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Removal of Chromium (VI) and Iron from waste water Using Rice straw as Adsorbent

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Abstract: Environmental pollution is currently one of the most important issues facing humanity. Heavy metal toxicity due to industrial wastewater has been a threat to the environment for the past many decades, especially in the developing countries such as India. The commonly used procedures for removing heavy metals from aqueous streams include chemical precipitation, coagulation, ion exchange, reverse osmosis etc. In this work, adsorption experiments were carried out using rice straw as an agricultural residue was assessed for heavy metals (Cr (VI) & Fe) adsorption from aqueous solutions. The aim of this study is to find out the effectiveness of rice straw as an adsorbent for the removal of Chromium (VI) and Iron. In this work, the adsorption behavior of rice straw was studied by a set of experiments at conditions of varying pH, contact time and adsorbent amount to reduce the heavy metal content viz. Chromium (VI) and Iron.
Keywords: Adsorption, Adsorption isotherms, Optimum pH, Optimum adsorbent

1. Introduction

The industrial and domestic wastewater is responsible for causing several damages to the environment and adversely affecting the health of the people. Industrial wastewater is often characterized by considerable heavy metal content and, therefore, treatment is required prior to disposal in order to avoid water pollution Excessive release of heavy metals into the environment due to industrialization and urbanization has posed a great problem worldwide. Unlike organic pollutants, the majority of which are susceptible to biological degradation, heavy metal ions do not degrade into harmless end products. Heavy metals are one of the most persistent pollutants in water. Unlike other pollutants, they are non-degradable, but can accumulate throughout the food chain, producing potential human health risks and ecological disturbances. Their presence in water is due to discharges from residential dwellings, groundwater infiltration; fertilize industries, tanneries, batteries, paper industries, pesticides and industrial discharges etc. These heavy metals pose serious health hazard, including cancer, organ damage, disorders of nervous system, and in extreme cases, death. The danger of heavy metal pollutants in water lies in two aspects of their impact. Firstly, heavy metals have the ability to persist in natural ecosystems for an extended period. Secondly, they have the ability to accumulate in successive levels of the biological chain, thereby causing acute and chronic diseases. For example, copper toxicity causes itching and dramatization, keratinization of the hands and soles of feet.

Heavy metals are non-degradable metals. Several industrial wastewater streams may contain heavy metals such as Cr, Fe, Cu, Pb, Zn, Ni, etc., including the waste liquids generated by metal finishing or the mineral processing industries. Heavy metals are natural components of the Earth's crust. They cannot be degraded or destroyed. To a small extent they enter our bodies via food, drinking water. Heavy metals can enter a water supply by industrial and consumer waste, or even from acidic rain breaking down soils and releasing heavy metals into streams, lakes, rivers, and groundwater.

1.1 Industrial wastewater

Water is a renewable resource, it is naturally renewed within the hydrological cycle; however, once used it gets polluted and of course the extent of pollution is directly correlated to the purpose it was used for Industrial wastewater is defined as any wastewater generated from any manufacturing, processing, institutional, commercial, or agricultural operation, or any operation that discharges other than domestic or sanitary wastewater. Due to the water scarcity problem that Egypt and many other countries all over the world are facing, which is expected to become more serious in the future, wastewater treatment technologies, whether domestic or industrial, are very vital; therefore, more efforts and finance are ought to be assigned for research work in that field. Treating and reusing wastewater will eventually allow conserving fresh water for potable and domestic use, while using lower quality water, treated wastewater, for other uses that does not require high quality of water, such as irrigation, landscaping and industrial re-use. High quality water should not be used for purposes that can bear lower water quality.

The common uses of treated wastewater by industrial facilities are the following

1. Evaporative cooling water, particularly for power stations
2. Boiler-feed water
3. Process water
4. Irrigation of landscaping surrounding industrial plants

2. Methodology

2.1 Materials

2.1.1 Rice straw

Rice straw which is an agricultural by product has been used as low cost adsorbent. Untreated rice straw was prepared by cutting the straw into small pieces, washed with distilled water, dried in an oven over a period of 24 hrs and then grind into fine powder. Treated rice straw was prepared by using sodium hydroxide solution, ie; 16 g of powdered rice straw was treated with 240 mL of sodium hydroxide solution and dried in oven at 100°C over a period of 24 hrs.

Figure.1 Rice straw

Figure.2 Chopped rice straw

Figure.3 Powdered Rice straw

2.1.2 Synthetic waste water

Potassium dichromate was used to prepare stock Chromium (VI) solution and Ferric Ammonium Sulphate is used to prepare stock Iron solution in distilled water. For the pH adjustments Hydrochloric Acid and Sodium hydroxide solutions were used.

