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Airi Paajanen[a]; Jukka Lehto[a]; Tarja Santapakka[a]; J. Philippe Morneau[a]
[a] Laboratory of Radiochemistry, Department of Chemistry, UNIVERSITY OF HELSINKI, Helsinki, Finland

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SORPTION OF COBALT ON ACTIVATED CARBONS FROM AQUEOUS SOLUTIONS

Airi Paajanen, Jukka Lehto, Tarja Santapakka, and J.Philippe Morneau
Laboratory of Radiochemistry, Department of Chemistry
P.O.Box 55, FIN-00014 UNIVERSITY OF HELSINKI
Helsinki, Finland

ABSTRACT

The efficiencies of 15 commercially available activated carbons were tested for the separation of trace cobalt (^{60}Co) in buffer solutions at pH 5.0, 6.7, and 9.1. On the basis of the results four carbon products, Diahope-006, Eurocarb TN5, Hydraffin DG47, and Norit ROW Supra, were selected for further study. These carbons represented varying (low, medium, and high) cobalt removal efficiencies and were prepared of three typical raw materials: peat, coconut shell, or coal. Study was made of the effects on sorption efficiencies of factors of interest in metal/radionuclide-bearing waste effluents. These factors were pH, sodium ions, borate, and citrate.

INTRODUCTION

Activated carbons are extensively used to remove organic contaminants in industrial and municipal waste-water treatment processes and to remove harmful gaseous agents in air purification and gas cleaning processes

(1,2). In the metallurgical industry they are used to recover valuable metals, gold and silver, in particular, from aqueous solutions (1). They are also known to take up organic metal complexes from solution (3). Separation of metal ions by activated carbons has not been extensively studied. The present work was undertaken to obtain fundamental data on the sorption of trace cobalt ions on activated carbons. The main tasks were to investigate the mechanism of cobalt ion sorption and to select the best carbon products for the removal of radioactive cobalt from nuclear waste solutions. A most interesting question was to find out whether cobalt ion sorption takes place by ion-exchange mechanisms. Activated carbons consist of randomly oriented graphite-type carbon layers with various oxidized groups in the layer edges (1). Some of these groups, such as carboxylic and phenolic, probably act as ion-exchanging groups.

MATERIALS AND METHODS

The commercially available activated carbons that were tested are listed in Table 1. All carbons were granular in form and had been activated by steam processing. Most of the carbons were recommended by the manufacturers for use in water treatment; several were recommended for air and gas purification, and two of these were impregnated for special gas purification: Pittsburgh Type HGR contains about 13% elemental sulfur and Eurocarb PHO 5KI 5% potassium iodide.

Sorption of cobalt ions on the activated carbons was investigated by a batch method: 20 mL of cobalt solution with either ^{60}Co or ^{57}Co tracer and 0.20 g of carbon was shaken in a sealed polyethylene vial. Because the particle size of the initial carbon products varied in a wide range, all carbons were crushed and sieved for the 0.14-0.30 mm (50-100 mesh) particle size fraction (Table 1).

Following equilibration, the carbon was separated from the solution by filtration through a filter with pore size 0.22 μm. The pH of the filtrate was measured

TABLE 1. ACTIVATED CARBONS TESTED IN THE EXPERIMENTS

Carbon		Manufacturer	Raw Material	Particle Size (mm)
Filtrasorb 400	a)	Chemviron Carbon	Coal	0.42-1.70
Chemviron Carbon BPL	b)	Chemviron Carbon	Coal	2.00-4.75
Pittsburgh Type HGR	b)	Chemviron Carbon	Coal	2.00-4.75
Diahope-006	a)	Mitsubishi Kasei Co.	Coal	0.42-1.68
Diahope-S80	a),c)	Mitsubishi Kasei Co.	Coal	0.42-1.68
Eurocarb PHO	b)	Eurocarb Products Ltd.	Coconut shell	0.35-1.41
Eurocarb PHO 5KI	b)	Eurocarb Products Ltd.	Coconut shell	1.68-3.36
Eurocarb TN5	d)	Eurocarb Products Ltd.	Coconut shell	1.68-3.36
Eurocarb YAO WW	a),b)	Eurocarb Products Ltd.	Coconut shell	0.35-0.84
Hydraffin 30	a)	Lurgi Aktivkohle GmbH	Coal	0.5-2.5
Hydraffin DG47	a)	Lurgi Aktivkohle GmbH	Coal	1.0-2.5
Hydraffin CC	a)	Lurgi Aktivkohle GmbH	Coconut shell	0.5-2.5
Norit PK	a)	Norit N.V.	Peat	0.25-1.0
Norit RB2	b)	Norit N.V.	Peat	dia. 2
Norit Row Supra	a)	Norit N.V.	Peat	dia. 0.8

