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Effect of pH on the Removal of Chromium (Cr) (VI) by Sugar Cane Bagasse

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تأثير درجة الحموضة في إزالة الكروم (VI) باستخدام بقاس من قصب السكر

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خلاصة: المناطق الصناعية في الهند تُسيطرُ عليها الصناعات الصّغيرةِ والمتوسطِة والتي تُشكّلُ تهديدا جدّيا بالنسبة للبيئةِ بما تطلقه من مخلفات ملوثة. ومما يزيد من تفاقم المشكلة وجود بعض المعادن الثّقيلةِ في هذه المخلفات. ويستخدم معدن الكروم على نحو واسع في عدد من الصّناعاتِ مثل طَلاء الأواني، وتلميع المعادن وأبراج التبريد والأصباغ ودبغ الجلود.. الخ. ومن المعروف جدا أن معدن الكرومِ **(VI)** سام جدا ويَعتبرُ خطرا على صحةِ البشر والحيواناتِ، كما أن تّركيزه بدرجة عالِية في البيئاتِ المائية يشكل خطراً كبيراً عليها. وقد تمت معالجة المخلفات المحتوية على معدن الكرومِ بعدة طرقِ، مثل التخفيض الكيميائي، والترسيب، والتبادل الايوني، والتخفيض الكهروكيمياوي، والتبخير، والتّنافذ والتناضح العكسى. وقد وجد أن طريقة التنافذ هى اكثر الطرق فعالية وهى طريقة رخيصة وسهلة. والهند بلد زراعيةُ وتنتجُ كميات كبيرة من الفضلات الزّراعية مثل بقاس سكر القصب، وجوت نبات جوزة الهندِ، وصدفة البندق، وقصب وقش الأرز، وقشور البقوليات ومخلفات الأسمدة ...الخ. والدِراسات الناجحة على هذه الموادِ يُمكنُ أَنْ تَكُونَ مفيدة في بلدان العالم الثالث ويُمكنُ أَنْ تُقدّمَ بشكل سهل كمكثّفاتِ لإزالةِ معدن الكرومِ من مياه الصرف الصناعي. وأغلب الأبحاث في السّابق تُبرزُ إستعمال الكاربون المنشّط بشكل تجاري. وهذه المكثّفاتِ عمليا غاليةُ جدا وغير ذات جدوى اقتصادية كبيرة في دول العالم الثالث. وبأخذ ذلك في الاعتبار فقد تم تصميم دراسات ميدانية لاستخدام بقاس سكر القصب لإزالة معدن الكروم (VI) من المحاليل المائيةِ.

ABSTRACT: The industrial estates in India are dominated by small and medium scale industries, which are posing a serious threat to the environment by virtue of discharging effluents of a polluting nature. The problems become severe due to the presence of heavy metals in the effluents. Chromium is widely used in a number of industries such as electroplating, metal finishing, cooling towers, dyes, paints, anodising and leather tanning industries. The toxicity of chromium (VI) is well known and is considered a hazard to the health of humans and animals. The presence of chromium (VI) in aquatic environments at high concentrations is also lethal to marine species. The treatment of chromium bearing effluents have been reported through several methods, such as chemical reduction, precipitation, ion exchange, electrochemical reduction, evaporation, reverse osmosis and adsorption. However among these, adsorption is found to be highly effective, inexpensive and an easy method to operate. India is an agricultural country and generates a considerable amount of agricultural wastes such as sugar cane bagassess, coconut jute, nut shell, rice straw, rice husk, waste tea leaves, ground nut husk, crop wastes, peanut hulls and fertilizer wastes. Successful studies on these materials could be beneficial to developing countries and could be easily applied as adsorbents for the removal of chromium from wastewater. Most of the previous work highlights the use of commercial activated carbon but these adsorbents are relatively expensive and less feasible to be used in developing countries. Keeping these in view batch experiments have been designed to study the feasibility of sugar cane bagasse to remove chromium (VI) from the aqueous solutions. While evaluationg the impact of various parameters, such as adsorbent does, contact time, initial concentration and pH on chromium removal efficiency, the results indicate a prominent effect of pH on the chromium reduction by the adsorbent used in the present study.