2.1.2.1 Chromium (VI) Solution

Standard Chromium (VI) solution was prepared by adding 2.8287g of Potassium dichromate ($K_2Cr_2O_7$) to distilled water and the solution is diluted into 1000mL. This solution is diluted to obtain standard solutions containing 20-100mg/L of Chromium (VI).

Figure.4 Standard Chromium (VI) metal solution

2.1.2.2 Iron Solution

Standard Iron solution was prepared by adding 4.975g of ferrous ammonium Sulphate in distilled water and the volume is made up into 1000mL. This solution is diluted to obtain standard solutions having concentrations 20-100mg/L of Iron.

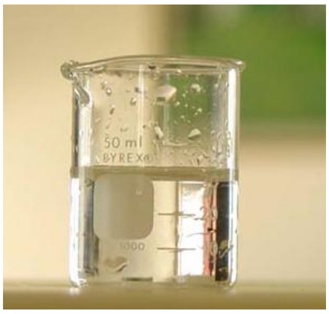

Figure.5 Standard Iron Solution

2.2 Treatment Methods

There are numerous methods currently employed to remove and recover the metals from our environment and many physico-chemical methods have been proposed for their removal from wastewater. Removal of heavy metals from wastewater is usually achieved by physical and chemical processes which include precipitation, coagulation reduction membrane procession change and adsorption. These methods have been found to be limited, since they often involve high capital and operational costs and may be associated with the generation of secondary waste which presents treatment problems. All the chemical methods have proved to be much expensive and less efficient than the adsorption process. In contrast, the adsorption technique is one of the preferred methods for removal of heavy metals because of its efficiency and low cost.

2.3 Batch Adsorption

The influence of rice straw on metal ions removal was investigated under the following experimental conditions. Batch experiments were conducted for varied pH, Adsorbent dose, Initial Chromium (VI) and Iron concentration and contact time. At desired intervals, effluent samples were collected, filtered using Whattman filter paper and analyzed for concentration of Chromium (VI) (VI). The amount of metal ion adsorbed was calculated as.

$$\%adsorption = (Ci-Cf)/Cf \times 100$$

Where, C**i**and C**f**are the initial and final concentrations of the metal ions in the solution (ppm).

2.4 Experimental Procedure

Adsorption experiments were conducted in batch process, that is, the solution was kept in separate beakers. First the different concentration solutions are mixed with same amount of adsorbent. Thus the effect of initial concentration on adsorption can be determined. Then same concentrated solution are mixed with 0, 2, 4,

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6, 8 or 10 g of treated rice straw thus the effect of adsorbent dosage can be determined and this mixture kept in contact for different time intervals to investigate the effect of contact period on removal efficiency. Also the the analysis for varied pH values are done. Finally samples were analyzed in batches for residual Chromium (VI) (VI) and Iron concentration.

Figure.6 Batch Chromium (VI) Adsorption

Figure.7 Batch Iron Adsorption

2.4.1 Spectrophotometer

Chromium (VI) ions and Iron ions are detected using spectrophotometer. Spectrophotometry is a method to measure how much a chemical substance absorbs light by measuring the intensity of light passes through sample solution. The basic principle used in spectrophotometer is that each compound absorbs or transmits light over a certain range of wavelength. Different concentrations of Chromium (VI) stock solutions were tested in the spectrophotometer at a wave length of 540nm and the optimum concentration is found out. Similarly the different stock Iron solutions are prepared and the absorbance of these solutions is measured in the spectrophotometer at a wavelength of 510nm.

Figure.8 Spectrophotometer

3. Results and Discussions

Adsorption studies have been conducted for the removal Chromium (VI) and Iron from synthetic waste water. In order to design adsorption system, optimization of various operating parameters such as Adsorbent dosage, pH, and Contact time are of vital importance. To ascertain the above parameters batch adsorption studies were conducted and the results are discussed below.

Table.1 Absorbance % of Standard Chromium (VI) solution

Concentration of solution	Absorbance %
10mg/l	0.012
20mg/l	0.018
30mg/l	0.024
40mg/l	0.031
50mg/l	0.039
60mg/l	0.047
70mg/l	0.055
80mg/l	0.064
90mg/l	0.072
100mg/l	0.082