Manufacturer's recommendation for general applications: a) water treatment, b) air and gas purification, c) food industry, d) precious metals recovery.

immediately after the separation of carbon. All solutions were prepared in deionized water and from *pro analysis* grade reagents. Experiments were done at ambient temperature (20-25 °C). The concentration of cobalt in the solution was determined by measuring the ^{60}Co or ^{57}Co tracer activity with NaI crystal and a single-channel analyser. As a measure of the cobalt sorption efficiency, the distribution coefficient (K_D) was calculated. The distribution coefficient is the ratio of the equilibrium concentration of cobalt in carbon to the concentration of cobalt in solution and is calculated in the following way:

$$K_D = (A_0/A - 1) \times V/m \text{ (mL/g)}, \qquad (1)$$

where A_0 and A are the activities of ^{60}Co/^{57}Co in the solution before and after the treatment, respectively; V is the solution volume (mL); and m is the mass (g) of the activated carbon.

The first set of experiments was carried out with all 15 activated carbons in three buffer solutions: buffer I was 0.05 mol/L sodium citrate solution at pH 5.01; buffer II, 0.05 mol/L sodium citrate/0.1 mol/L NaOH solution at pH 6.66; and buffer III, 0.03 mol/L sodium borate/0.1 mol/L HCl solution at pH 9.07. All buffer solutions were adjusted to 0.1 mol/L with respect to sodium ion concentration, and they contained 0.3 μmol/L inactive cobalt together with ^{60}Co tracer. The equilibration time was 18 hours.

On the basis of these first tests (Table 2), four carbons, Diahope-006, Eurocarb TN5, Hydraffin DG47 and Norit ROW Supra, were selected for further investigation. The effects of the following factors on the cobalt sorption were studied: pH, concentrations of sodium ions, and complexing agents.

The effect of pH on the cobalt sorption was studied by determining the distribution coefficient of trace cobalt (^{57}Co, Co concentration, $1.8 \cdot 10^{-8}$ mol/L) in deionized water at various pH levels adjusted with NaOH or HCl. Carbon samples of 1.0 g were shaken in 50 mL of cobalt solution until the pH leveled off. This took 7-10 days; pH values were recorded in nitrogen atmosphere to avoid the intrusion of carbon dioxide into the system at higher pH values. ^{57}Co tracer, which has a higher specific activity than ^{60}Co, was used to avoid precipitation of cobalt hydroxide in alkaline solutions.

The effect of sodium ion concentration on the distribution of ^{60}Co (Co concentration, 0.3 μmol/L) was determined in the concentration range 10^{-5} mol/L to 1.0 mol/L. Equilibration time was 42 hours. Before these experiments, a 30- to 40-g sample of each carbon was treated in a column with 1.0 L of 1.0 mol/L NaCl/1.0 mmol/L NaOH solution and then rinsed with 50 mL deionized water. The purpose of this treatment was to convert the presumed ion-exchange sites into Na^+ form. After NaCl/NaOH/H_2O treatment, the carbon was dried at 110°C for 18 hours.

The effects of complexing agents, sodium tetraborate ($Na_2B_4O_7$) and sodium citrate ($Na_3O_7C_6H_5$), on the distribution coefficient of ^{60}Co (Co