KEYWORDS: Adsorption, Toxicity, Sugarcane, Bagasse and Chromium.

1. Introduction

Most of the wastewater in industrial estates contains trace quantities of many heavy metals such as nickel, manganese, lead, chromium, cadmium, zinc, copper, iron and mercury. Some of these metals are essential to the growth of biological life and absence of sufficient quantities of them could limit their growth (Metacalf and Eddy *et al,* 1994). Larger concentrations, however, could cause adverse effects on humans, animals and plants. The rapid industrialization has resulted in accelerating the flux of heavy metals into surfacial environment. Pollution, due to these heavy metals, has been a major source of concern to scientists and environmental engineers. The presence of any of the above mentioned heavy metals in excessive quantity will interfere with many usages of water because of their toxicity. Therefore, it is desirable to measure and control the concentrations of these substances. Several mishaps related to heavy metal concentrations in the aquatic environment have increased the awareness about heavy metal toxicity. Among these, Minamata tragedy in Japan (1953-60) due to metallic mercury escaping from the laboratories and industries, mainly from chlorine manufacturing. It was acquired by aquatic life and passed along through natural food chains to humans, largely by fish. Another disease "Itai-Itai" that occurred among the farmers who drank water-containing cadmium supplied from the Jentsu River in Japan (Benefield ; Jadleins and Weand *et al,* 1982).

Chromium (VI) causes many adverse effects on humans, aquatic life and soil. Some of the effects are summarized as follows; Humans: Nausea, vomiting (Kerishnamurthy and Vishwanathan) , epiesgestric pain, severe diarrhoea, haemorrhage, dermatitis by skin contact, nasal mucous membrane, ulcer (Satyanarayan *et al,* 1995), lung cancer and tissue necrosis. Aquatic life: reduction in fish production at high concentrations, chromium accumulates in fish tissues and reaches to consumers. Gold fish and trout are killed at a concentration of 180 mg/l. Land: Soil fertility is reduced if chromium-bearing effluents are discharged on land (Sohail, 1997).

Table 1: Comparative study of different adsorbents (Siddiqui, Z. M. and Paroor, S. 1994).

Adsorbent	Initial conc.Cr (VI) mg/l	Equilibrium time(hr)	Dose (g/100ml)	pH	Cr (VI) removal %
Activated GHC [8]	10	3	0.24	2	80
Activated charcoal [2]	100	-	5	-	100
Calcinate coke [5]	5	-	-	2	100
Bagasse ash [10]	10	3	6	2	53.2
Activated bagasse carbon [10]	10	1.5	1.0	0.85-2	99.97
Raw bagasse [10]	10	1.5	1.0	1.0	93.5
Activated coconut jute [10]	10	1.5	1.0	1.4-2	99.7
Waste tea leaves carbon [7]	-	-	1.2	2	100
Activated charcoal, Flyash & rice husk [11]	-	7,- ,0.5	-	0-2	50,- ,100
Carbon slurry [12]	-	1.0	0.8	2.5	91.50
Rice straw [3]	10	24	1.0	1-3	100
Activated charcoal [6]	10	-	0.5	3	Max at pH 3
Peat [9]	100	24	0.4-4	>2	50
Fe(III) hydroxide [1]	50.8	-	0.30	4-6	99
Lignite [13]	3000	24	0.4	2	73.33
Activated carbon [4]	5.0	2	0.2	2.5	100

2. Adsorption of Heavy Metals on Agricultural Wastes

The treatment of chromium bearing effluents has been reported through several methods, such as, chemical reduction and precipitation, ion exchange, electrochemical reduction, evaporation and reverse osmosis. Most of these methods need high capital costs and recurring expenses such as chemicals. Less attention has been paid towards the treatment of effluent containing chromium by means of the adsorption technique using agricultural wastes. (Sohail *et al*, 1998). Potential Agricultural waste adsorbents are activated ground nut husk carbon (Periasamy, 1991), calcinate coke (Satyanarayan, 1995), bagasse ash , activated coconut jute, waste tea leaves carbon, activated charcoal, fly ash and rice husk, and rice straw (Deo, 1992). The comparative studies of different adsorbents are shown in Table 1 (Lal, 1992; Huang, 1975; Sharma, 1993; Shrichand, 1994).