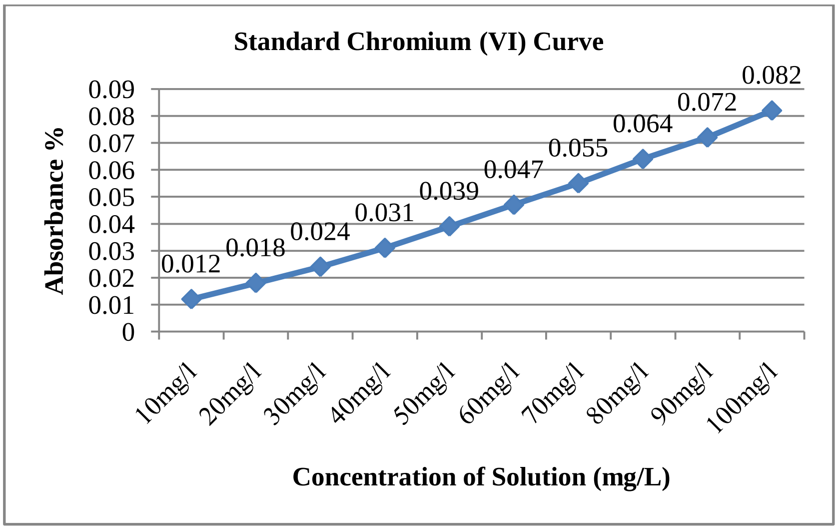

Figure.9 Standard Chromium (VI) Curve

Table.2 Absorbance % of Standard Iron solution

Concentration of solution	Absorbance %
10mg/l	0.012
20mg/l	0.021
30mg/l	0.032
40mg/l	0.041
50mg/l	0.051
60mg/l	0.059
70mg/l	0.068
80mg/l	0.076
90mg/l	0.083
100mg/l	0.091

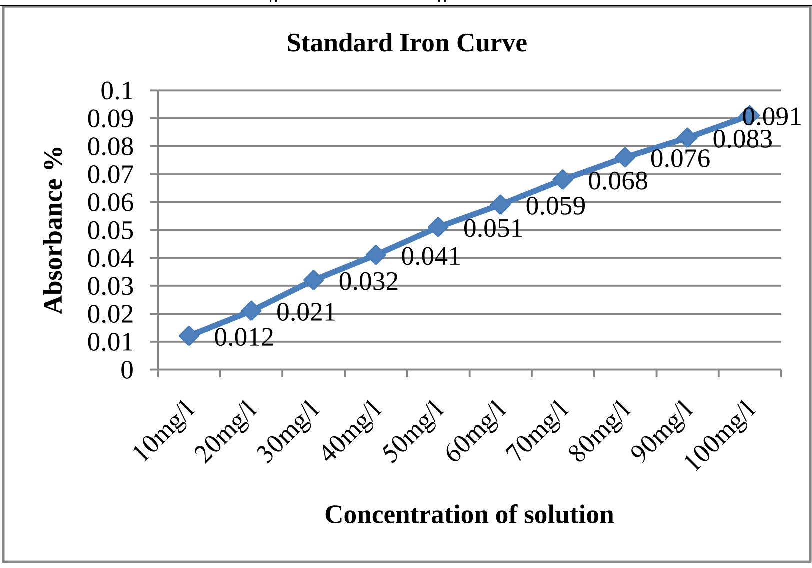

Figure.10 Standard Iron Curve

3.1 Effect of Initial Concentration

The initial concentration in the solution is a major factor affecting the adsorption. Thus the efficiency of Chromium (VI) and Iron removal was affected by the initial metal ion concentration. For the study 20-100mg/l concentrated Chromium (VI) and Iron solutions are adopted and 10g of adsorbent is chosen and analyzed at different time intervals. The removal efficiency decreases while increasing the initial metal ion concentration. At lower initial concentration rapid adsorption occurring and thus the removal efficiency for low concentrated solution are more as compared to large concentration solution.

Table.3 Chromium (VI) Absorbance % for different concentration solution at different time

Concentration of Solution	Amount of Adsorbent	Absorbance %				
		1hr	2hr	3hr	4hr	5hr
20 (mg/L)	10g	0.019	0.016	0.015	0.015	0.015
40 (mg/L)	10g	0.024	0.022	0.021	0.017	0.017
60 (mg/L)	10g	0.039	0.032	0.027	0.022	0.019
80 (mg/L)	10g	0.061	0.042	0.035	0.028	0.023
100 (mg/L)	10g	0.076	0.068	0.048	0.036	0.031

