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Functionalized activated carbons for the removal of inorganic pollutants

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ABSTRACT

Activated carbon (AC) is an effective adsorbent for organic molecules but not for small and polar compounds, such as metals and oxyanions. This study presents preliminary results of a series of commercially prepared specifically modified activated carbons, aiming at removal of oxyanions and heavy metals. Breaktrough experiments were performed for chromate, arsenate, perchlorate and nickel, with concentrations between 700–9000 ppb. Complete removal of pollutants is observed for hundreds to thousands of bed volumes depending on the pollutant concentration. Exhausted columns with chromate were regenerated for reuse during at least seven cycles, and performance was slightly reduced (270 pore volumes at the 7th cycle, compared with 300 pore volumes at the 1st cycle). A pilot filtering device of 60 l was established in a metal plating factory, which has operated successfully for five months at least. A sorption kinetics experiment was performed at the pilot site, by adding a known amount of chromate and measuring reduction in its concentration with time. Measured results follow first order sorption kinetics, coinciding fully with theoretically evaluated rate constant, indicating complete removal.

Keywords: Adsorption; Activated carbon; Arsenic; Chromium; Nickel; Perchlorate; Breakthrough diagram; Sorption kinetics

1. Introduction

In arid and semi-arid zones the amount of water is limited. In addition, in many developed as well as developing and underdeveloped countries, sewage and industrial waste have contaminated water reservoirs with organic and inorganic pollutants, thus threatening health and environment. Water reuse and purification of polluted water reservoirs could be the key for increased development, but it should be ensured that quality of the reused water and the purified water does not impose environmental hazards. Industrial and household sewage might contain several chemicals that must be removed, especially chemicals defined by the US Federal Clean Water Act as “priority pollutants”, which might be hazardous to human health and the environment [1].

Among other inorganic chemicals that should be removed before almost any water reuse, are trace elements, such as arsenic, nickel, chromium, as well as toxic specific species of relatively non-toxic elements, as the oxyanion perchlorate, which has been reported to pose neurodevelopmental risk to infants [2,3].

Carbon has been used as an adsorbent for water treatment for hundreds of years. The first documented use of carbon for water treatment was in 200 BC “to remove tastes” [4]. In 1785, experimental chemists learned that

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carbon could accumulate unwanted disagreeable contaminants from water. Carbon in the activated form was first used as a filter medium in the late 1800s. The use of carbon for adsorption progressed in the late 19th and early 20th centuries, when vapor phase organic carbon was developed and given its first widespread use as a defense against gas warfare during the First World War. Activated carbon (AC) is a natural material derived from bituminous coal, lignite, wood, coconut shell, etc., activated by several means. Carbon particles are "activated" by exposing them to an activating agent, such as steam at high temperature. This process develops a porous, three-dimensional graphite lattice structure. The size of the pores depends on the exact treatment. Longer exposure times result in larger pore sizes. Granular activated carbon (GAC) filters used for water treatment were first installed in Europe in 1929. In the 1940s, GAC was found to be an efficient purification and separation technology for the chemical industry. By the late 1960s and early 1970s, GAC was found to be very effective for removing a broad spectrum of synthetic chemicals from water and gases (i.e., from the vapor phase). GAC, in granular form, is designated by sizes for liquid or vapor phase applications. The most popular aqueous phase carbons are the 12×40 and 8×30 sizes because they have a good balance of size, surface area, and head loss characteristics [4].

Activated carbon (AC) is considered an effective adsorbent for large organic molecules but not for small and polar compounds [4] such as metals and oxyanions [5]. In the case of chromium and arsenic, for example, activated carbon only removes a few milligrams of metal ions per gram of sorbent and severe regeneration problems exist [6,7]. Several studies have suggested different modifications for activated carbon by various chemical treatments [8]. Such modifications might result in different physical and chemical properties and therefore different sorption characteristics [5,9–11]. For example, acid treated activated carbon (Calgon F400, Calgon Carbon Corp., USA) was shown to have different sorption characteristics for phenol due to changes in the functional groups on the AC surface [10]. Başar et al. [11] studied the effect of modification of AC by surfactants on the electrostatic properties of the surface (zeta potential) and concluded that adsorption of ionic surfactants by hydrophobic interactions might lead to charged AC surface.