3. Materials and Methods

The wastewater to be used in the investigation was prepared by dissolving a known amount of potassium dichromate in a known volume of distilled water in order to have waste of uniform characteristics and to avoid the interference with other elements. To evaluate the potential of bagasse to remove hexavalent chromium, batch experiments were carried out. Wastewater containing known concentrations of Cr (VI) were prepared from the stock solution and taken separately in glass stoppered conical flasks. Then known quantities of the adsorbent were added to the wastewater. The system was equilibrated by shaking the contents of the flask at room temperature so that adequate contact time between adsorbent and the metal ion was maintained. The suspension was filtered through Whatman No.1 filter paper and the filtrate was analyzed to evaluate the concentration of Cr (VI) metal in the treated wastewater. All the analyses were performed according to Standard Methods (Standard Methods, 1989). Metal analysis was carried out by using Atomic Absorption Spectrometry (model: GBC- 902).

4. Results and Discussion

While evaluating the effect of adsorbent dose, contact time and pH on chromium removal, the initial concentration of Cr (VI) was kept as 50 mg/l because in chrome plating wastes, chromium concentrations vary from 3-30 mg/l [ISI 7453-1977].

5. Effects of Contact Time at Different Adsorbent Doses on Cr (VI) Removal

The response of contact time on the removal of Cr (VI) is presented in Figure1. The observations reveal that the percentage of removal of Cr (VI) increases with an increase in contact

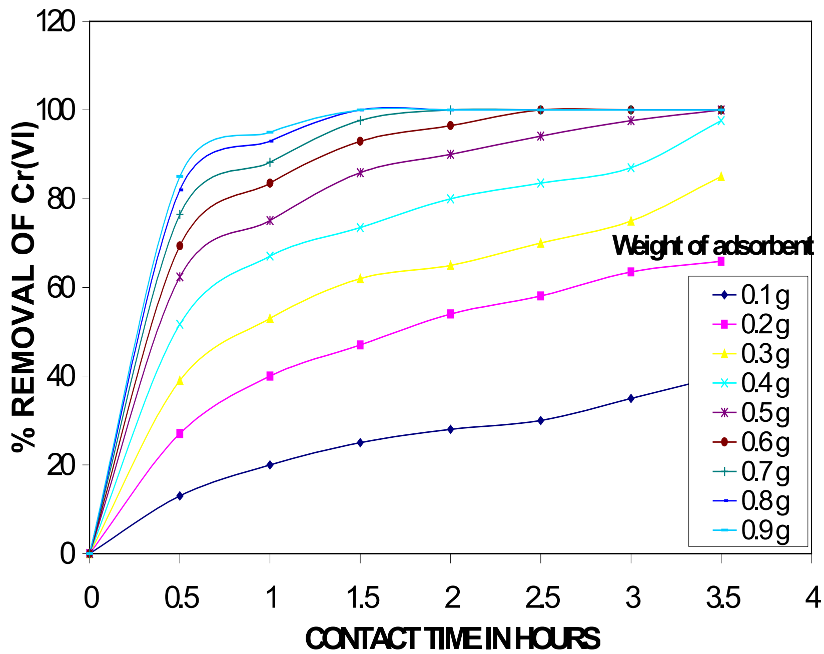

Figure 1. Effects of contact time at different adsorbent (bagasse) doses on Cr (VI) removal.

time. The removal efficiency is further increased as the dose of bagasse increases from 0.1 to 0.9 g and the contact time varies from 0.5 to 3.5 hr. It is also observed that at 0.5 hr the removal efficiency increased from 27-80% as the adsorbent dose increased from 0.2 to 0.8 g. If the contact time is raised to 1.0 hr, the removal efficiency varies from 38 to 93% for the same variation of dose (0.2 to 0.8 g).

