ADSORPTION OF CHROMATE ANIONS FROM AQUEOUS SOLUTIONS AT DIFFERENT PH VALUES

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Abstract

The objective of the studies was to determine an effect of pH on adsorption of hexavalent chromium onto activated carbons. The static studies of pH (in range from 4 to 9) on adsorption effect Cr (VI) onto activated carbon F-300 was investigated. The best results at lowest pH value were obtained. The highest varies in chromium removal - from 5 to 10% - achieved between pH values of 6 and 7, in dependence on initial concentration. In this range of pH and low concentrations of chromium, transformation hydrochromate into bichromate takes place.

The investigations ash disposal methods was carried out on carbon WD-extra washed 10% solution of HCl and H_2SO_4 and distilled water for the purpose of acid remains removal. Maximum adsorption occurred on ash removed carbon by hydrochloric acid. The efficiency of adsorption was varied in dependence on ash disposal method and reached 35%. The lowest results of adsorption for not ash removed carbon was obtained, because of process took place at high pH values, wherein ion exchange on weak exchangers, including activated carbon was the worst.

Itroduction

Chromium, especially its hexavalent form, is one of these heavy metals whose toxicological properties have been proved, however it still causes some problems at classical methods of treating water. Hexavalent chromium is easy to dissolve (as opposed to trivalent chromium which creates insoluble hydroxide) and is the most toxic. It can create chromates, hydrochromates and dichromates [1] in water. Over normative amounts of hexavalent chromium are found not only in surface water but also in groundwater. Acceptable concentration of general chromium in drinking water is 50 µg/dm^3 [2]. The research conducted on the possibility of oxidizing trivalent chromium showed that there is a danger that while adding ozone at the water treatment stations it may happen that less toxic form of trivalent chromium will change into its hexavalent form. It will cause that the water will contain Cr(VI) which has not been found in raw water [3].

The conducted research on application of activated carbons as selective ion exchangers in order to remove hexavalent chromium showed the possibilities of removing from water these ions which are concentrated at the low level to the demanded final concentration[4-6]. However, the fact that removal of ion (especially anions) is complex and unexplained in a sufficient way causes that it is advisable to make detailed research. It will enable to carry out the process under optimal conditions. This is crucial particularly in this case because activated carbons have relatively low absorption capacity in comparison to unlimited ions. The determination of optimal adsorption conditions and the choice of proper activated carbon have got great influence on economical aspect of the suggested method.

This paper presents the results of research concerning the influence of pH of a solution on the effects of chromate anion adsorption.

Methods

The research on the influence of pH on adsorption effects was conducted under static conditions on carbon F-300 which has not got large alkalinity and has got neutral reagent of water extract (table 1).

pH value was corrected by means of HCl or NaOH solution. The adsorption took place in 250 cm ^{3} of solution and at the chromium concentration of 0,8, 1 and 6 mgCr/dm^3. Then it was added 1g of activated carbon dried at the temperature of 140 °C. The prepared samples were shaken for 2 hours and put away for further 22 hours so that they reached equilibrium [7].
The investigation concerning the influence of removing ash from carbon by means of HCl or H_2SO_4 was carried out on carbon WD-extra which have got high capacity of mineral compounds in ash [8].

Table 1. Physicochemical properties of active carbons used in the research

No	Index	The quantity of index for carbon	
		WD-extra	F-300
1	Embankment mass, g/dm^3	415	542
2	Water logging, cm^3/g	0,78	0,61
3	Mechanical durability, %	98	97
4	Alkalinity, %	2,63	0,19
5	pH of water extract	9,8	6,8
6	Iodine adsorption, mg/g	967	1050
7	Methylene figure, mg/g	156	162
8	Grain number – grain sieve analysis		
	> 2,0 mm	4,9	31,4
	2,0 ÷1,5 mm	57,4	23,4
	1,5÷1,0 mm	34,3	30,2
	1,0 ÷ 0,5 mm	2,2	10,2
	< 0,5 mm	1,0	4,6
9	Capillary volume cm^3/g	1,069	0,987
10	Capillary area, m^2/g	753,6	792.1
11	Outside area, m^2/m^3	2235	2912

Results

One of the most important parameters which have influence on the results on ion exchange adsorption is pH of a solution. In this paper there was made a research on the impact of pH on carbon F-300, which is a rinsing carbon and the fact that we added it to the investigated water did not change its reagent. There were made some measurements of balanced concentrations for the following pH values: 4; 5; 6; 7; 8 and 9 and for initial concentrations: 0,8; 1,0; and 6,0 mg/dm^3 (Fig. 1). Within the range of pH = 4 ÷ 9 the increase in pH of water causes the decrease in adsorption results. The reduction of hexavalent chromium concentration (Table 2) is inversely proportional to pH value and to initial concentration. There are great differences among them especially when pH of water is changed from pH value 6 to pH = 7 (from 5 to 10 %).