Monser and Adhoum [5] studied the removal of heavy metals by AC treated with cationic (tetrabutyl ammonium) or anionic (diethyldithiocarbamate) modifiers and found that the modification with tetrabutyl ammonium led to a better sorption capacity for Cr(VI). However, the cations used as modifiers in this study did not adsorb completely to the AC and, therefore, there is a high probability that modifier molecules might leak from the AC to the treated effluent, polluting by themselves, and even releasing the chromate previously adsorbed.

Garcia-Martin et al. [12] described the adsorption of two pyrimidine-containing compounds on the surface of activated carbon and the removal of chromate ions from aqueous solutions.

Methods for removal of perchlorate have been proposed, by passing the polluted fluid over activated carbon, wherein the activated carbon has been either preloaded with an organic cation functional group or organic cation polymer or cationic monomer, or tailored with ammonium or other reduced nitrogen-containing compound [13].

Yin et al. [8] review several studies that suggested different modifications for activated carbon by various chemical treatments, resulting in different physical and chemical properties and therefore different sorption characteristics. However, most modifications showed only moderate improvement, increasing sorption of heavy metals two to four times, when compared with virgin AC. Moreover, even in cases where application was evaluated as increasing effectively sorption of an inorganic pollutant, the regeneration of the sorbent, required thermal treatment, and was not demonstrated [13].

In general, regeneration procedures might be crucial for cost effectiveness of the sorbent. Reuse of the sorbent and recycling and sale of the recovered substance might lower prices and solve the problem of solid waste disposal. However, the quality of the recycled product is always in question [7].

This article reports a series of commercially prepared specifically modified activated carbons based on ionic organic modifiers or chelates added at 10–15% of the total weight of the sorbent, designed for the removal of oxyanions such as chromate, arsenate, selenate, etc., or heavy metals as nickel, copper, zinc, cadmium, etc. Sorbents were tested for chromium, arsenic, nickel and perchlorate, and complete removal of pollutant was observed for hundreds to thousands of bed volumes depending on the pollutant concentrations. In experiments performed with chromium, the exhausted sorbent may be regenerated for reuse during at least seven cycles, with only slight decrease in the performance, while chromium was recovered aiming for its possible reuse as resource. A pilot device for chromium is presented, and sorption kinetics test of it was performed, showing a first order kinetics process, fully coinciding with theoretical evaluations.

2. Materials and methods

Modified granular AC for arsenic (As-N2LF02, containing 10.4% modifier), chromate (Cr-Y12AYJ04, 12.2% modifier), nickel (Ni-Y12OGM05, 9.9% modifier) and perchlorate (ClO_4-Y12CAH04, 15.5% modifier) were supplied by ToxSorb Ltd. (Kfar Giladi, Israel). Modifications are based on the binding of aromatic molecules to the activated carbon matrix. Organic modifiers consist of a hydrophobic part based on one or several separated or fused aromatic rings, which anchors the modifier to the AC, and an ionic or polar part, which interacts with the pollutant [14]. Modifications make the sorbent suitable for removal of metal and other inorganic molecules, without hindering the capabilities of sorption of organic pollutants. Modifiers were tested by washing several times with distilled water, and no release of organic compounds was detected.

Breakthrough diagrams were prepared separately for each of the following pollutant solutions: (a) As 100 μM (7490 ppb As) added as $NaHAsO_4$, (b) Cr 100 μM (5200 ppb Cr) added as K_2CrO_4, (c) Ni 150 μM (8670 ppb Ni) added as $NiCl_2$, (d) 7.04 μM perchlorate (700 ppb ClO_4^-) added as $KClO_4$. All pollutants were purchased from Sigma-Aldrich, except Ni which was obtained from a commercial Ni plating compound. Filtering columns for As, Cr and perchlorate experiments were prepared on 15 ml plastic cylindrical columns (26.5 cm length and 0.567 cm^2 cross section), with pore volume of 7–7.5 ml, depending on the sorbent. Ni adsorption columns had 50 ml volume (5.07 cm^2 cross section, and 10.4 cm length, cylindrical for about 85% of the length, and conical for the rest of it), with pore volume of 24.8 ml.

