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Flotation-Separation of Chromium(Ⅵ) and Chromium(Ⅲ) from Water and Leathers Tanning Waste Using Active Charcoal and Oleic Acid Surfactant

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An experimental procedure is presented for the separation of Cr(Ⅵ) and Cr(Ⅲ) from aqueous solutions, natural water and leather tanning waste using powdered active charcoal (PACh) as an adsorbent and oleic acid (HOL) as a surfactant. Several parameters (namely: the initial concentrations of surfactant and active charcoal, pH value, ionic strength, shaking time, temperature and foreign ions) that influence the separation process were studied. Good results were obtained, according to which more than 98% of Cr(Ⅵ) at pH 2.0 or Cr(Ⅲ) at pH 7.5 were removed. The selective separation of Cr(Ⅵ) from Cr(Ⅲ) was also examined, since the system Cr(Ⅲ)/Cr(Ⅵ) is toxic, and occurs in industrial effluents and some surface waters. The procedure may find analytical applications for speciation studies. Moreover, a flotation mechanism is suggested.

In recent years, chromium has received considerable attention owing to uses of its compounds in metallurgy, refractory materials, chemical industries, tanning of leather, oxidative dying, electroplating, fungicides, rust inhibition and catalysis.[1,2] Chromium enters the environment from the effluent discharge of the aforementioned industries. It is present in natural water in the trivalent and hexavalent states. The former is considered an essential element for biological activity in mammals, whereas the latter is considered to be a toxic material.[3–5] From both environmental and geochemical viewpoints, accurate and selective methods are required to remove, distinguish and separate these oxidation states.

Numerous techniques exist to remove metal ions from aqueous solutions.[6–8] These techniques may involve: chemical precipitation, ion exchange, reverse osmosis, adsorption on active carbon, solvent extraction and flotation separation processes. Of these, adsorption onto powdered activated carbon (PAC) has proved to be a very effective technique for removing low concentrations of organic compounds and inorganic toxic species from water supplies and wastewater, for the enhancement of activated sludge and water treatment.[9–11] PAC has the advantage of being less costly to manufacture; it also offers more surface area for adsorption and distributes more easily and uniformly in water. PAC also offers the advantage that the dose and the reaction time can be adjusted according to the composition of the liquid streams to be treated, as in the case of color or odor removal. PAC requires a minimal capital expenditure for feeding and contacting equipment. Economic limitations have been placed on the use of PAC due to difficulties encountered in separating it from suspension in order for it to be regenerated.[10] To compensate for this, a combination between flotation and adsorption is a vital process. Moreover, flotation techniques are considered to be an attractive, more effective and less expensive method for the removal, recovery and/or preconcentrating of trace substances.[12–17]

The only published similar work with the present one was the separation of Cr(Ⅵ) loaded carbon with an anionic surfactant.[10] Therefore, the aim of this work is to establish a selective, rapid and simple flotation procedure for the separation of different chromium species from natural water and leather tanning wastes using charcoal as an inexpensive adsorbent and oleic acid as a surfactant at the recommended parameters.

Experimental

Reagents: All reagents, unless specified otherwise, were of analytical-reagent grade. Aqueous solutions were prepared in doubly distilled water. Chromium stock solutions (1×10^{-3} mol dm^{-3}) were prepared from $CrCl_3\cdot6H_2O$, $K_2Cr_2O_7$ and K_2CrO_4 by weighing the appropriate quantity and dissolving in doubly distilled water. The active charcoal (purchased from Sigma Co.) was crushed and pulverized in the Laborabory. It was dried for 2 h at 125 °C and subsequently kept in a desiccator. A freshly powdered active charcoal (PACh) stock suspension (2.5 g dm^{-3}) was prepared daily before use. An oleic acid (HOL) stock solution (6.36×10^{-2} mol dm^{-3}) was prepared by dispersing 20 cm^3 of HOL, food grade (*d* 0.895), in 1 dm^3 kerosene.

