from wastewater by ion exchange and the use of natural zeolites, excellent results in the removal of heavy contaminants using this adsorbent Khosravi *et al.,* (2011).

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