TABLE 2. SORPTION OF COBALT ON DIFFERENT ACTIVATED CARBONS IN THREE BUFFER SOLUTIONS

Carbon	Buffer I		Buffer II		Buffer III	
	K_D	pH_{eq}	K_D	pH_{eq}	K_D	pH_{eq}
Filtrasorb 400	105	5.28	4610	7.74	910	9.06
Chemviron Carbon BPL	120	5.26	6400	7.55	1450	9.13
Pittsburgh Type HGR	40	5.02	220	7.23	930	9.03
Diahope-006	250	5.26	13260	7.59	1900	9.10
Diahope-S80	220	5.27	12620	7.63	1300	9.10
Eurocarb PHO	90	5.31	2300	7.47	2830	9.09
Eurocarb PHO 5KI	75	5.32	1470	7.38	3570	9.08
Eurocarb TN5	20	5.25	460	7.36	760	9.06
Eurocarb YAO WW	130	5.24	2530	7.35	5560	9.07
Hydraffin 30	100	5.24	4160	7.77	2970	9.06
Hydraffin DG47	130	5.24	6550	7.47	6920	9.07
Hydraffin CC	70	5.31	1970	7.57	2030	9.05
Norit PK	30	5.25	210	7.84	3560	9.09
Norit RB2	90	5.36	390	7.67	2670	9.13
Norit ROW Supra	85	5.38	430	7.84	2920	9.10

concentration, 10 μmol/L) were studied in the concentration range 10^{-6} to 10^{-3} mol/L. Prior to the sorption experiments, the solutions were left standing for 70 hours at room temperature to allow the complexation of cobalt with the agent.

Adsorption of cobalt onto the vials and filters. The polyethylene vials used in the equilibration of carbon adsorbed 6% of the cobalt from 0.3 μmol/L Co solution at pH 4, but no adsorption from the buffer solutions was found. Three different syringe filters were also tested: Millex GV (Millipore, filter polyvinylidene fluoride, housing polyethylene), I.C. Acrodisc (Gelman, filter polyethersulfone, housing polypropylene) and Acrodisc LC (Gelman, filter polyvinylidene fluoride, housing polypropylene). From 0.3-μmol/L Co solution at pH 4, the Millex GV filter adsorbed about 50% of the cobalt and the

I.C.Acrodisc filter 4%. There was found to be virtually no adsorption from the buffer solutions. In the experiments described above, Acrodisc filters were used. Thus, the interference due to adsorption onto the vials and filters was assumed to be negligible.

RESULTS AND DISCUSSION

Sorption of Cobalt from Buffer Solutions

Cobalt sorption efficiencies of the 15 activated carbons varied in a wide range (Table 2), the distribution coefficients being 20 - 250 mL/g in the citrate buffer at pH 5.0, 210 - 13,260 mL/g in the citrate buffer at pH 6.7, and 760 - 6,920 mL/g in the borate buffer at pH 9.1. All carbons sorbed cobalt very poorly from solutions at low pH, but the sorption efficiency increased rapidly with pH. This is as would be expected, if the cobalt ions were taken up in an ion-exchange process. Any ion-exchange groups present, for example, carboxylic and phenolic groups, would be weakly acidic and not dissociate in the acidic region and thus not be capable of taking up metal ions.

Some carbons had a sorption maximum at equilibrium pH about 7.5, while the others had the highest K_D value at pH 9.1 (Table 2). It is interesting that all five coconut shell carbons took up cobalt most efficiently at pH about 7.5 and all three peat carbons at pH 9.1. The behaviour of the coal carbons was not so straightforward: five materials had a maximum efficiency at pH about 7.5 and two materials at pH 9.1. As will be seen below, distribution coefficients determined in plain water increased systematically with pH, with no maxima (Fig. 1). Probably, therefore, the maxima in the distribution coefficients of some carbons at pH 7.5 were due to the change in buffer anion from citrate at initial pH values 5.0 and 6.7 to borate at pH 9.1. Citrate ions (L) form monocomplexes with Co^{2+}, the logK (stability constant) for the reaction $Co^{2+} + L = CoL$ being 5.00 (4). Boric acid ($L = B(OH)_4^-$), in turn, forms a tetracomplex, with the logK for CoL_4 being 10.03 (4). Study of the initial buffer solution species of cobalt with the SPE programme (6) revealed that cobalt was 97% in the form of citrate complex at pH 5.1 and 100% in that form at pH 7.5. The stability constant of the borate complex is so low, by contrast, that no borate complex was present at pH 9.1, but 65.2% of cobalt was present as Co^{2+}, 18.4% as $CoOH^+$, and 16.4% as soluble $Co(OH)_2$.