Apparatus: The atomic absorption data were measured on a Perkin–Elmer Model 2380 atomic absorption spectrophotometer (AAS) using an air-acetylene flame. A Shimadzu (Model 240) ultraviolet/visible instrument was used to conduct spectrophotometric measurements for Cr(Ⅵ) determination at 540 nm. An IR analysis was carried out using a MATTSON 5000 FTIR spectrometer. The pH was measured with an Orion Model 330 digital pH meter.

Flotation Cells: Two types of flotation cells[19] were used throughout. The flotation cell (a) was a test tube of 1.5 inner diameter and 29 cm length with a stopcock at the bottom. Such a cell was used to study the factors affecting the flotation efficiency. The flotation cell (b) was a cylindrical tube of 6 cm inner diameter and 45 cm length with a stopcock at the bottom and a quick-fit stopper at the top. Such a cell was used to separate chromium from 1 dm^3 samples.

Procedure: To study the factors affecting the flotation process, 20 cm^3 aliquot of a solution containing defined amounts of Cr(III) or Cr(VI), PACh, H_2SO_4 and/or NaOH (for controlling pH) was introduced into flotation cell (a). The cell was shaken for 10 min (optimized time) to complete the adsorption of Cr(III) or Cr(VI) onto PACh. To this solution 4 cm^3 HOL with a specified concentration was added. Again, the cell was inverted upside down 20 times by hand and kept standing for 5 min to complete the flotation. Residual Cr(III) or Cr(VI) in the mother liquor was analyzed by AAS at 242.8 nm. Hexavalent chromium was additionally analyzed by applying the standard diphenylcarbazide method.[20] The floatability percentage ($F\%$) was calculated from

$$F = (1 - C_f/C_i) \times 100\%,$$

where C_i and C_f denote the concentrations of Cr(III) or Cr(VI) before and after flotation, respectively.

To study the flotation of PACh alone, the previous procedure steps were performed in the absence of chromium ions. After complete flotation, the float containing PACh was filtered through a G_5 sintered-glass filter (porosity 1–1.5 μm) and dried in an oven at 125 °C to a constant weight. The percentage PACh flotation ($F\%$) was calculated from

$$F = C_f/C_i \times 100\%,$$

where C_i and C_f denote the initial and floated concentrations of PACh. The flotation experiments were carried out at room temperature, ca. 25 °C.

Results and Discussion

Floatability of Charcoal: An initial series of flotation experiments (using a constant concentration of 1×10^{-4} mol dm^{-3} HOL at pH 7) was carried out in an effort to establish the optimum concentration of PACh required for this investigation. The obtained results showed a maximum flotation (~100%) of PACh in a wide concentration range of 0.5–5.0 mg dm^{-3}. Therefore, after preliminary measurements, the concentration of charcoal favorable for flotation of Cr(III) and Cr(VI) was presumed to be 2.0 mg dm^{-3} at a suitable pH for each ion.

Another series of experiments was conducted to determine the effect of pH on the flotation of 2.0 mg dm^{-3} PACh using 1×10^{-4} mol dm^{-3} HOL. Fortunately, the maximum flotation (~100%) of charcoal was obtained over a broad pH range of 1–10. This gives the advantage of carrying out flotation experiments in both acidic and alkaline solutions using charcoal as an adsorbent and oleic acid as a surfactant.

The optimum proposed concentration of PACh (2.0 mg dm^{-3}) was confirmed by floating 5 mg dm^{-3} of each of Cr(VI) and Cr(III) using 1×10^{-4} mol dm^{-3} HOL at pHs of 1.5 and 7.5, respectively. The results are graphically represented in Fig. 1. It is noted that the maxdimum floatability of both Cr(III) and Cr(VI) was obtained in the concentration range 1.5–5.0 mg dm^{-3} of PACh. Therefore, 2.0 mg dm^{-3} of PACh was recommended for subsequent experiments.

