

Pilot plant studies for the removal of heavy metals from industrial wastewater using adsorbents

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Abstract: Due to carcinogenic and toxic effects of heavy metals on the environment and living beings, the necessity of proper removal systems for these harmful elements is obvious. Additionally, conventional methods in wastewater treatment are mainly biological; therefore, removal of heavy metals should occur by using adsorbents. In this study, activated carbon along with other cheap and available materials such as sawdust and bentonite in seven different adsorbent mixtures is applied to remove heavy metals from wastewater. Wastewater was applied to the system with a flow rate of $0.2 \frac{L}{min}$. Assuming fixed pH, biochemical oxygen demand, chemical oxygen demand, and total suspended solids, amounts of Fe, Mn, Cu, Al, and Mg from the wastewater were measured. Finally, adsorption capacity results were analyzed according to Langmuir and Freundlich theories for each mixture of adsorbents. Based on the results, sawdust is introduced as a desirable adsorbent for most heavy metals. For each element, an optimized adsorbent is also suggested, which, due to similar atomic and cationic properties, can be generalized for other similar elements.

Key words: Advanced treatment, heavy metal, adsorbent, Freundlich equation, Langmuir equation, adsorption isotherms

1. Introduction

Currently, adsorption, as a simple and effective technique in water and wastewater treatment, can be a successful solution to remove toxic and harmful elements such as heavy metals. Heavy metals are among the loosely defined subset of elements that exhibit metallic properties. Many definitions have been suggested, some based on atomic number, density, or atomic weight, and some on chemical properties or toxicity. Some of these heavy metals are dangerous to health or to the environment (e.g., mercury, cadmium, lead, and chromium), some may cause corrosion (e.g., zinc and lead), and some are harmful in other ways (e.g., arsenic may pollute catalysts). Within the European Union, the eleven elements of highest concern are arsenic, cadmium, cobalt, chromium, copper, mercury, manganese, nickel, lead, tin, and thallium. Some of these elements are actually necessary for humans in minute amounts (cobalt, copper, chromium, manganese, and nickel), while others are carcinogenic or toxic, affecting, among others, the central nervous system (manganese, mercury, lead, and arsenic), the kidneys or liver (mercury, lead, cadmium, and copper), or skin, bones, or teeth (nickel, cadmium, copper, and chromium). Usually high amounts of these toxic elements can endanger the environment and all living systems [1–4]. On the other hand, advances in technology and population growth cause industries to use harmful chemicals to satisfy their desires, while they may pollute the surface water and groundwater resources. Currently wastewater treatment plants in Iran might not be able to remove these toxic elements efficiently and the necessity of an

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advanced treatment unit is sensible. This unit is more essential when industrial wastewater enters the municipal sewage system. Activated carbon, clay minerals, biomaterials, zeolites, and some industrial solid wastes have been widely used as adsorbents for adsorption of ions and organics in wastewater treatment [5]. Using new and advanced carbon-based materials as the adsorbents often yields a physical adsorption system with high adsorptive capabilities [6]. Among all carbon-based materials, activated carbon (AC) is the most desirable adsorbent. AC is a crude form of graphite with a random or amorphous structure, which is highly porous, exhibiting a broad range of pore sizes, from visible cracks to crevices and slits of molecular dimensions [7]. AC's adsorptive properties are due to factors such as high surface area, well-developed internal microporosity, and wide spectrum of surface functional groups [8]. AC's properties depend upon the raw material it is made of and the activation process. Two types of activation, thermal/physical and chemical activation, impart a porous structure within a starting material of relatively low surface area.

AC is classified as granular (GAC) or powder (PAC) based on its size. Because there is no absolute method to regenerate PACs, their application may not be economical. Usually 4% to 10% of AC is lost during the regenerating process, which depends on the method of regeneration. Table 1 shows some properties of GAC and PAC. GAC is used in this study despite the proper features of PAC.

Table 1. Properties of granular and powder activated carbon.