Of the 15 activated carbons screened, Diahope-006, Eurocarb TN5, Hydraffin DG47, and Norit ROW Supra were selected for further investigation. The objectives of this further study were to identify active carbon products with good sorption properties for cobalt removal applications and to gain a better understanding of the sorption process. Activated carbons prepared of different materials and having different cobalt separation efficiencies—low, medium and high—were accordingly selected. Table 3 shows the K_D values of these four carbons in the three buffer solutions and in plain water at the same pH value (values in water taken from Figure 1).

As seen in Table 3, the K_D values obtained in buffer solutions were comparable to the values obtained in plain water, except those obtained in citrate buffers with Hydraffin DG47 and, especially, with Diahope 006. One would expect complexation of cobalt with citrate to compete with ion exchange and, in that way, decrease the sorption on active carbons, but this was not the case. One feasible explanation for the increase in K_D is that carbons, such as Hydraffin DG47 and Diahope 006, may take up cobalt complexes even more effectively than cobalt ions. This is discussed further below.

Effect of pH on the Distribution Coefficient of Cobalt

More detailed investigations with the selected activated carbons Diahope-006, Eurocarb TN5, Hydraffin DG47, and Norit ROW Supra showed that these carbons take up virtually no Co^{2+} ions at pH 4 or below (Fig. 1). Above pH 4 the distribution coefficient increased sharply. At pH 11 the highest

TABLE 3. DISTRIBUTION COEFFICIENTS OF ^{60}Co ON FOUR ACTIVATED CARBONS IN THREE BUFFER SOLUTIONS AND IN PURE WATER SOLUTIONS AT THE SAME pH VALUES

Carbon	Distribution coefficient (K_D)					
	Buffer I	Water at pH 5.3	Buffer II	Water at pH 7.5	Buffer III	Water at pH 9.1
Diahope-006	250	10	13260	170	1900	1400
Eurocarb TN5	20	35	460	310	760	1400
Hydraffin DG47	130	20	6550	280	6920	1500
Norit Row Supra	85	40	430	680	2920	6500

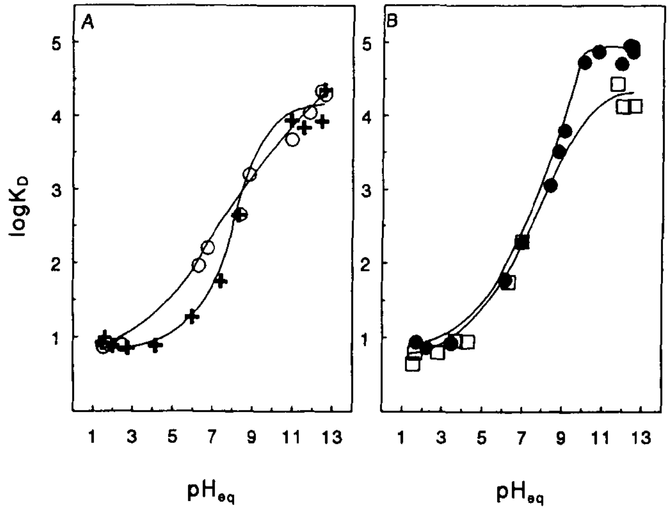

FIGURE 1. Distribution coefficient (K_D) of cobalt on activated carbons as a function of pH. A: Diahope-006 (✚), Eurocarb TN5 (○); B: Hydraffin DG47 (□), Norit ROW Supra (●).

distribution coefficient was obtained with Norit ROW Supra (75,000 mL/g), while the K_D for the other carbons was approximately one order of magnitude lower. The K_D for Norit ROW Supra, Hydraffin DG47, and Diahope-006 seemed to level off at pH 10-11, but that of Eurocarb TN5 was still increasing at pH 12.6. The pH behaviour of the cobalt ion sorption suggests that there is a weakly acidic group (or groups) in the carbons responsible for the ion uptake. The carboxylic group is a likely candidate since it typically starts to dissociate at pH values 4-6 in weakly acidic ion-exchange resins. Eurocarb TN5 may contain an additional, even more weakly acidic group, such as the phenolic group, which dissociates only at relatively high pH values.