A removal efficiency of 94% of Cr (VI) is observed at a contact time of 1.5 hr with a dose of 0.70 g/50 ml. Chand *et al*. (Shrichand, 1994) observed 30% removal efficiency of Cr (VI) having initial Cr (VI) concentration of 10 mg/l, at pH 4.38, the contact time was 1.5 hr and dose of adsorbent was 1.2 g/100 ml.

6. Effects of Adsorbent Dose at Different Contact Time on Chromium Cr (VI) removal

The effect of various bagasse dose on the removal of Cr (VI) from the wastewater are shown in Figure 2 .The results indicate an increase in the removal efficiency of Cr (VI) with increase in the dose of raw bagasse up to a certain level, beyond which the removal efficiency remains constant. It is evident that a dose of 0.8 g/50 ml is sufficient to remove 75-100% Cr (VI) in 0.5-3.5 hr. The increase in the removal efficiency with a simultaneous increase in adsorbent dose is due to the increase in surface area and hence more active sites are available for the adsorption of Cr (VI).

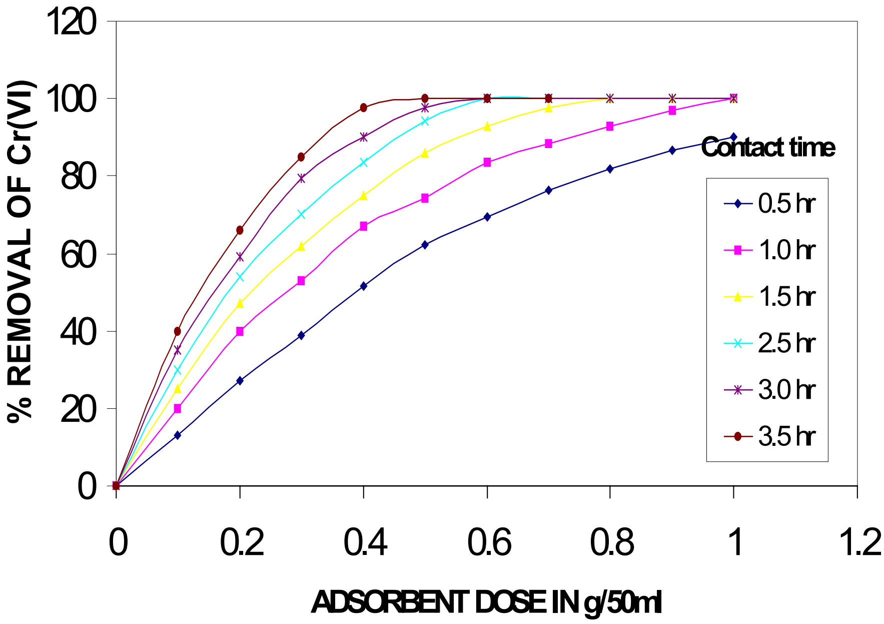

Figure 2. Effects of adsorbent dose at different contact time on Cr (VI) removal.

7. Effect of pH on Chromium (VI) Removal

Effect of pH on Cr (VI) removal shows that at lower pH, the Cr (VI) removal efficiency is higher and at higher pH the removal efficiency is reduced considerably (Figure 3). At pH 1.0 the removal efficiency is 100%, whereas on increasing the pH to 3.0 the removal efficiency is reduced to 15%. One of the reasons for the better adsorption capacity observed at low pH values may be attributed to the large number of H^+ ions present at these pH values, which in turn neutralizes the negatively charged hydroxyl groups (-OH) on the adsorbed surface thereby reducing hindrance to the diffusion of dichromate ions. At higher pH, the reduction in adsorption may be due to an abundance of OH^- ions causing increased hindrance to diffusion of positively charged dichromate ions.