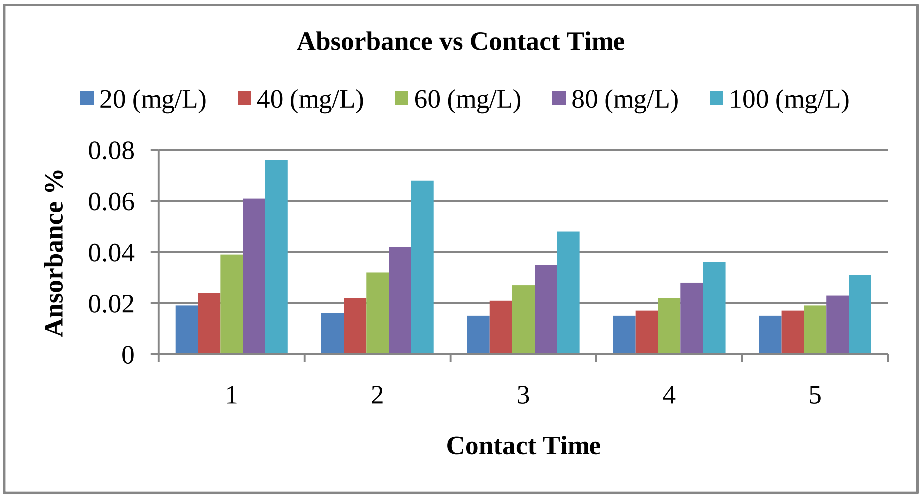

Figure.11 Chromium (VI) Absorbance % for different concentration solution at different time

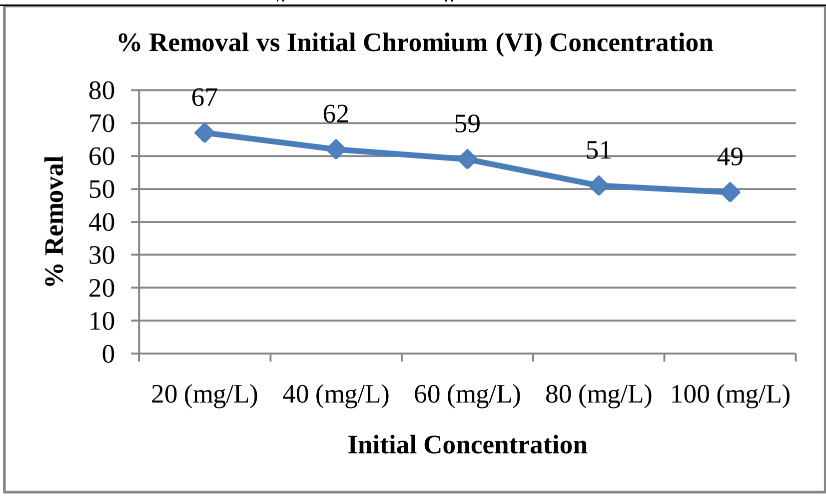

Figure.12. % Removal vs Initial Chromium (VI) Concentration

Table.4 Iron Absorbance % for different concentration solution at different time

Concentration of solution	Amount of Adsorbent	Absorbance %				
		1hr	2hr	3hr	4hr	5hr
20 (mg/L)	10g	0.025	0.021	0.018	0.016	0.015
40 (mg/L)	10g	0.065	0.056	0.043	0.034	0.029
60 (mg/L)	10g	0.067	0.061	0.049	0.038	0.034
80 (mg/L)	10g	0.073	0.066	0.051	0.043	0.039
100 (mg/L)	10g	0.089	0.075	0.059	0.048	0.044

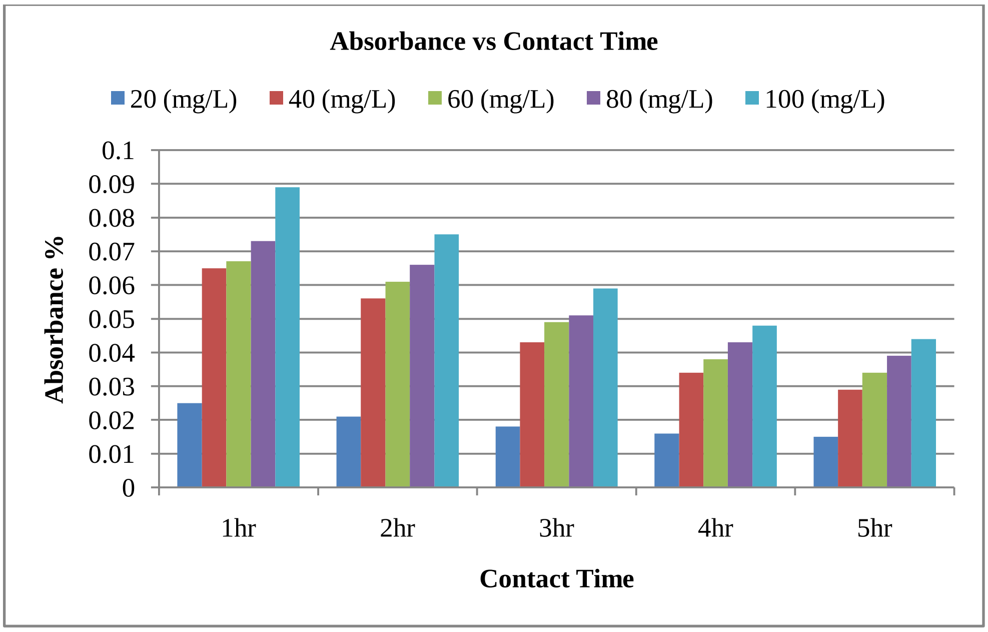

Figure.13 Iron Absorbance % for different concentration solution at different time