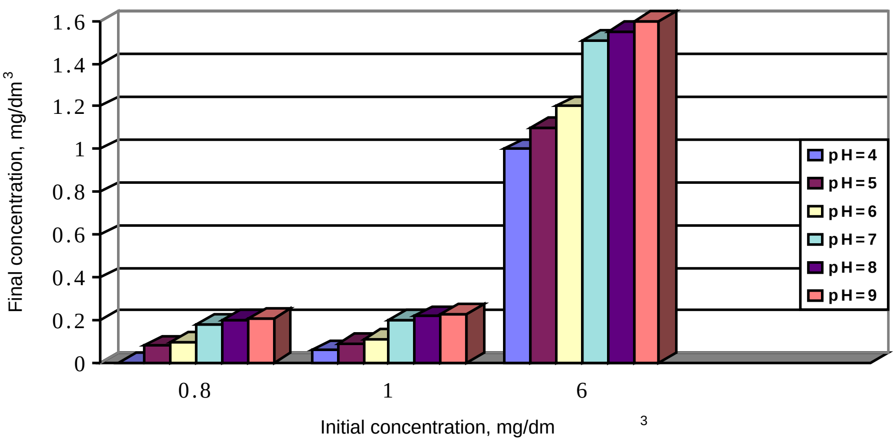

Fig. 1. The adsorption of chromate anions from water solutions at different pH values

The results of the measurements which show the impact of pH (even a few dozen percentage) on adsorption effects (Fig.1, table2) were the foundation of the initial modification of the used WD-extra carbon, which has got high pH values of water extract. The alkaline character of the reagent is caused by the presence in carbon some mineral compounds containing alkaline salts: mainly of calcium, magnesium, sodium and potassium. There is also a small amount of sulphides which can be responsible for the change of hexavalent chromium into trivalent one and for its precipitation as hydroxide. Therefore further research was carried out on carbons which had been partially ash handled by means of 10% HCl or H_2SO_4.

Table 2. The level of hexavalent chromium removal ($1-C_k/C_0$) depending on pH of the solution

Initial concentration, Mg/dm^3	pH					
	pH = 4	pH = 5	pH = 6	pH = 7	pH = 8	pH = 9
0,8	1	0,91	0,88	0,78	0,75	0,73
1,0	0,94	0,91	0,89	0,80	0,78	0,77
6,0	0,83	0,82	0,80	0,75	0,74	0,73

As a result of preliminary research it was established for static adsorption twenty-four-hour time of contact at constant pH = 7. Under such conditions and at changeable concentration of hexavalent chromium solution, there was carried out the next cycle of research. Its aim was to determine the influence of agent used to ash handle on anion exchange capacities of activated carbon.
The static adsorption was carried out on ash-free activated carbons at different initial concentrations (Fig. 2 and 3).

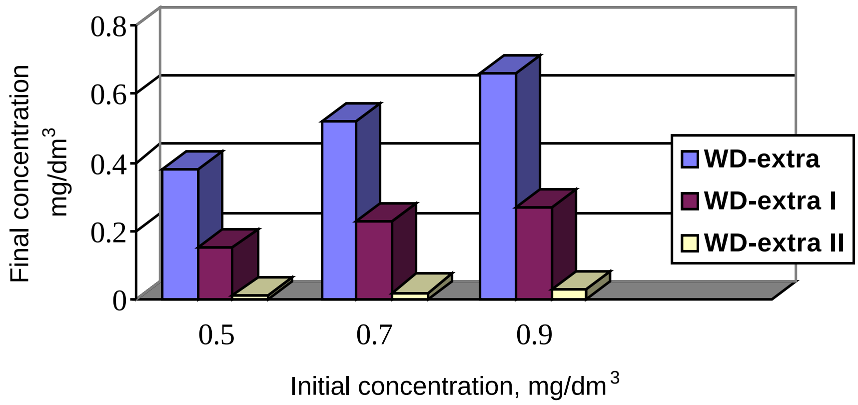

Fig. 2. The adsorption of chromate anions from water solutions
WD-extra - carbon containing ash
WD-extra I - ash-free carbon (ash removed by means of H_2SO_4)
WD-extra II - ash-free carbon (ash removed by means HCl)