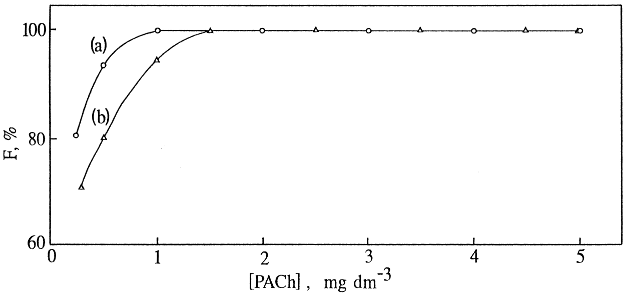

Fig. 1. Floatability of Cr(VI) and Cr(III) vs PACh concentration. Cr(VI) and Cr(III), 5.0 mg dm^{-3}, each; HOL, 1×10^{-4} mol dm^{-3}; (a) Cr(VI) at pH 2; (b) Cr(III) at pH 7.5.

Flotation of Chromium(VI): First of all, it must be taken into consideration that the Cr(VI) species were present in aqueous solutions in the forms $HCrO_4^-$ and $Cr_2O_7^{2-}$ according to the following equilibrium:[21] $2HCrO_4^- \rightleftarrows Cr_2O_7^{2-} + H_2O$; K at 25 °C = 40.0 at $\mu = 0$, and it is probable that only about 7% of the Cr(VI) species were present as $Cr_2O_7^{2-}$ ions in the initial solutions of pH 4.1. Moreover, the surface of the most active carbons contains oxo groups[11,12] (C_xO and C_xO_2), which are expected to be strongly ionized, react in a similar way as the organic compounds, and are mainly responsible for the adsorption of anions from solution.[23]

Figure 2 (Curve a) indicates the influence of the pH on the floatability of 5 mg dm^{-3} Cr(VI) using 2 mg dm^{-3} PACh and 1×10^{-4} mol dm^{-3} HOL. As can be seen, a maximum flotation efficiency (~100%) was attained in the pH range of 1.5 to 2.5. This may be attributed to the adsorption of hydrogenchromate ions, $HCrO_4^-$ (predominant species at this pH range) with hydrolized carbon oxo groups (C_xO^{2+} and $C_xO_2^{2+}$) according to the following schematic reaction equations:[10,11]

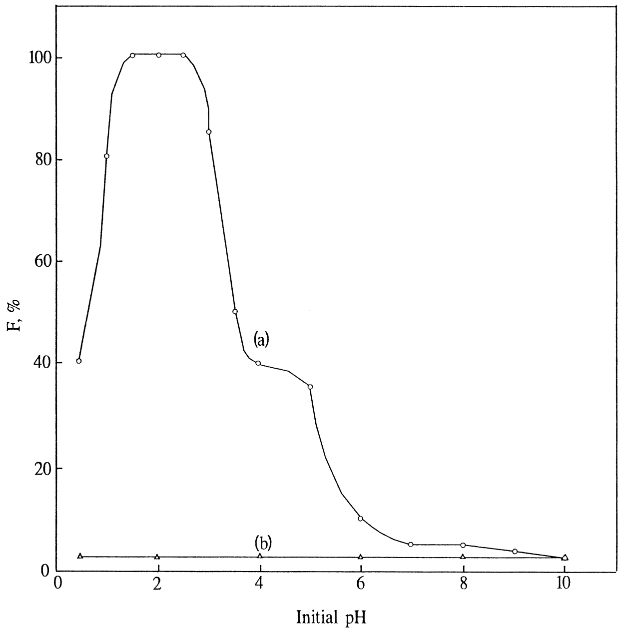

Fig. 2. Floatability of Cr(VI) vs pH. Cr(VI), 5.0 mg dm^{-3}; HOL, 1×10^{-4} mol dm^{-3}; PACh, 2.0 mg dm^{-3}; in the presence (Curve a) and absence (Curve b) of PACh.

$$C_xO + H_2O + HCrO_4^- = C_xOH_3Cr^+ + 2OH^-$$

or

$$C_xO_2 + H_2O + HCrO_4^- = C_xO_2HO_3Cr^+ + 2OH^-.$$

At very low pH, the flotation of hexavalent chromium is mainly governed by the active reduction of $Cr_2O_7^{2-}$ and $HCrO_4^-$ to Cr(III) not capable of adsorption, and hence the flotation efficiency decreases.

