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REMOVAL OF CHROMIUM (VI) IONS FROM SOLUTIONS WITH ACTIVE CARBON PREPARED FROM RICE HULLS

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In this study, the active carbon was prepared from rice hulls by activating with and without zinc chloride at the different tempeatures. Then the obtained active carbon has been used for Cr(VI) removal from solution. The effects of carbonization temperature of hulls, concentration of Cr (VI), and adsorbate-adsorbent ratio on adsorption of Cr (VI) ions were examined in order to find out the optimum conditions. The removal of Cr (VI) ions ranged from 30.5% to 99.4% when 20, 100 and 200 ppm solutions were used.

Key words : Adsorption, Active carbon, Rice hulls.

Introduction

Removal of heavy metals from waste waters has become a major concern to minimize environmental problems in recent years [1-4]. The most heavy metals are responsive to conventional treatment methods which have already been developed and utilized for water purification and metal recovery operations.

Treatment methods for waste waters include chemical precipitation, solvent extraction, cementation, reverse osmosis, electrodeposition and adsorption on active carbon or a synthetic resin [5-7]. Active carbon adsorption appears particularly competative and effective in the removal of heavy metals at trace quantities [8]. In addition, if agricultural by-products are used to prepare active carbon, the process must be more economical.

Interest has arisen recently in the investigation of some unconventional methods and use of agricultural by-products, such as rice hulls, peanut skins, rice straw, bagasse and garlic skins, etc., for waste water treatment. Rice hull ash has been found to be very effective in water treatment as a filter medium and coagulant [9]. The adsorption abilities of dyestuff-treated rice hulls against some heavy metals were investigated [3]. Some modified agricultural wastes were used for heavy metal removal from solutions [1,2]. Usmani *et al.* [10] reported that active carbons prepared from rice hulls have shown good adsorptive capacity in aqueous systems.

Rice hulls, the largest milling by-product of rice, are not used as fodder, because they have hard tissue containing a lot of silica. Approximately 168.000 tonnes of rice annually harvested with the yield of 2625 kg per hectar in Turkey [11]. Rough rice is milled for removing the hull from kernel for human consumption. During this step, it is possible to obtain 33.600 tonnes rice hulls from one-year rice production.

The present study is concentrated on the utilization of rice hull as a source of active carbon. The active carbon obtained at the different temperatures was used for the removal of Cr(VI) ions from aqueous solution.

Experimental

Preparation of active carbon. Rice hulls obtained from district of K.Maras were dried at 105° for 12 hr and then divided into two portions. One of them was mixed with 60% zinc chloride solution by 1/1 (w/v) ratio [12]. Zinc chloride was used as an activating agent since it has the highest solvent action on cellulose and it reacts with the inorganic matter in the raw material at the temperature of carbonization, rendering them into a form in which they are easily removeable by washing [10]. The treated and untreated samples were carbonized at 300, 500, 600, 700, 800, 900 and 1000° for 1/2 hr under the nitrogen atmosphere (Fig. 1). The cooled mixture was washed with distilled water and dried at 105° Finally, all the active carbon samples obtained were grinded and passed through 100-mesh sieve.

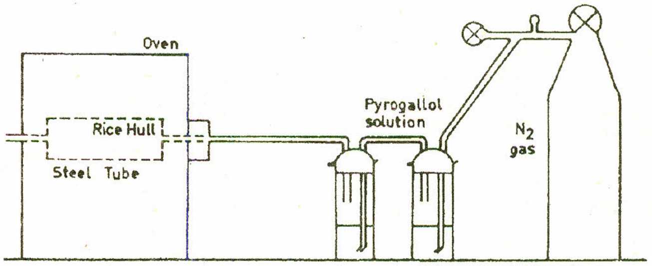

Fig. 1. Active carbon preparation apparatus.