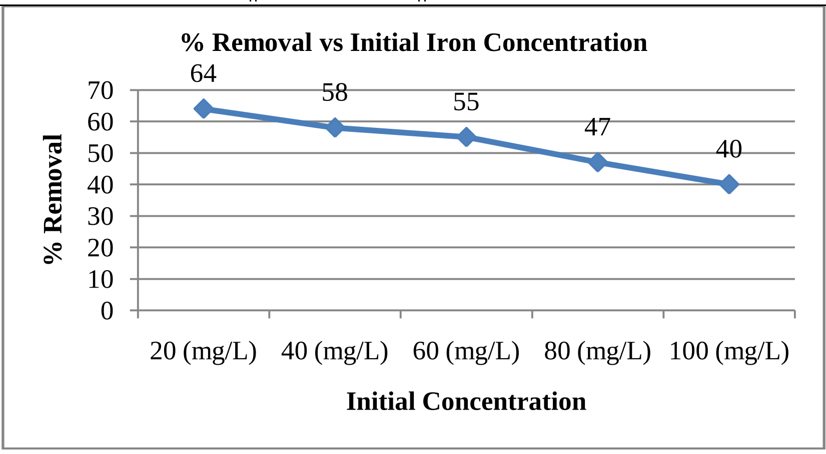

Figure.14 % Removal vs Initial Iron Concentration

3.2 Effect of Adsorbent Dosage

The main parameter affecting the adsorption is the concentration of adsorbent, because the adsorbent dosage helps to determine the capacity of adsorbent for the given initial concentration of metal solution. The effect of the adsorbent on the adsorption process can be determined by a plot of %Removal vs Adsorbent dosage for fixed concentration of Iron and Chromium (VI) (VI) solutions. For the study 100mg/l concentrated Chromium (VI) and Iron solutions are adopted. From the curve it is found that the adsorption increases with the increase of adsorbent dosage for both Iron and Chromium (VI) solutions. It is because of the increased adsorption surface area of adsorbent. But the adsorption increases up to an optimum amount of adsorbent and then decreases. The optimum amount of adsorbent is 10g for both the metals.

Table.5 Absorbance of 100mg/l Chromium (VI) solution with different amount of adsorbent

Concentration of Adsorbent	Absorbance %				
	1hr	2hr	3hr	4hr	5hr
2 g	0.053	0.048	0.042	0.036	0.031
4 g	0.049	0.045	0.039	0.032	0.024
6 g	0.043	0.038	0.032	0.025	0.019
8 g	0.032	0.027	0.021	0.016	0.012
10 g	0.025	0.021	0.018	0.015	0.006
12g	0.028	0.024	0.022	0.016	0.009

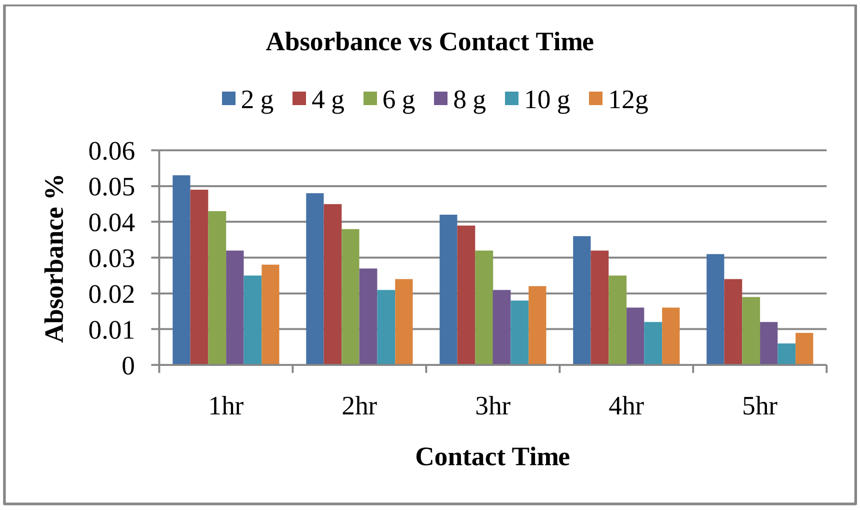

Figure.16 Absorbance of 100mg/l Chromium (VI) solution with different amount of adsorbent