Property	Unit	GAC	PAC
Specific area	M ² /g	700–1300	800–1800
Density	kg/m ³	400–500	360–740
Wet density	kg/L	1.0–1.5	1.3–1.4
Particle size	-	0.1–2.36 mm	5–50 μm
Effective size	mm	0.6–0.8	–
Average porous radius	Å	16–30	20–40

Bentonite is an absorbent aluminum phyllosilicate that usually forms from weathering of volcanic ash, most often in the presence of water. Specific characterizations such as ion exchange, formability, and expansion make this material a useful product. In addition, its reasonable price and availability suggest that researchers use it as an adsorbent in many civil projects. Sawdust, as a byproduct of the wood industry and a cheap material, can also be an efficient candidate to be used as adsorbent. One important aspect of sawdust application in wastewater treatment can be the environmentally friendly usage of this product in industry. Previous studies indicated that the heavy metal removal process is based on filtration of granular materials, which, according to atomic properties of the metals, can occur as hydroxide, sulfate, and carbonated sedimentation [9–12]. Many researchers around the world investigate adsorption and filtration processes of sludge resulting from these processes, which are typically toxic and harmful. Meanwhile, financial aspects usually require countries to choose cheap and available adsorbents with high adsorption rates. In order to find a practical solution for heavy metals in water and wastewater treatment plants, in this study, GAC, sawdust, and bentonite are used as adsorbents to remove iron, copper, manganese, aluminum, and magnesium.

2. Experimental work

2.1. Materials and methods

In order to consider the removal process of heavy metals including Fe, Cu, Mn, Al, and Mg, two sets of horizontal filters are used. These filters contain an injecting pump for metal solutions in definite concentrations, storage

tank for sewage effluent, discharge divider box for each filter along with a V-notch weir to control discharge, and finally two horizontal filters of 20 cm diameter and 40 cm column height. Figure 1 represents the schematic set-up. Based on the adsorption theory and in order to reduce the error caused by particle collision of metal solution in adsorption site, the testing process includes two steps. In the first step, measurement is done for Al and Mg, and in the second step for Fe, Cu, and Mn. The reason for this classification is the similar atomic weight of the elements, which eliminates any possible error and leads to an ideal adsorption for each of the metals.

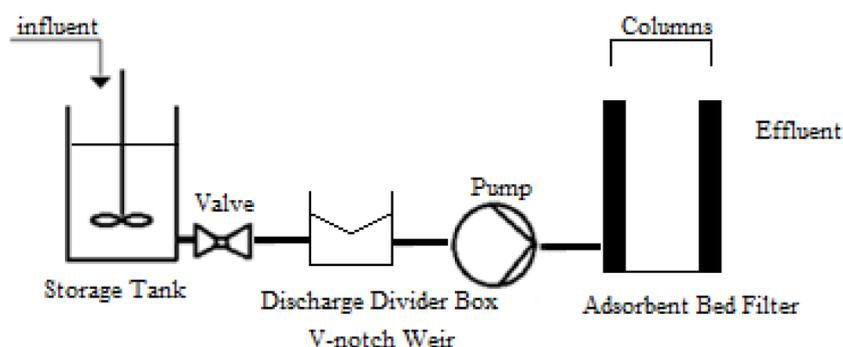


Figure 1. Experimental set-up of the pilot.

Due to the fact that metals at high pH values may make hydroxide sedimentations and coagulation, pH values are usually controlled and constant at low levels. On the other hand, pH values in municipal and industrial wastewater treatments are about 7–8, and therefore the pH value was determined to be at a constant level (pH 7). Meanwhile, biochemical oxygen demand (BOD) and chemical oxygen demand (COD) should not exist at advanced treatment levels; therefore, in order to run the tests, definite concentrations (1.5 ppm) of heavy metals were added to raw water that contained no remarkable BOD or COD. In other words, for all heavy metals including Fe, Cu, Mn, and Al, the feed concentration was 1.5 ppm, and for Mg, due to the importance of its initial concentration, the value of 36.5 ppm was investigated. According to the statistics received on Iranian water quality, it was determined that the higher concentration of Mg may make better sense in reality.

Hydraulic loading on filters for seven different mixtures of adsorbents and two kinds of sewage effluent containing Fe, Cu, Mn, Al, and Mg was conducted. Mixtures of adsorbents included AC, sawdust, and bentonite, and their mixing proportions are shown in Table 2. Density for AC, bentonite, and sawdust were 530, 600, and 245 kg/m³, respectively.

Table 2. Mixing proportions of filtration site.