The active carbon prepared from untreated hull at 900° was heated at 1000° to determine the ignitable fraction. The unignitable fraction was considered as inorganic compounds and analyzed by atomic absorption spectrophotometer and flame photometry. The composition was found to be, ignitable fraction 62.96%, SiO_2 34.97%, Al_2O_3 0.28%, CaO 0.75%, MgO 0.22%, K_2O 0.12% and MnO 0.15%.

Adsorption tests and analysis. The chromium solutions were prepared by dissolving chemically pure $Na_2Cr_2O_7\ 2H_2O$ in deionized water.

A known quantity of active carbon sample (1,2,3,4 g) was shaken with 100 ml of the chromium solution for 30 min., at room temperature. The mixture was then filtered and analyzed for Cr(VI) ions by atomic absorption spectrophotometer (Perkin Elmer 370). The amount of the Cr (VI) ions adsorbed on the active carbon was estimated by considering the initial and final concentrations of the chromium in solution.

Results and Discussion

The results obtained from adsorption experiments (batch methods) are given in Tables 1-2. The Cr (VI) ions have been effectively removed from solutions by the active carbon

TABLE 1. REMOVAL OF Cr (VI) IONS BY ACTIVE CARBON, PREPARED FROM UNTREATED HULLS.

Symbol	C_0 (ppm)	Intial pH	C_f (ppm)	Final pH	Absorbed Cr %	Absorbed Cr mg/kg	C_o-C_f (ppm)	m (g)	log(C_o-C_f)/m	logC_f
AK-300	20	2.07	13.9	4.89	30.5	610	6.1	1	0.78	1.14
	100	3.09	56.3	5.85	43.7	4370	43.7	1	1.64	1.75
	200	3.74	78.4	6.92	60.8	12160	121.6	1	2.08	1.89
AK-500	20	2.07	12.7	4.71	36.5	730	7.3	1	0.86	1.10
	100	3.09	43.4	5.73	56.6	5660	56.6	1	1.73	1.63
	200	3.74	68.2	6.81	65.9	13180	131.8	1	2.11	1.83
AK-600	20	2.07	4.0	4.53	80.0	1600	16.0	1	1.20	0.60
	100	3.09	18.9	5.69	81.1	8110	81.1	1	1.90	1.27
	200	3.74	23.4	6.72	88.3	17660	176.6	1	2.24	1.36
AK-700	20	2.07	3.2	4.48	84.0	1680	16.8	1	1.22	0.50
	100	3.09	14.2	5.54	85.5	8580	85.8	1	1.93	1.15
	200	3.74	19.9	6.33	90.0	18000	180.0	1	2.25	1.29
AK-800	20	2.07	4.8	3.82	76.0	1520	15.2	1	1.18	0.68
	100	3.09	22.3	5.33	77.7	7770	77.7	1	1.89	1.34
	200	3.74	34.4	6.27	82.8	16560	165.6	1	2.21	1.53
AK-900	20	2.07	6.0	3.71	70.0	140.0	14.0	1	1.14	0.77
	100	3.09	24.7	5.27	75.3	7530	75.3	1	1.87	1.39
	200	3.74	38.2	6.13	80.9	16180	161.8	1	2.20	1.58
AK-1000	20	2.07	6.9	3.60	65.5	1310	13.1	1	1.11	0.83
	100	3.09	29.4	5.13	70.6	7060	70.6	1	1.87	1.46
	200	3.74	42.1	6.09	78.9	15780	157.8	1	2.19	1.62

TABLE 2. REMOVAL OF Cr (VI) IONS BY ACTIVE CARBON, PREPARED FROM HULL TREATED WITH ZINC CHLORIDE.