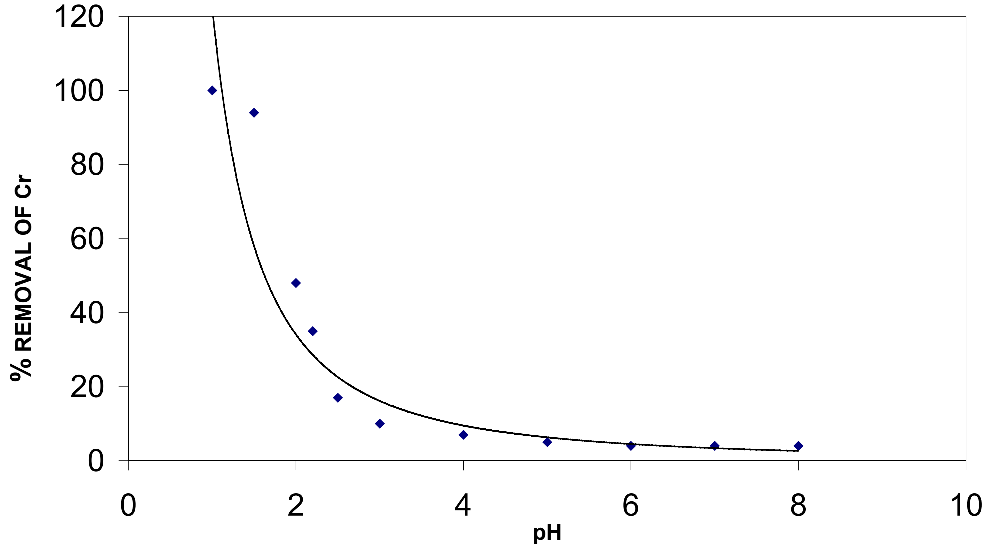

Figure 3. Effects of pH on Cr (VI) removal.

8. Effects of Various Initial Cr (VI) Concentrations on Cr (VI) Removal

The results of Figure 4 show that at low initial concentrations of chromium (VI) (5 to 10 mg/l) the removal efficiency is higher (70-100%). The removal efficiency of chromium decreases when chromium concentration is increased beyond 10 mg/l. The removal efficiency is 60% at a concentration of 20 mg/l and it decreases to 47% when chromium concentration was increased to 50 mg/l. In a similar study Chand *et al*. (Shrichand, 1994) obtained 90% removal efficiency at a Cr (VI) concentration of 10 mg/l in a dose of 1.0 g/100 ml at a contact time of 1.5 hr when the pH of the solution was 2.0.