	Granular active carbon		Bentonite		Sawdust		Total weight of filter (kg)
	Percentage (v/v %)	Weight (kg)	Percentage (v/v %)	Weight (kg)	Percentage (v/v %)	Weight (kg)	
Mixture 1	100	6.7	0	0	0	0	6.7
Mixture 2	80	5.32	0	0	20	0.615	5.935
Mixture 3	80	5.32	20	1.734	0	0	7.054
Mixture 4	80	5.32	10	0.866	10	0.307	6.493
Mixture 5	70	4.7	0	0	30	0.922	5.622
Mixture 6	70	4.7	10	0.866	20	0.615	6.181
Mixture 7	70	4.7	15	1.299	15	0.461	6.480

Loading discharge for both filters were 0.2 L/min and both filters were parallel with similar discharge; therefore, the output discharge from the tank that enters the dividing box was 0.4 L/min. It is notable that the reason to select 0.2 L/min as the input discharge is to offer sufficient time for heavy metals to come in contact with the adsorbents. According to this assumption, $(Q \times A)$ can be evaluated as follows:

$$Q \times A = 0.2 \times \left(\frac{\pi}{4} \times 0.2^2 \right) = 6.28 \times 10^{-6} \left(\frac{m^3}{min} \frac{m^2}{1} \right) \quad (1)$$

The initial concentration for each metal to form the sample was 13.4 ppm; therefore, output discharge was 0.4 L/min and desirable output concentration was 1.5 ppm. Initial concentrations of heavy metals in raw water (before conducting tests) were not measurable (besides magnesium) and assumed as zero ($C_1 = 0$). The input concentration (from injector pump) was thus $C_D = 13.4$ ppm. Finally, the mass balance equation was:

$$\frac{(Q_D \times C_D) + (Q_1 \times C_1)}{Q_D + Q_1} = C_0 \quad (2)$$

Based on this equation, the injecting pump discharge of initial solution into the storage effluent sewage tank was 3.04 L/h, which for every pump would be 1.52 L/h. Thus, specifying the injecting pump discharge, initial solution concentration, output discharge of tank, and output concentration of tank, a permanent concentration of 1.5 ppm for all metals (beside magnesium 36.5 ppm) in the tank will be available.

Hydraulic loading of the filter must be continued until the entire adsorption column capacity is saturated and heavy metal concentrations in input and output are equal to the initial concentration. Due to different adsorption capacities of adsorbent materials, 480 min was the base time to run the experiment. This meant that sampling of adsorbent output had to be conducted in different times (0, 30, 60, 90, 150, 240, 330, 420, and 480 min). After each sampling and at the end of the hydraulic loading, tests were conducted on the samples and their heavy metal concentrations were measured.

2.2. Adsorption isotherms

After conducting the tests, obtained results were analyzed according to Freundlich and Langmuir equations. In the beginning, adsorption capacity of every adsorbent mixture for each heavy metal element was evaluated individually $(C_i - C_e)$, where C_i is the initial concentration of adsorbate (mg/L) and C_e is the final equilibrium concentration of adsorbate after adsorption has occurred (mg/L). The value of $\frac{(C_i - C_e)V}{m}$ was then calculated, where V is the volume of liquid in the reactor (L) and m is the mass of adsorbent (g).

Finally, the adsorption coefficient based on Langmuir $\left[\frac{C_e}{\left(\frac{x}{m}\right)} = \frac{1}{ab} + \frac{1}{a}C_e \right]$ and Freundlich $\left[\log \frac{x}{m} = \log k_f + \frac{1}{n} \log C_e \right]$ equations can be accessed and output concentration can be evaluated [13–15]. In these relations, $\frac{x}{m}$ is the mass of adsorbate adsorbed per unit mass of adsorbent, $\frac{mg \text{ adsorbate}}{g \text{ activated carbon}}$; a , b are the empirical constants; k_f is the Freundlich capacity factor; and $\frac{1}{n}$ is the Freundlich intensity parameter.

3. Test results and discussion

3.1. Optimized mixture of adsorbent based on experimental and theoretical values

The theoretical concentrations (calculated from adsorption isotherms) were compared with experimental concentrations and optimized adsorbent for each heavy metal obtained. Figures 2–6 show the optimized mixture

of adsorbent for each heavy metal. For every heavy metal (Fe, Mg, Mn, Cu, and Al), all seven adsorbent mixtures were run and their graphs as drawn in Figures 2–6 only show the optimized mixture of adsorbent for each heavy metal. It is notable that the optimum mixture was achieved based on the exhaust time. The value of heavy metals was measured using an atomic adsorption spectrophotometer (PerkinElmer 1100B) in the chemical laboratory of the Water Research Institute of Tehran.