Symbol	C_o (ppm)	Initial pH	m*	C_f (ppm)	Absorbed Cr %	Absorbed Cr mg/kg	m*	C_f (ppm)	Absorbed Cr %	Absorbed Cr mg/kg	m*	C_f (ppm)	Absorbed Cr %	Absorbed Cr mg/kg
ZAK-300	20	2.07	2	4.8	76.0	1520	3	4.0	80.0	1600	4	3.5	82.5	1650
	100	3.09	2	19.3	80.7	8070	3	11.4	88.6	8860	4	8.5	91.5	9150
	200	3.74	2	35.4	82.3	16460	3	17.9	91.0	18200	4	11.2	94.4	18880
ZAK-500	20	2.07	2	3.2	84.0	1680	3	3.1	84.5	1690	4	2.9	85.5	1710
	100	3.09	2	15.4	84.5	8460	3	8.4	91.6	9160	4	5.5	94.5	9450
	200	3.74	2	24.2	87.9	17580	3	13.0	93.5	18700	4	6.9	96.5	193000
ZAK-600	20	2.07	2	2.4	88.0	1760	3	2.3	88.5	1770	4	2.2	89.0	1780
	100	3.09	2	6.0	94.0	9400	3	4.7	95.3	9530	4	3.9	96.1	9610
	200	3.74	2	5.7	97.1	19420	3	4.3	97.8	19560	4	3.7	98.1	19620
ZAK-700	20	2.07	2	1.2	94.0	1880	3	0.9	95.5	1910	4	0.5	97.5	950
	100	3.09	2	2.6	97.4	9740	3	2.3	97.7	9770	4	1.9	98.1	9810
	200	3.74	2	2.1	98.9	19780	3	1.7	99.1	19820	4	1.1	99.4	19880
ZAK-800	20	2.07	2	1.7	91.5	1830	3	1.3	93.5	1870	4	1.1	94.5	1890
	100	3.09	2	4.5	95.5	9550	3	3.9	96.1	9610	4	3.1	96.9	9690
	200	3.74	2	4.1	97.9	19580	3	3.4	98.3	19660	4	2.7	98.6	19720
ZAK-900	20	2.07	2	2.2	89.0	1780	3	1.9	90.5	1810	4	1.4	93.0	1860
	100	3.09	2	11.3	88.7	8870	3	10.7	89.3	8930	4	9.3	90.7	9070
	200	3.74	2	10.7	94.6	18920	3	9.2	95.4	19080	4	3.4	98.3	19660
ZAK-1000	20	2.07	2	2.7	86.5	1730	3	2.2	89.0	1780	4	2.0	90.0	1800
	100	3.09	2	14.9	85.1	8510	3	13.1	86.9	8690	4	11.2	88.8	8880
	200	3.74	2	12.4	93.8	18760	3	11.3	94.3	18860	4	4.2	97.9	19580

m*: Adsorbent (g/100ml)

samples prepared at the different temperatures. The percentage removal of Cr(VI) ions from the solutions ranges from 30.5% to 99.4%. The best results were obtained with active carbon prepared at 700° (ZAK-700). This can be partially attributable to the transition of amorphous silica to crystaline form occured at this temperature [11]. In addition, a maximum porous structure develops in the material at 700° and thus creates a larger internal surface area. It can be concluded that the optimum temperature for the production of active carbon from rice hull is 700°. The active carbons produced by adding zinc chloride (ZAK) have higher adsorption capacities than the untreated ones (AK). It is understood that the use of zinc chloride has a definite effect on the adsorption capacities of active carbons. The chemical treatment of rice hull with zinc chloride prior to carbonization must be considered as a pre-requisite for producing an active carbon with high adsorption capacity. Zinc chloride has a dehydrating action as it causes hydrogen and oxygen atoms in the raw material to be