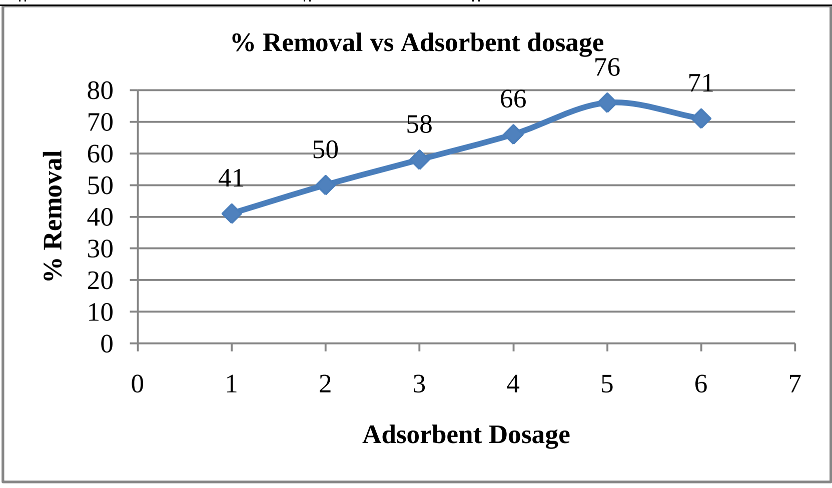

Figure.17 %Removal vs Adsorbent dosage

Table.6 Absorbance of 100mg/l Iron solution with different amount of adsorbent

Concentration of Adsorbent	Absorbance %				
	1hr	2hr	3hr	4hr	5hr
2 g	0.511	0.431	0.382	0.295	0.255
4 g	0.381	0.342	0.293	0.234	0.022
6 g	0.321	0.285	0.251	0.197	0.165
8 g	0.265	0.222	0.191	0.123	0.111
10 g	0.234	0.185	0.153	0.095	0.065
12g	0.245	0.201	0.183	0.111	0.083

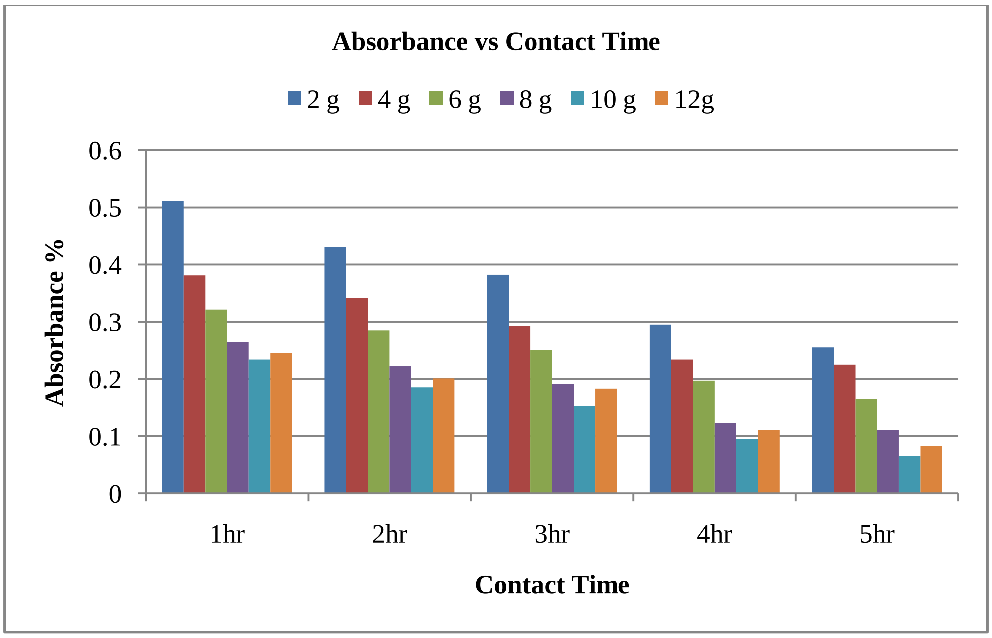

Figure.18 Absorbance of 100mg/l Chromium (VI) solution with different amount of adsorbent