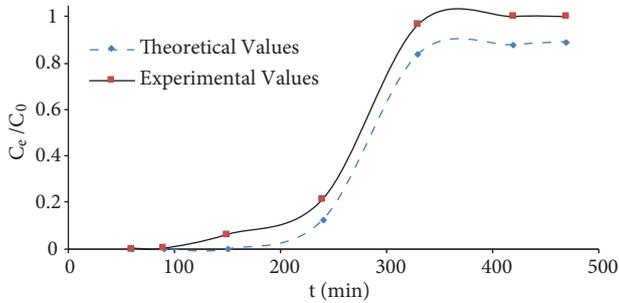


Figure 2. Theoretical and experimental graphs for iron adsorption (mixture 4).

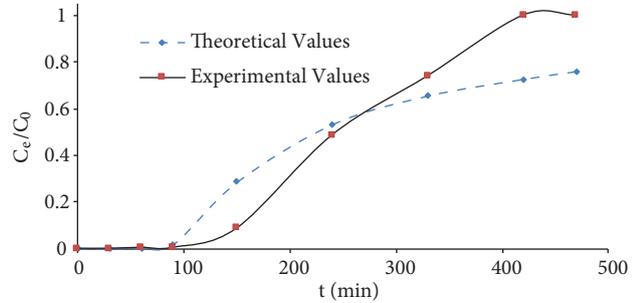


Figure 3. Theoretical and experimental graphs for copper adsorption (mixture 3).

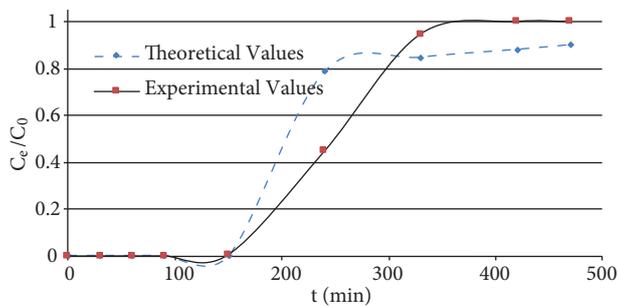


Figure 4. Theoretical and experimental graphs for manganese adsorption (mixture 5).

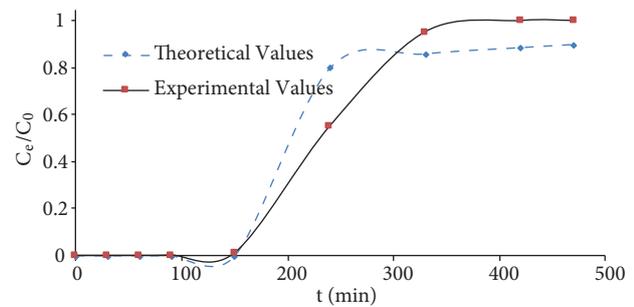


Figure 5. Theoretical and experimental graphs for aluminum adsorption (mixture 5).

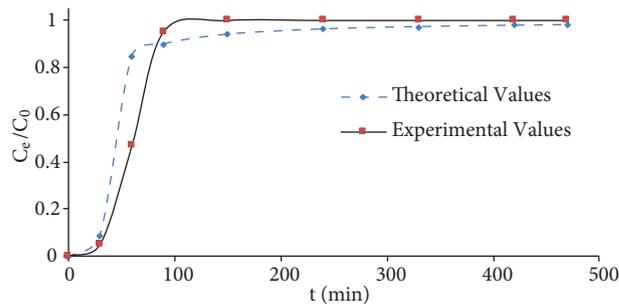


Figure 6. Theoretical and experimental graphs for magnesium adsorption (mixture 7).

According to the results, and comparing the graphs, it can be concluded that the order of cation adsorption depends on atomic number (cation weight), i.e. for metallic cations, higher atomic numbers show more efficient removal capacity, and therefore this order is obtained: $\text{Cu} > \text{Fe} > \text{Mn} > \text{Al} > \text{Mg}$. Another remarkable factor is the cationic capacity. Comparing the test results of Al^{3+} and Mg^{2+} shows that with higher cationic capacity, better removal occurs. The main reason for this phenomenon is that the main mechanism in adsorption

sites is physicochemical forces whereby higher cationic capacity improves the physical adsorption capability. Cationic capacity is the determinant factor in comparison with atomic number. It is remarkable that Mg feed concentration was much higher than Al, which is effective in the adsorption process, and it should be considered that this high initial concentration may affect the results, as well. In this regard, early bed saturation may occur for Mg.

Comparing the kinds of adsorbents, it can be concluded that powder adsorbents can have better contact with pollutants. This can cause a higher adsorption in early times in comparison with granular adsorbents. Therefore, granular adsorbents have slower adsorption rates and require more time to get saturated, while their final efficiency is lower than powder adsorbents. As a general conclusion, sawdust had a more efficient performance in comparison with bentonite, and mixtures containing sawdust had better adsorption quality.