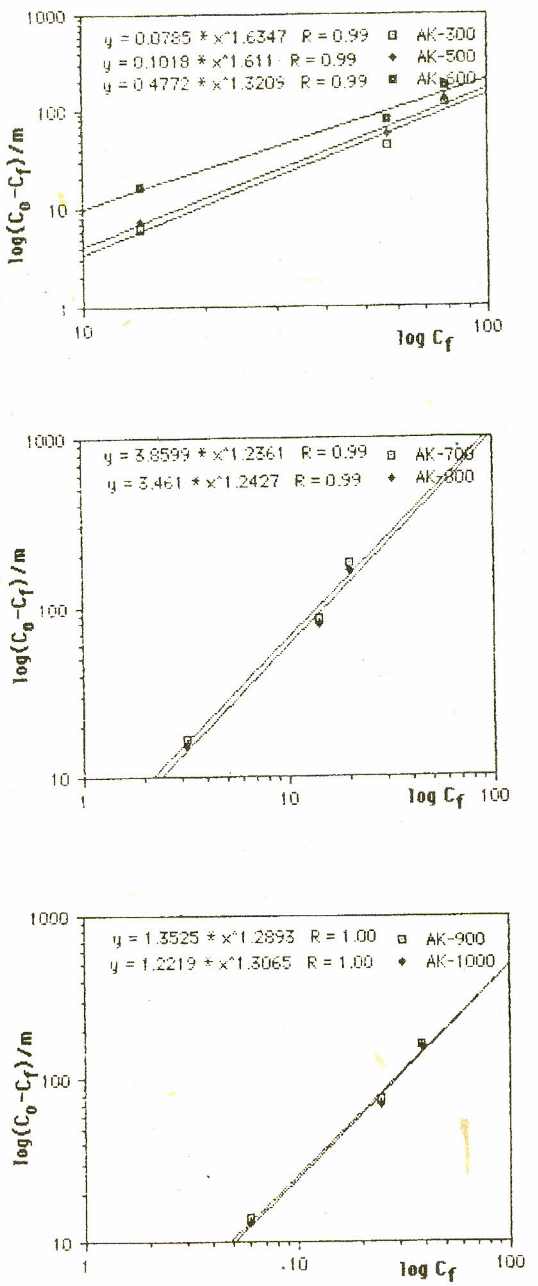

Fig. 2. Absorption isotherms for the removal of Cr(VI) ions by active carbon, prepared from untreated hull.