Concentrations of pollutants were determined as follows: (a) As was measured by a colorimetric procedure [15] by means of a diode-array HP 8452A UV-Visible spectrophotometer. (b) Chromium concentration were measured by means of the UV-Visible spectrophotometer mentioned, ($\varepsilon_{372} = 4986\ M^{-1}cm^{-1}$) after NaOH spiking, in order to insure that chromate is present as a divalent anion. (c) Nickel concentrations were measured by a SPECTRA ICP-AES. (d) Perchlorate concentrations were measured by IC, according to EPA 314 standard method.

The chromium sorbing column was brought to saturation and regenerated for seven times. Regeneration procedures are available for all the four sorbents, and differ slightly depending on the pollutant [14]. For the Cr sorbing platform, the procedure is based on washing the filter with the equivalent of two pore volumes of a highly concentrated chloride solution, followed by two pore volumes of water to wash excesses of regenerating solution. The amount of chromate recovered was precipitated at each cycle by reduction of the eluent, obtaining >95% recovery, when compared with amounts adsorbed as evaluated from breakthrough experiments. The same regeneration solution (after chromium separation) was used for all cycles.

A pilot device for the removal of chromate is fully operational in a plating factory in Northern Israel. The device filters the washing tank of a Cr-passivation process, and returns the filtered water to the tank, allowing its reuse. Washing tank size is 530 l, and the filter is based on 65 l of Cr-Y12AYJ04, with a pore volume of 30 l. The pump might be calibrated for flow rates ranging between 1.7–17 l min^{-1}. Additional details are described in the Results section.

For the kinetic experiment 100 ml of highly concentrated commercial Cr compound were poured to the washing tank, achieving an initial concentration of 650 ppb Cr. 20 ml of water from the outlet of the filter and from the washing tank were sampled at variable time lapses, for approximately 5 h, and Cr concentrations were determined as described above. From the results, the rate constant was evaluated and compared with the calculated value.

3. Results

Fig. 1a presents removal of perchlorate from a 7.040 μM (700 ppb) effluent, by means of a ClO_4-Y12CAH04 filtering column, with a flow rate of 3.1 ml min^{-1}, yielding a retention time of approximately 5 min. The ClO_4-Y12CAH04 sorbent removed completely the perchlorate for more than 5500 pore volumes, whereas with regular, non-modified activated carbon a considerable concentration of ClO_4^- was measured already after 50 pore volumes. The results imply more than 1000 fold improvement when compared with the non-modified AC. The matrix was tap water, containing 22 ppm chlorides, electric conductivity of about 350 mSi cm^{-1} and pH = 7.8. For this experiment a spiking concentration of 40,000 ppb nitrate was added. Nitrate is known to reduce performance of several perchlorate sorbing platforms, but it did not hindered efficiency of removal of the ClO_4-Y12CAH04.

Fig. 1b shows a breakthrough diagram of a 100 μM arsenate (7490 ppb As) solution removed by means of a As-N2LF02 column, with a flow rate of 33 ml min^{-1}, yielding a very short retention time of less than 0.5 min. The matrix was tap water (described above). Complete removal can be observed for more than 100 pore volumes. A similar breakthrough 50 ml column based on Ni-Y12O-GM03 sorbent, with a flow rate of 5.1 ml min^{-1}, yielding a retention time of approximately 10 min, was prepared for a Ni solution of 150 μM (8670 ppb) concentration. The matrix in this case was tap water, with additional 0.43 mM SO_4^{2-}, coming from the industrial Ni solution. Complete removal of Ni was observed (Fig. 1b) for more than 300 pore volumes.

Fig. 1c shows breakthrough diagram of a 100 μM chromate (5200 ppb Cr) solution on a Cr-Y12AYJ04 column. Different lines show adsorption after first cycle (with a flow rate of 1.78 ml min^{-1}, yielding a retention time of approximately 8.5 min) and seventh cycle of regeneration (with a flow rate of 5.36 ml min^{-1}, yielding a retention time of less than 3 min). The experiment demonstrated (results not shown) that the slight decrease in performance occurs mainly at the first two regeneration cycles, whereas afterwards the amounts adsorbed remain unchanged for the rest of the experiment (5 additional cycles).