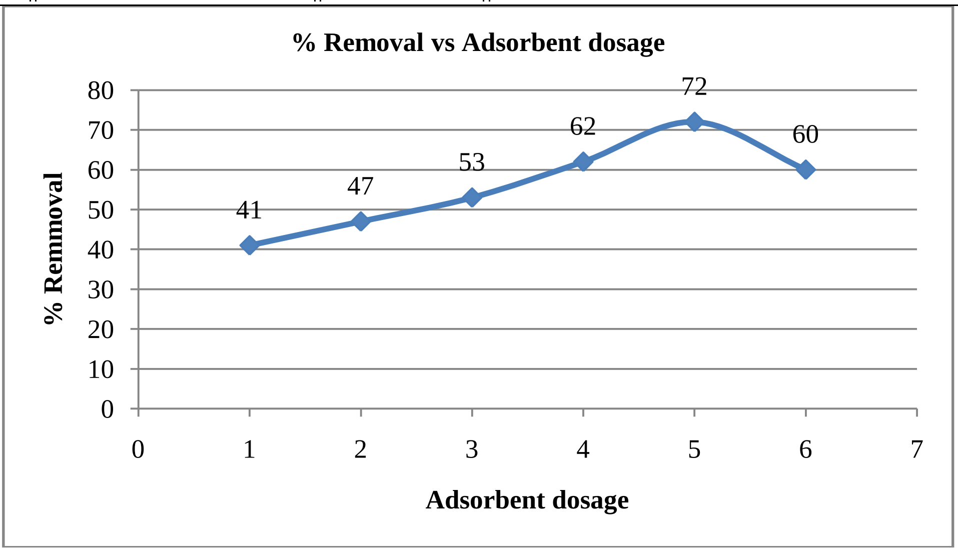

Figure.19 %Removal vs Adsorbent dosage

3.3 Effect of Contact Time

The contact time is a major factor affecting the adsorption. The effect of contact time is determined by analyzing the Chromium (VI) and Iron solution at different time intervals with 10g of adsorbent dose. The plot between the % Removal and the contact time shows the variation in adsorption with the increase of time. From the graph it is found that the adsorption increases gradually with the increase of contact time.

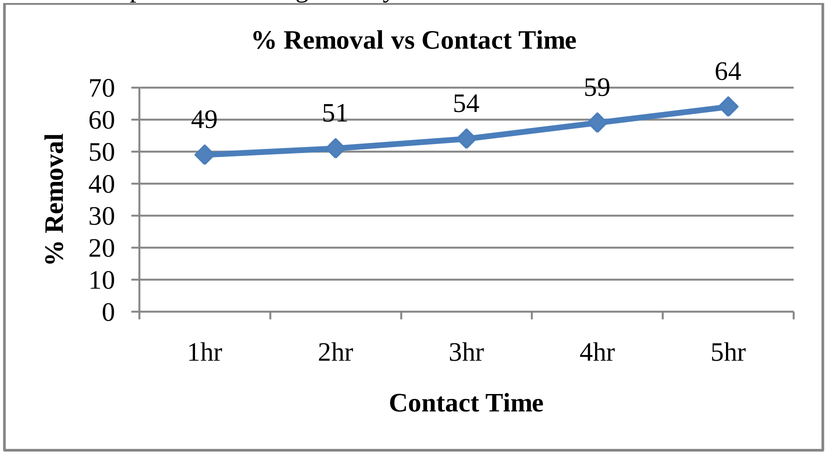

Figure.20 % Chromium (VI) Removal vs Contact Time

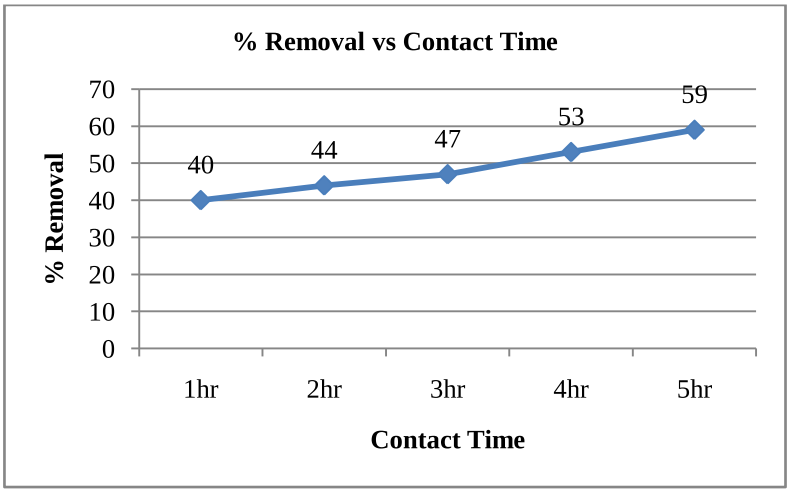

Figure.21 % Iron Removal vs Contact Time

3.4 Effect of pH

The pH of aqueous solution plays a vital role in controlling the adsorption process. The pH governs the adsorption of metal ions. The effect of pH on the adsorption of Chromium (VI) and Iron are determined by analyzing the Chromium (VI) and Iron solutions at different pH levels. A plot between the % removal and pH gives the variation in adsorption of metal ion. The % removal increases with increase in pH and reaches a maximum and then decreases in both metal solutions. The optimum pH for the Chromium (VI) is 4.9 and for Iron is 6.2