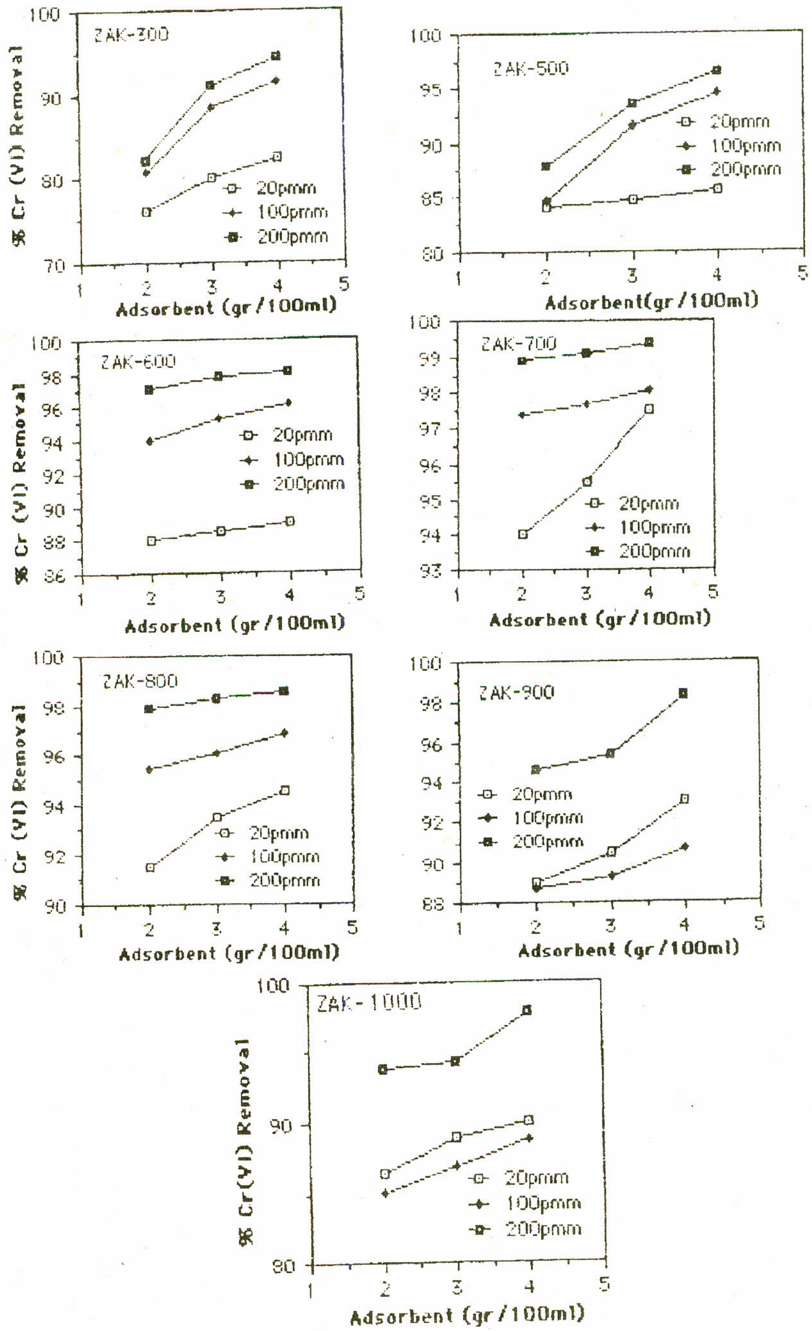

Fig. 3. Cr (VI) removal capacity of active carbon prepared from hull with treatment of zinc chloride as a function of carbon doze.

stripped away as water and thus creates a vast network of molecular capillaries to increase the adsorptive power of active carbons [10].

The initial Cr (VI) concentration has a considerable effect on the adsorbed amount of Cr (VI) ions on the active carbons prepared from rice hull. The amounts of Cr(VI) ions taken up by the active carbons increased with increase in the initial Cr(VI) concentration.

It is well known that adsorption of heavy metal ions by active carbon depends on pH of the solution. The adsorption capacity generally increases as the pH decreases. Thus, removal of Cr(VI) ions has been performed under acidic conditions, in the range of 2.07-3.74 to reach maximum adsorption. In all cases there was an increase in pH after adsorption. Increasing in pH may be attributed to the ion exchange phenomenon. The changes in pH decreased by increasing carbonization temperature of hulls.

Adsorption tests were carried out by using fourteen different active carbons and Cr(VI) solutions at various concentrations in order to determine the conditions for the most effective removal of Cr(VI) ions. It is seen in Table 2 that the most effective carbon for removal of Cr(VI) ions has been found to be zinc chloride added carbon prepared at 700° (ZAK-700).

The Cr(VI) ions are removed probably by reduction of Cr(VI) to Cr(III) and by the adsorption of Cr(VI) species at the active carbon surface. Reduction reaction may take place at the external surface and the adsorption and reduction reactions occur simultaneously.

The adsorption isotherms may be developed from the data shown in Table 1 (Fig. 2). The Freundlich isotherm describes the adsorption according to the following relation:

$$C_o - C_f / m = k C_f^{1/n}$$

where: C_o = Initial concentration of Cr(VI) ions (ppm),
C_f = Final concentration of Cr(VI) ions (ppm),
m = The amount of active carbon used (g/100 ml solution),
K,n = Empirical constants.

It is seen that the adsorption process is in agreement with the Freundlich isotherm. The value of k and n are given on the isotherms. The adsorption is generally proportional to the concentration of Cr (VI) ions in the solution and the amount of active carbon used (Fig. 3).

In conclusion, the present investigation demonstrates that the active carbon prepared from rice hull can be used for Cr(VI) removal from solution. The use of these active carbons represents another unconventional and inexpensive method for removing of heavy metals from waste waters. It may be potentially useful for treatment of industrial and domestic waste waters.

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