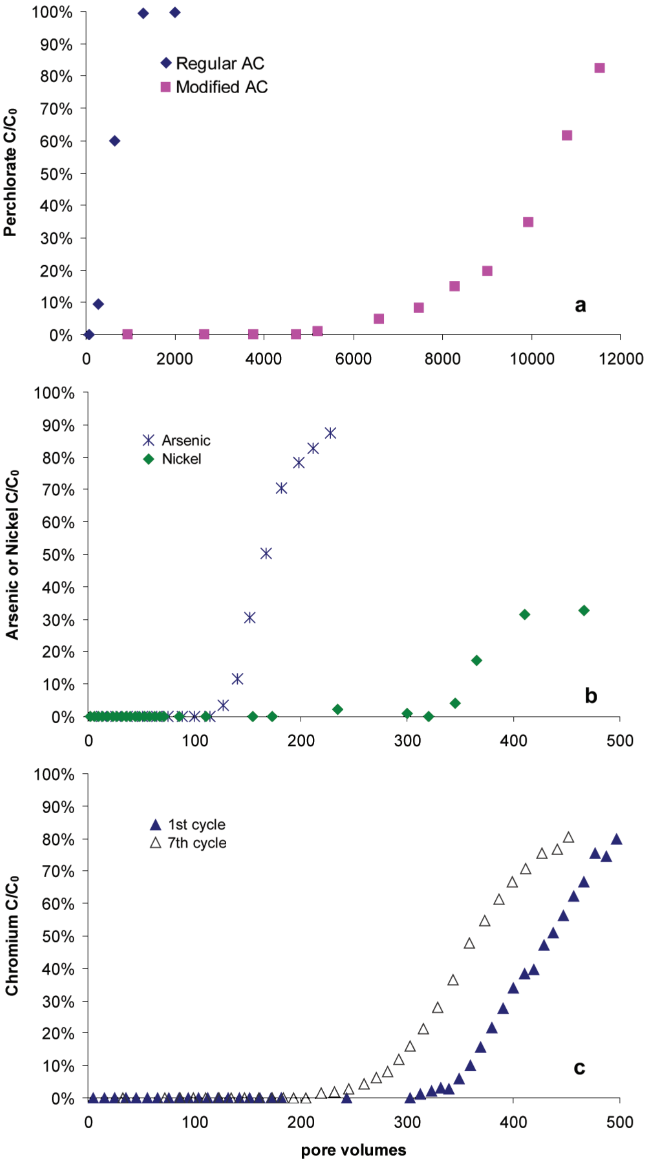

Fig. 1. Breakthrough diagrams for modified activated carbon columns (1a) perchlorate removal from a 700 ppb effluent by regular AC (rhombus) and modified AC (squares), (1b) arsenic (asterisk) and nickel (rhombus) removal from 7490 and 8670 ppb effluents, respectively (1c) chromium removal from a 5200 ppb effluent. Full triangles show first filtering cycle, empty triangles show behavior for a filter polluted and regenerated for 7 cycles.

Cr-Y12AYJ04 was also used for the preparation of a fully operational pilot filtering device, established in a metal plating factory at Tefen Industrial Zone, in Northern Israel. Approximate cost of the sorbing material when prepared in relatively small amounts was about 4$/kg. The Cr filtering device was installed on April 30th, 2009, and started working the next day. Fig. 2 shows a schematic diagram of (a) the filtering process and (b) the regeneration cycle. Basically- the filtering device is connected to a washing bath (see Fig. 2a). Metal parts produced by the factory are dipped in the high Cr-concentration plating solution for a given period of time depending on the treatment (Fig. 2a-1). Dipped parts are afterwards introduced in the washing bath, and surplus of Cr from the dipped parts enters the washing bath. Water with Cr (50–1000 ppb) from the washing bath is pumped through NP1-Cr filter at a rate controlled by the rate of removal required (Fig. 2a-2). At the filtering column the solution flows in contact with the sorbent material for 1–5 min, and Cr is removed from the effluent for 1000–10,000 bed-volumes, depending on the input concentration (Fig. 2a-3). The effluent leaves the filter (Fig. 2a-4), while Cr concentration and electrical conductivity are monitored (Fig. 2a-5) to ensure safe Cr levels and monitor filter saturation. As long as the filter is not saturated, and outlet Cr concentrations are low, effluent is returned to the washing bath (Fig. 2a-6).