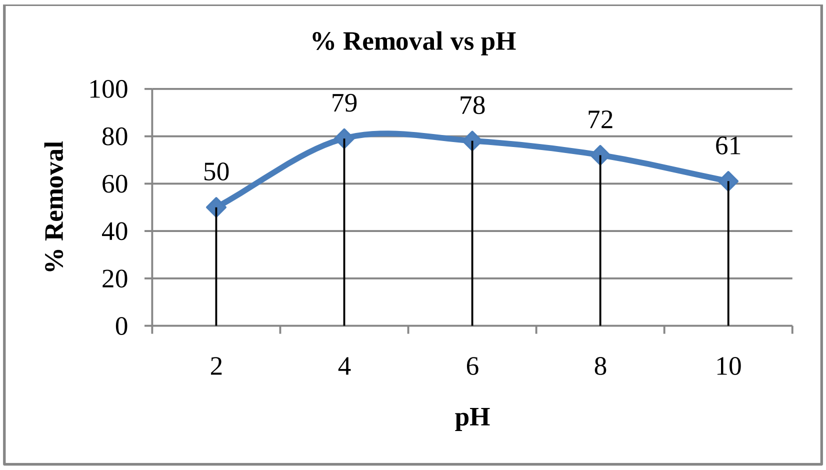

Figure.22 % Chromium (VI) removal vs pH

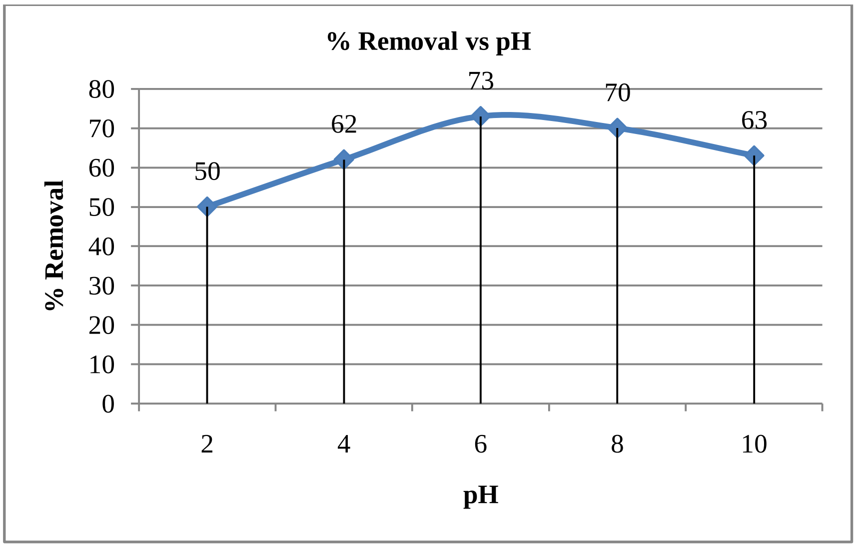

Figure.23 % Iron removal vs pH

4. Conclusions

Rice straw is an environmentally friendly potential adsorbent for heavy metals. This work examined the efficiency of this adsorbent in removal of some metal ion from aqueous solution. In the present study, batch adsorption tests were conducted on the removal of Chromium (VI) and Iron present in wastewater. The present investigation showed that the rice straw is an effective and inexpensive adsorbent for the removal of Chromium (VI) and Iron. And it is found that the main factors affecting the adsorption of heavy metals from waste water are the initial Concentration of the solution, Amount of adsorbent used, Contact time and the pH of the solution.

The adsorption of the heavy metals depends on the initial concentration of metal solution. The adsorption decreases with the increase of the initial concentration of metal ions in the solution. Thus the removal efficiency also decreases. The amount of adsorbent is another factor depending the adsorption. The adsorption increases with increase of the amount of the adsorbent used. But at after an optimum amount of adsorbent the adsorption gets decreased. The increase of the adsorption is due to the availability of lager adsorbing sites and contact area on the adsorbent. Thus better removal efficiencies are obtained at an increased amount of adsorbent. The optimum amount of adsorbent is obtained as 10g for both the metal solutions. The contact time is another depending factor for adsorption of heavy metals. The adsorption rate increases with the increase of contact time with the adsorbent. Thus the use of a better amount of adsorbent and with sufficient contact period result better removal of heavy metals from the waste water. pH is another factor depending the adsorption. The pH of the solutions is adjusted using adequate amount of Acid or Alkali. The optimum pH for the removal of Chromium (VI) is obtained as 4.9 and for Iron is 6.2. Thus Rice straw, natural adsorbent can be used for the treatment of heavy metals in waste water. The operation and processing cost of the rice straw is comparatively lesser and thus it is economical. The adsorption of the heavy metals can be increased by providing sufficient amount of adsorbent and providing enough contact time at the optimum pH value. The maximum % adsorption of Chromium (VI) is obtained as 95% and for iron is 98.5%. Thus the rice straw can be used as a good natural adsorbent for treatment of heavy metals of Chromium (VI) and Iron.

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