It is obvious that the dissociation of the weakly acidic groups was not the only factor affecting the cobalt uptake in the alkaline region. Solution phase hydrolysis of cobalt is also important since it competes with ion exchange. The concentration of cobalt was so low that no precipitation of cobalt hydroxide took place. Soluble hydrolysis species, however, form in alkaline solutions. Below the pH value 8 the prevailing species is Co^{2+}, whereafter $CoOH^+$, soluble $Co(OH)_2$, and $Co(OH)_3^-$ start to form, having their maximum concentrations at pH 9.4 (22%), pH 10.9 (97%), and pH 13.7 (85%), respectively.

Effect of Sodium Ion Concentration on the Distribution Coefficient of Cobalt

Increasing sodium ion concentration had a relatively large and peculiar effect on the cobalt sorption (Fig. 2). If the uptake of cobalt ions by active carbons (AC) (previously treated with NaCl to convert them into Na^+-form, NaAC) was exchange of Co^{2+} ions, then increasing sodium ion concentration should decrease the distribution coefficient according to the following reaction equation:

$$2NaAC + Co^{2+} <==> Co(AC)_2 + 2Na^+. \qquad (2)$$

This should occur because the equilibrium would be shifted to the left-hand side. A decrease of this kind was found only for Eurocarb TN5 carbon. For other

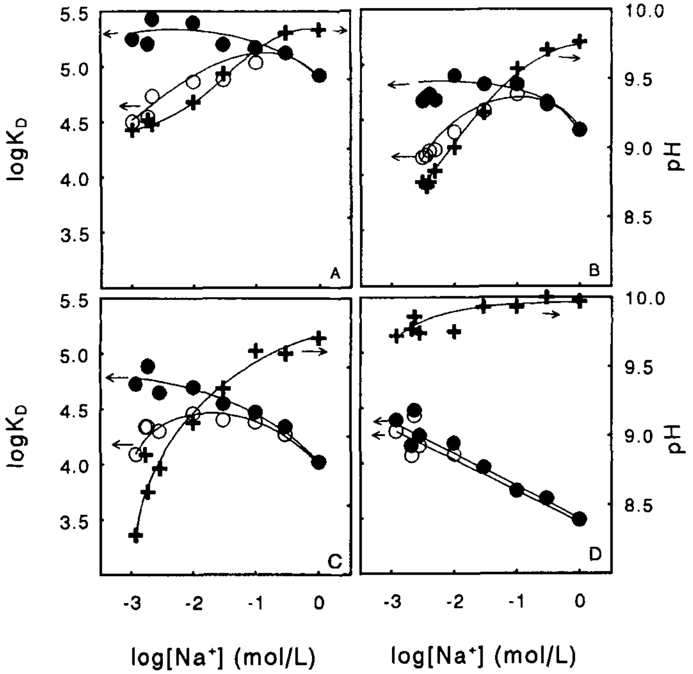

FIGURE 2. Distribution coefficient (K_D) of cobalt on activated carbons as a function of sodium ion concentration. A: Norit ROW Supra, B: Diahope-006, C: Hydraffin DG47, D: Eurocarb TN5. ✚ = equilibrium pH, ○ = K_D at equilibrium pH, ● = K_D values normalized to constant pH.

carbons, a maximum in K_D was found in sodium concentrations between 0.01mol/L and 0.1mol/L (Fig. 2, circles). The equilibrium pH increased with these carbons by approximately one unit (Fig. 2, pluses). Normalization of the K_D values to a constant pH of the 1mol/L NaCl solutions results in a more expected behaviour: decrease in K_D with increasing sodium ion concentration (Fig. 2, filled circles). For an ideal Co^{2+} for Na^+ exchange, a straight line with a slope of -2 should be obtained. Presence of the hydrolysis species of cobalt, however, obviously distorts the ideal picture (5). With inorganic ion exchangers it is a common phenomenon that they peptize, i.e., release colloidal particles, which are very difficult to remove by filtration (5). This is especially true for dilute solutions. Thus, it is possible that the K_D values in low sodium concentrations were somewhat lower than would have been the case if all the carbon colloids had been removed.