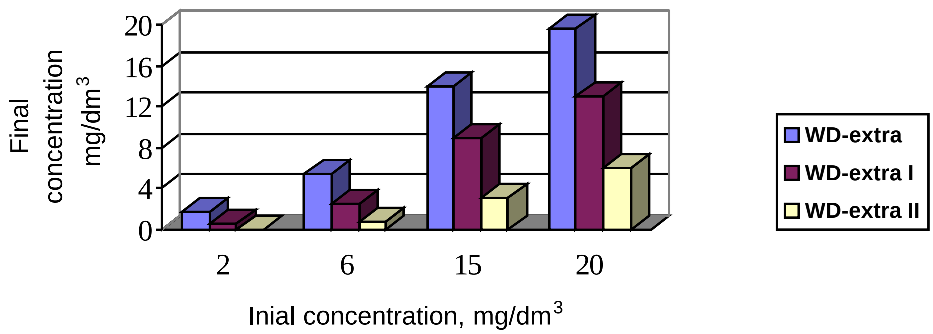

Fig. 3. The adsorption of chromate anions from water solutions on WD-extra carbon from which ash was removed in different ways

Discussion

The above shown results indicate that pH value of the solution is a very important parameter within the process of ion exchange adsorption. It has a great influence especially on dissociation of function groups on carbon surface. Activated carbons have got different function groups, however, in the case of anion exchange groups, it is hard to analyse them. According to reports presented in literature, these carbons can be treated as weak anions [9]. The dissociation of alkaline groups can take place in acid environment or at least neutral one. The reports presented in literature do not formulate unambiguous and optimal pH value of environment for Cr(VI) adsorption.

The research carried out by Perez-Candela [10] proved that optimal pH value during adsorption of hexavalent chromium is depended on material of which carbon is made and on the method of its production (especially activation process). Huang and other researchers [11] while investigating Calgon Filtrosorb carbon calculated the optimum adsorption of chromate anion at pH = 6, whereas the investigations shown in [12] concerning activated carbons from coconut shells and in [13]concerning the usage of bagasse indicate that the best results of adsorption were obtained at low pH values (max at pH=2).

According to the research [14] on mineral-carbon sorbent , the dissociation of alkaline groups took place only up to pH value = 4. Therefore the investigation of this parameter should be made on a specific carbons and every time [15]. Carbon F-300 is a rinsing carbon and adding it to the solution does not change its pH value. Within the range pH 4 ÷ 9, analyzed in the paper, the increase in pH value causes decrease in adsorption (Fig.1). There are especially great differences while changing pH = 6 to pH = 7. The increase in adsorption values in this case is 5 to 10 %. Within this range of pH hydrochromates change into chromates [16]. At lower water pH chromium appears as single-valued anion $HcrO_4^-$, at higher pH of water it appears as chromate anion CrO_4^{2-}. In the process of exchanging one chromate anion into another there can participate two active centers, however in the case of hydrochromate anion there is only one center. Simultaneously, the decrease in ionic charge has got a negative impact on strengths which cause the process of ion exchange. The sophisticated nature of ion exchange contributes to the fact that the effects of adsorption are not, as expected, twice bigger. The effects of adsorption obtained at high pH values can indicate that there are oxygen groups on the surface of carbon which are strongly alkaline and they can also show that other bonds are essential as they cause that chromate anion is stopped on carbon sorbents. The investigations made by Jankowska and other researchers [9], concerning the amount of sorbent anions in relation to desorbent groups OH^-,confirmed the occurrence of other chromium bonds than ion exchange bonds with carbon surface.

The positive influence of ash handling from carbon on the effects of adsorption is seen clearly for the whole investigated range of concentrations. The lowest values of the adsorption of chromate anion are obtained in the case of carbon which has not been subject of ash handling. For lower concentrations the decrease in contaminations on this carbon is about 26%. Higher results were obtained on ash-free carbon where ash had been removed by means of sulphuric acid. In this case the decrease in contaminations for the concentration 0,5 mg/dm^3 was 72%, and for the concentration 0,9 mg/dm^3 - 70%. That is unquestionable that the best results were obtained in the case of ash handling by means of sulphuric acid. The decrease in contaminations for concentrations under 1mg/dm^3 was over 90%. The reason is that in the case of adsorption on ash-free carbon, the process took place at high pH values, which has got the influence on lower adsorption values. The differences among the amounts of removed chromium on carbons which have been ash handled by means of different acids and the carbons which have not been ash handled are considerable. The differences can come even to 72% between ash handled carbon by means of sulphuric acid and fresh carbon.