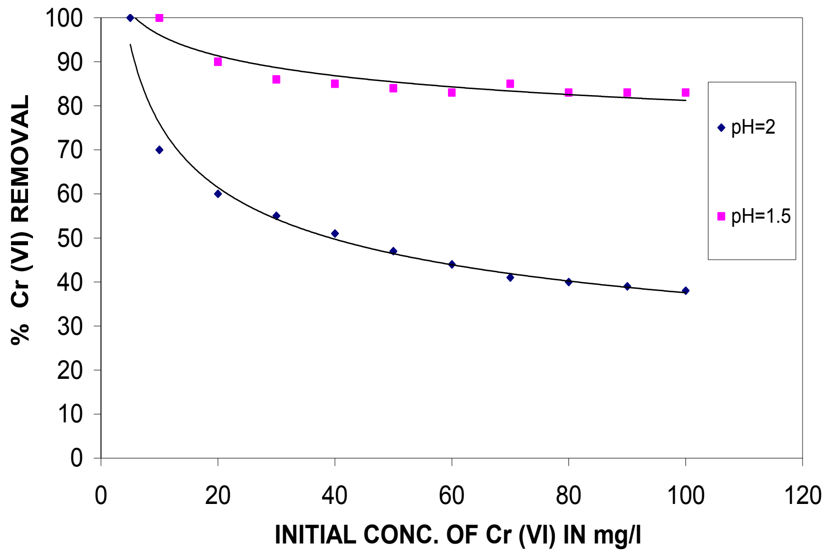

Fig.4 EFFECTS OF INITIAL Cr (VI) CONCENTRATION ON Cr (VI) REMOVAL

9. Rate Kinetics

The adsorption studies (Figure 5) conducted at a fixed initial concentration and varying adsorbent doses were fitted to the linearized Freundlich adsorption isotherm given below,

$$\text{Log}\,(x/m) = \log K + 1/n \log Ce$$

where, x/m is the amount of Cr (VI) adsorbed per unit mass of adsorbent (mg/mg) and Ce is the equilibrium concentration of aqueous solution. K is a constant, which is a measure of adsorption capacity, and 1/n is a measure of adsorption intensity. The values of the constant K and 1/n are 0.0032 and 0.235 respectively.Since the values are less than 1, it indicates a favorable adsorption (Shrichand, 1994).

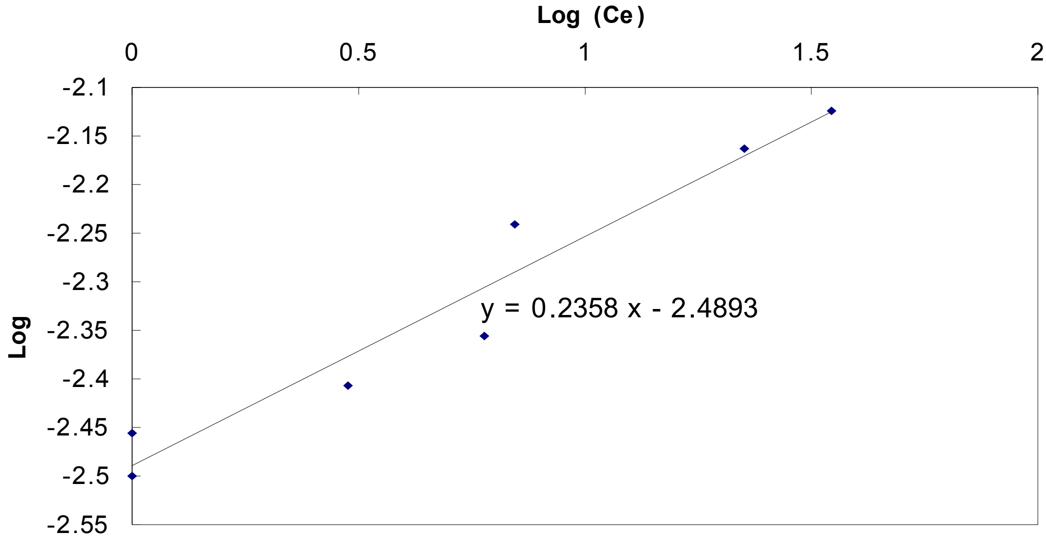

Figure 5. Plot for freundlich isotherm.

10. Conclusions

The following conclusions can be drawn from the present study.

- An adsorbent dose of 0.8 g/50 ml is sufficient to remove 80-100 % Cr (VI) from a solution having an initial concentration of 50 mg/l.
- The data obtained during the present study may be quite helpful in designing a full-scale adsorber for the treatment.
- Before applying raw bagasse for the treatment of wastewater there is a need for further investigations as the acid hydrolysis of cellulose in acidic medium produces alcohol that may increase the expand of the wastewater.
- Raw bagasse exhibits a high degree of Cr (VI) removal and it can be utilized for the treatment of industrial wastes containing chromium (VI) concentrations between 10-100 mg/l.
- The raw bagasse after adsorption can be burnt for heat recovery and the bagasse ash containing small quantities of Cr (VI) can be disposed off on low-lying areas.

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