At higher solution pH, more than 6, the flotation efficiency decreases sharply, which may be due to the fact that the unadsorbed bichromate ions change into chromate ions (which do not effectively take part in the adsorption reaction and remain unadsorbed), as shown below:[24]

$$HCrO_4^- = H^+ + CrO_4^{2-}. \qquad (\log K = 9.0)$$

For a comparison, the results of Cr(VI) flotation without the use of PACh (Curve b) are shown. As can be seen, the effectiveness of the addition of PACh as an adsorbent is evident for Cr(VI) flotation. For subsequent flotation experiments, pH 2 was selected as the optimum value.

Flotation of Cr(III): It has been reported[25] that in aqueous solution chromium(III) has the following soluble Cr^{3+}, $CrOH^{2+}$, $Cr(OH)_2^+$ and $Cr(OH)_4^-$ and insoluble $Cr(OH)_3$ species; their presence is a function of the pH. Below pH 7 the concentration of $CrOH^{2+}$, $Cr(OH)_2^+$ increases, while between pH 7 and 8.8 $Cr(OH)_3$ is the present species and above pH 10.4 $Cr(OH)_4^-$ is the predominant soluble one. $Cr(OH)_3$ is positively charged with a zero point of charge at pH 8.2–9.3.[2,25] Moreover, most carbon surfaces are negatively charged.[10] These results represent the basis of discussing the floatability of chromium(III) in this investigation.

The influence of the pH on the floatability of Cr(III) is presented in Fig. 3. The experimental conditions are listed as a caption in the figure. In this figure both the system with (Curve a) and that without (Curve b) the addition of 2.0 mg dm^{-3} PACh are shown. As can be seen from Curve a, the floatability reaches its maximum value (~100%) in the pH range 6.0–8.5, outside of which the floatability of Cr(III) is unsatisfactorily. Enhanced removal of metal ions as the solution pH is increased can be attributed to the adsorption of hydrolyzed products and/or the surface precipitation of the metal as the metal hydroxide.[26,27] The surface precipitation model, especially successful in predicting pH adsorption edges, is described by a series of adsorption and precipitation reactions.[27] Because metal is adsorbed on a surface, a new hydroxide phase is formed, allowing a further mass transfer of sorbate (metal) to the solid phase. In other words, as the sorbate concentration increases, the surface complex concentration and the mole fraction of the surface precipitate both increase until the surface sites become saturated. Surface precipitation then becomes the dominant sorption mechanism.[27]

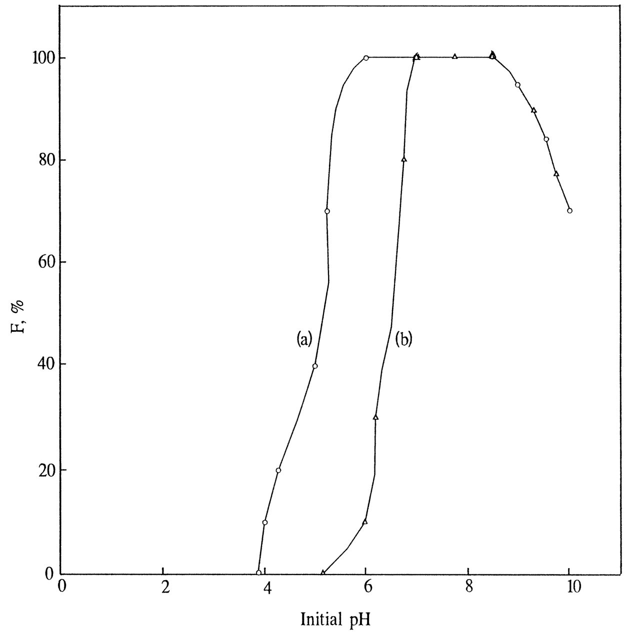

Fig. 3. Floatability of Cr(III) vs pH. Cr(III), 5.0 mg dm^{-3}; HOL, 1×10^{-4} mol dm^{-3}; PACh, 2.0 mg dm^{-3}; in the presence of (Curve a) and absence (Curve b) of PACh.