In the solutions with the initial concentration of 10^{-4} to 10^{-5} mol/L, the sodium concentration increased to about 0.001 mol/L during the equilibration. This can be rationalized in terms of ion exchange on the assumption that the exchangers partly hydrolyze, i.e., take up hydronium ions from water, according to the following equation:

$$NaAC + H_2O <==> HAC + Na^+ + OH^- \qquad (3)$$

Exchanger hydrolysis, a common occurrence with weakly acidic ion exchangers (5), brings a constant sodium ion concentration into the solution. This means that the sodium concentration levels off in solution where the hydrolysis-related sodium concentration exceeds that of the initial, adjusted one. The assumption of exchanger hydrolysis is also supported by the increase in pH during the contact, from the initial pH value of the NaCl(^{60}Co) solution (see Eq. 3). Although increasing sodium ion concentration should decrease the equilibrium pH, this was not the case, but rather the pH increased. This is uncharacteristic behaviour for cation exchangers and cannot yet be explained.

Effect of Complexing Agents on the Distribution Coefficient of Cobalt

The effect of tetraborate anion on the sorption of cobalt on the activated carbon was minor for Norit ROW Supra and Diahope-006 and moderate for Hydraffin DG47 and Eurocarb TN5 (Fig. 3A). The distribution coefficient of ^{60}Co on Hydraffin DG47 and Eurocarb TN5 decreased by approximately one order of magnitude when the tetraborate concentration increased from 10^{-6} mol/L to 10^{-3} mol/L. Since the pH of the solutions varied in the range 8-10, all the distribution coefficient values were normalized to the same pH value of 9.0 by using Fig. 1.

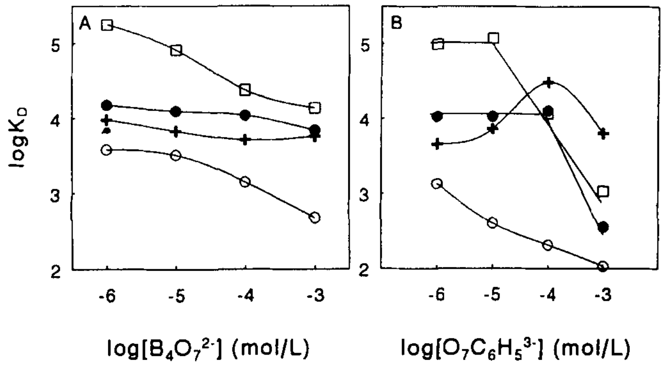

FIGURE 3. Distribution coefficient (K_D) of cobalt on activated carbons as a function of tetraborate (A) and citrate (B) concentration. Diahope-006 (✚), Eurocarb TN5 (○), Hydraffin DG47 (□), Norit ROW Supra (●).

Citrate concentration had a much stronger effect than tetraborate concentration on the uptake of cobalt, especially at concentrations higher than 10^{-4} mol/L (Fig. 3B). This is understandable, considering that the citrate complex with cobalt is stronger than that of borate and that solution phase complexation competes with the uptake of cobalt ions by carbons. Analysis of the solution phase species with the SPE programme (6) showed that cobalt was present almost completely (99%) as citrate complex at the highest ligand concentration. At ligand concentrations 10^{-4} mol/L, 10^{-5} mol/L, and 10^{-6} mol/L, the fraction of the citrate complex decreased, with the concentration ratio of cobalt citrate complex to the free cobalt ion being 87/10, 17/20, and 2/20, respectively (the rest of the cobalt was present as hydrolyzed species).

It is interesting that the distribution coefficient of cobalt on Diahope-006 increased when the concentration of citrate increased from 10^{-5} mol/L to 10^{-4} mol/L. This is in agreement with results obtained in the three buffer solutions. Diahope-006 had an approximately ten times higher K_D in the citrate buffer at pH 7.5 than in plain water at the same pH value (Table 3). As discussed above, it is possible that cobalt is taken up as citrate complex by certain carbons, Diahope-

006 being an example. Rivera-Utrilla et al. obtained similar results with several complexing anions (3). The capability of activated carbons to sorb large organic molecules is well known and extensively exploited in waste-water treatment processes. It has also been utilized in the impregnation of carbon with hydroxyquinoline to be used for cobalt removal (7).

CONCLUSIONS

Efficiencies of 15 activated carbons for cobalt sorption varied in a wide range. All active carbons took up cobalt only in alkaline solutions. The probable uptake mechanism is ion exchange of cobalt ions with weakly acidic groups of the carbons, but more experimental work needs to be done to verify this. With most of the activated carbons, complexing agents interfered with the cobalt sorption by competing with the uptake process. However, some active carbons may have also taken up cobalt complexes, even better than pure ions.

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