The Langmuir isotherm in this study had no appropriate compatibility with experimental values, whereas the Freundlich isotherm had better performance. The main reason for this difference is the assumption made in the experiment. The Langmuir isotherm is based on laminar adsorption, which means that adsorptive materials remain as a layer on the adsorbent and if the first layer is not filled, the next layer will not be made. Thus, the Langmuir adsorption relation is linear and shows an ideal condition, which is not practical. On the other hand, the Freundlich isotherm is based on bulk adsorption. This means that particles are adsorbed due to physicochemical interactions of the filtration site and electromagnetic interactions of adsorbed material. This equation is more compatible with experimental values and practical uses and was applied in this research.

3.2. Required time for output concentration to reach standard values

One of the most important issues related to filtration is the operation time until the pollutant concentration is lower than standard values. These standard values in Iran for each heavy metal considered in the study are shown in Table 3. To reach the required time, these steps should be followed.

Table 3. Standard values for the effluent discharges.

Elements	Allowable concentration in agricultural soil (mg/g soil)	Allowable concentration for irrigation (mg/L)	Allowable concentration for drinking water (mg/L)
Fe	0.3	3	0.3
Cu	130	0.1	1
Mn	0.5	0.5	0.1
Al	0.2	0.2	0.2
Mg	50	50	50

- Evaluation of $\left(\frac{x}{m}\right)_t$, which means: $\frac{\text{Adsorbate mass}}{\text{Adsorbent mass}}$.
- Evaluation of x_i , which means the mass adsorbed by the adsorbent: $m \times \left(\frac{x}{m}\right)_t$.
- Evaluation of $t = \frac{x_i}{Q(C_i - C_e)}$, where Q is 0.2 L/min and C_e is the standard value for each calculation step.

According to this, another optimized adsorbent mixture can be gained for each metal. Table 4 shows the optimized mixture for each heavy metal according to required time to reach the standard value. These values are considered for all metals except manganese.

According to the tables, it can be generalized that if the sawdust values are higher, compatibility between experimental and theoretical data improves for Fe, Al, and Mg, which means that sawdust had better

performance in comparison with bentonite. In contrast, bentonite was a more sufficient adsorbent for Cu, while the performance of sawdust and bentonite was almost equal for Mn.

Table 4. Optimized mixture of adsorbent according to allowable operating time.

Heavy metal	Optimized mixture of adsorbent	Activated carbon (%)	Sawdust (%)	Bentonite (%)
Fe	4	80	10	10
Cu	7	70	15	15
Mn	4	80	10	10
Al	6	70	20	10

The required time for each metal and each mixture was obtained and the required time for the optimum mixture is shown in Table 5, with which we can figure out the necessary time of contact for each metal to reach the allowable limit concentration. The effluent is then ready to be discharged into nature. Only data on required time of the optimum mixture are given here.

Table 5. Required time to reach allowable limits for optimum mixture.

Heavy metal	Required time (min)	Allowable value
Fe	188.3	0.3 ppm
Cu	415.5	1 ppm
Mn	153.3	0.1 ppm
Al	142.5	0.2 ppm

4. Conclusion

In this study, the main objective was to find a practical solution to remove heavy metals in water and wastewater treatment plants. In many cases, municipal wastewater contains heavy metals that need to be treated. This becomes more crucial when industrial wastewater is combined with municipal water. Therefore, researchers try to find cheap and available adsorbents while also being practical. Sawdust as a byproduct and bentonite as an available material along with AC were applied in this study to remove heavy metals including Fe, Mn, Mg, Al, and Cu. Atomic number and cation capacity are two important factors that control the adsorption rates of metals. Metallic cations with higher atomic numbers are typically heavier and have more effective removal in comparison with lighter metals because they possess lower hydration water. Based on the figures given in the text, we can summarize the following trend for the experimented cations: $\text{Cu} > \text{Fe} > \text{Mn} > \text{Al} > \text{Mg}$.

As a general result, powder adsorbents perform more efficiently in comparison with granular adsorbents. Comparison of sawdust and bentonite showed that sawdust had a better adsorption rate and could be efficiently applied to Al, Mg, and Fe, while bentonite was more efficient for Cu and both of them were appropriate for Mn. In addition, the Langmuir isotherm was not very compatible in this study, whereas the Freundlich isotherm made more sensible predictions.

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