When monitoring indicates beginning of increase of Cr concentration, saturation of the filter is assumed. At this stage, the filtering column is replaced, and the saturated cartridge is treated for regeneration of the sorbent (Fig. 2b). The saturated column (Fig. 2b-1) is connected to a pump, and high chloride regeneration solution is pumped through the filter (Fig. 2b-2). Cr is released from the filter by means of 2–3 bed volumes of regeneration solution (Fig. 2b-3), and washed with additional 1–2 bed volumes of water to remove excess of regeneration solution compounds. The very high Cr concentration solution (together with water use to flush excess of regeneration solution) is pumped to a separate container (Fig. 2a-4), where by means of a simple redox process, chromium is separated from the regeneration solution (Fig. 2a-5). The cleaned regeneration solution is returned to the regeneration storage tank (Fig. 2a-6), whereas the chromium might be returned as a resource to the industrial process (Fig. 2a-7).

An experiment aiming to test the sorption kinetics of the pilot filter was performed as described in Materials and Methods. It was assumed and confirmed that the process should follow a first order kinetic behavior. Thus, C_t — the concentration of the pollutant at time t, should obey the "first order integrated rate law" [16]:

$$C_t = C_0 e^{-\lambda t} \qquad (1)$$

where C_0 is the initial concentration (meaning C at $t = 0$. In this case $C_0 = 650$ ppb), λ is the kinetics rate constant, and the minus sign indicates decreasing concentrations.

A theoretical estimate for the rate constant λ may be obtained: considering the total volume of liquid at any moment is 560 l (530 at the tank and additional 30 l in the filter), and the flow rate is 600 l/h (thus, 10 l min^{-1}). Assuming complete removal at the filter implies that at any given minute 10 l out of a total of 560 l are purified,

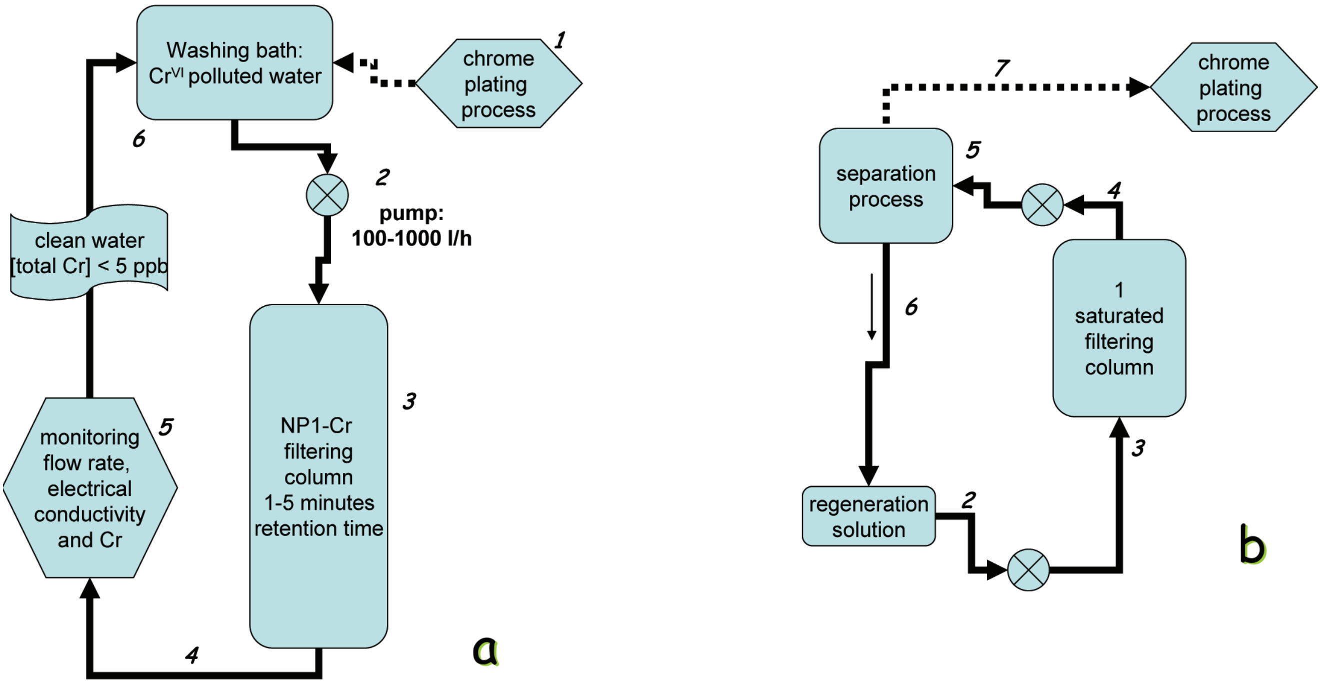

Fig. 2. Schematic diagram of (a) the filtration and (b) the regeneration processes. Detailed explanation for each stage is presented in the text.