Conclusions

1. The most important feature in the case of removing Cr(VI), apart from the presence of oxygen groups on the surface of carbon, is reagent of water extract of activated carbon. The presence of alkaline and mineral compounds in the ash of activated carbons is disadvantageous and the choice of carbon should be determined by this parameter.
2. Ash handling of activated carbons allows to create better conditions for adsorption of Cr(VI) and to eliminate the reduction and precipitation chromium in the form of hydroxide which blocks pores of carbon. The removal of alkaline, mineral compounds of activated carbons by means of acids causes the adsorption of acidic groups on alkaline oxides. Therefore better results are obtained after using sulphuric acid, which is easier displaced by chromate anion than sulphate groups.

3. In the case of ion exchange adsorption, pH of a solution, in which the adsorption takes place, is of great importance. In the case of the adsorption of hexavalent chromium, there are better results during the adsorption of acidic solutions and at the lowest investigated pH values (pH = 4).

References

1 R.M.STERN i in: Biological and Environmental Aspects of Chromium. ed. Langaard. Elsevier Biomed. Press, Amsterdam (1983).

2 Rozporz¹dzenie Ministra Zdrowia z dnia 19 listopada 2002r w sprawie wymagañ dotycz¹cych jakoœci wody przeznaczonej do spo¿ycia przez ludzi. (Dz.U.Nr 203).

3 A.BI£YK, R. MICHAŒ Przemiany zwi¹zków chromu w procesach uzdatniania wody. Ochrona Œrodowiska . **46-47**, 33-36 (1992).

4 Z.DÊBOWSKI, J.LACH: Usuwanie zwi¹zków chromu z wody na wêglu aktywnym. Ochrona Œrodowiska. **59**, 63-64 (1995).

5 J.LACH, Z. DÊBOWSKI: Sorpcja jonów chromu szeœciowartoœciowego na wybranych wêglach aktywnych. Mat. Konf. na temat „Zaopatrzenie w wodê miast i wsi”, Poznañ, Polska, 201-207 (1996).

6 J. LACH: Wp³yw obecnoœci anionów siarczanowych i chlorkowych na sorpcjê anionu chromianowego. Mat. Konf. na temat „Wêgiel aktywny w ochronie œrodowiska”, Czêstochowa, polska, 158-168 (2002).

7 Z.DÊBOWSKI, J.LACH, E.OCIEPA.: Wp³yw w³asnoœci fizyczno-chemicznych wêgli aktywnych na usuwanie chromu (III) i (VI) z wody. Ochrona Œrodowiska, **66**, 47-50 (1997).

8 B.BUCZEK. L.CZEPIRSKI: Adsorbenty wêglowe-surowce, otrzymywanie, zastosowanie, Gospodarka Surowcami Mineralnymi, **17**, 29-61 (2001).

9 H.JANKOWSKA i in.: Adsorpcja jonów na wêglu aktywnym. WN PWN, Warszawa (1991).

10 M.PEREZ-CANDEELA, J.M.MARTIN-MARTINEZ AND R.TORREGROSA-MACIA.: Chromium (VI) removal with activated carbons. Wat. Res**., 9**, 2174-2180 (1995).

11 C.P.HUANG, M.H.WU:The removal of chromium (VI) from diilute aqueous solution by activated carbon. Wat. Res.,l **11**, 673-679, (1997).

12 R. S. PADAKI SRINIVAS, R. SHASHIKANTH, G.S. MANJUNATHA: Kinetic studies adsorption of chromium by coconut shell carbons from synthetic effluents. J. Environ. Sci. Health, **27(8),** 2227-2241 (1992).

13 R. SHASHIKANTH, G.M.SHANTHA: Adsorption studies of chromium (VI) from synthetic aqueous solution by activated carbon derived from bagasse. J. Environ. Sci. Health, **28(10),** 2263-2280 (1993).

14 M.KORCZAK, J.KURBIEL:Wp³yw specyficznych w³asnoœci adsorbentu mineralno wêglowego na adsorpcjê wybranych barwników i zwi¹zków powierzchniowo czynnych. Materia³y Konferencyjne nt. Wêgiel Aktywny. Kraków, Polska, (1987).

15 A.D.SMIRNOW: Sorbcjonnaja oczystka wody. Chimija. Leningrad 1982.

16 D.C.SHARMA, C.F.FORSTER: A comparison of the Sorptive Characteristics of leaf Mould and Activated carbon Columns for the Removal of Hexavalent Chromium. Process Biochem., **31**, no.3, 213-218 (1996).