thus: $\lambda = 10\text{ l min}^{-1}/560\text{ l} = 0.01786\text{ min}^{-1}$. In first order processes "half life period", $t_{0.5}$, can be defined as the time taken for the concentration to fall to half its initial value [16]. Reordering Eq. (1) and introducing $C_t/C_0 = 0.5$, yields

$$t_{0.5} = \frac{\ln 2}{\lambda} = 38.81\text{ min}$$
.

Fig. 3 shows results of the kinetic experiment. It can be seen that no Cr is detected at the filter outlet, during the whole experiment, and the measured values for the Cr concentration at the washing tank fully coincide with the theoretical estimate. By performing exponential regression to the measured results, an actual initial concentration of 701 ppb and a rate constant of 0.0191 min^{-1} are obtained ($t_{0.5} = 36.3$ min), with $R^2 = 0.9904$. Those values fit very well the theoretical estimates of $C_0 = 650$ ppb and $\lambda = 0.0179\text{ min}^{-1}$, respectively.

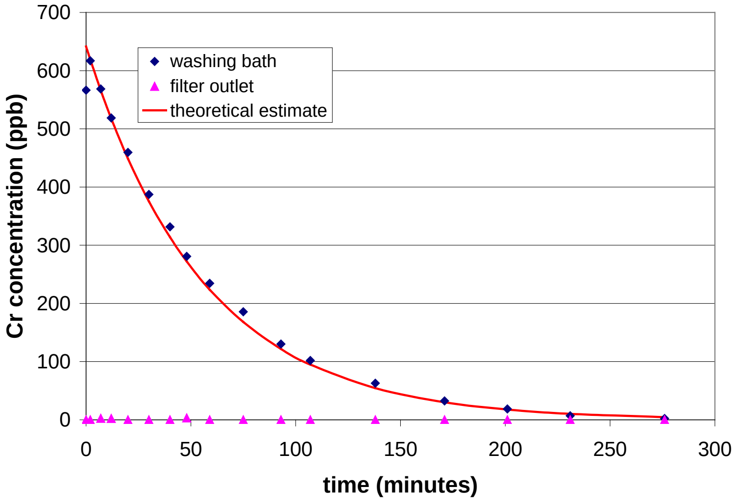

Fig. 3. Cr concentration at the washing bath (rhombus) and at the filter outlet (triangles) as a function of time, after addition of 650 ppb Cr. Line represents calculated concentrations assuming a first order reaction with $C_0 = 650$ ppb and rate constant of 0.01786 min^{-1}.

4. Conclusions

This study presents a series of commercial sorbents based on modified activated carbon, which successfully removed perchlorate, arsenic, chromium and nickel for hundreds to thousands of bed volumes, depending on the pollutant concentration. Regeneration of the chromium filters is presented indicating a slight decrease in performance, but even after seven regeneration cycles the sorbent still succeeds in removing Cr from a 5200 ppb solution, for more than 250 pore volumes. A pilot device based on that sorbent was built and has operated for at least five months. Evaluations based on chloride concentration at the washing tank (results not shown) assuming average rate of use of the chromium plating line remains unchanged, indicate that first regeneration cycle of the pilot filter will be performed after approximately six months.

A sorption kinetic experiment was performed. The importance of such experiment is that it can monitor the performance of the device: if rate constant found is considerably lower than theoretical evaluations, yielding half-live period considerably larger than 39 min, that could imply that incomplete removal is achieved because the actual pore volume of the filter is smaller than planned due to clogged pores or preferential flow in large cracks at the filter. The fact that measured results coincide fully with theoretical estimates indicate that the filter removes completely the Cr, and the total pore volume of the sorbent is in contact with the polluted solution.

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Abbreviations

AC — Activated carbon
GAC — Granular activated carbon
UV — Ultraviolet

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