The effect of adding PACh is evident from a comparison with Curve b, where the maximum flotation (~100%) is obtained in a narrow pH range of 7–8.5. In the absence of PACh, Cr(III) may be floated as its $Cr(OH)_3$ (with a positive surface charge) with oleate ions, since oleic acid begins to dissociate at $pH \geq 5.2$.[28]

Above pH 8.5, Cr(III) is present mainly as $Cr(OH)_4^-$, which is not capable of adsorption onto PACh having a negative surface charge or reaction with oleate ions, thus giving rise to a decrease in the flotation efficiency. The optimum pH selected for further flotation experiments of Cr(III) was 7.5

Effect of Surfactant Concentration: In order to find a suitable concentration of HOL for floating Cr(VI) or Cr(III) ions (5 mg dm^{-3}, each) from aqueous solutions, a series of experiments was conducted at pH 2 for the former and another series at pH 7.5 for the latter using 2.0 mg dm^{-3} of PACh in the presence of different concentrations of HOL. The results are shown in Fig. 4. It can be seen that both ions (Curves a and b) reach their maximum flotation (~100%) in the HOL concentration range of 1.5×10^{-5} to 1.0×10^{-3} mol dm^{-3}. A higher concentration of the surfactant impaired flotation. This impairment has been discussed by Klassen and Mokrousov,[29] who concluded that the poor flotation at high surfactant concentration is caused by the formation on the air bubble surface of a stable, hydrated envelope of surfactant or, perhaps, by forming a hydrated micelle coating on the solid surface. As a result, the

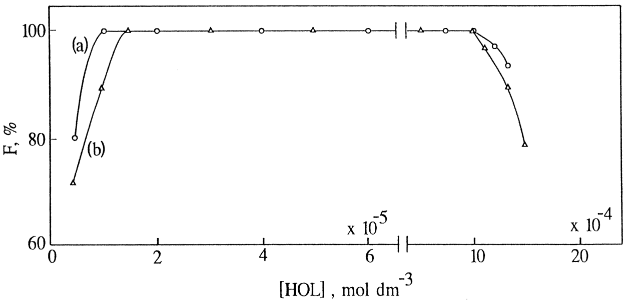

Fig. 4. Floatability of Cr(VI) and Cr(III) vs HOL concentration. Cr(VI) and Cr(III), 5.0 mg dm^{-3}, each; PACh, 2.0 mg dm^{-3}, (a) Cr(VI) at pH 2; (b) Cr(III) at pH 7.5.

hydrophobicity of this surface was not satisfactory for flotation. Therefore, 1×10^{-4} mol dm^{-3} HOL was fixed throughout.

Effect of Shaking Time: Figure 5 presents the effect of the shaking time of the original solutions (i.e. before flotation) on the floatability of Cr(VI) at pH 2 (Curve a) and Cr(III) at pH 7.5 (Curve b) in the presence of 2.0 mg dm^{-3} PACh, and then adding 1×10^{-4} mol dm^{-3} HOL at room temperature (~25 °C). As can be seen, the flotation efficiency of both ions reaches its maximum value (~100%) rapidly after 5 min, beyond which it remains constant. Shaking may promote the adsorption of chromium particles on the surface of charcoal and, hence, enhances the flotation. Shaking for 10 min was recommended for carrying out other experiments in this investigation.

Effect of Temperature: To study the effect of temperature on the flotation efficiency, a solution containing 5 mg dm^{-3} of each of Cr(VI) at pH 2 or Cr(III) at pH 7.5 after shaking with 2 mg dm^{-3} PACh for 10 min and surfactant solution were either heated or cooled to the same temperature. The surfactant solution was quickly poured into the chromium solution (inside a cell Jacketed with 1 cm thick fiberglass insulation) at time equal to zero. The mixture was then floated according to the previous procedure under the optimum conditions. The obtained results show that a change in temperature over a wide range (15–80 °C) has no appreciable effect on the flotation efficiency of Cr(VI) or Cr(III) ions.

Another series of experiments was carried out to float only PACh with HOL surfactant over a wide temperature range (15–80 °C) at pH 2.0 and pH 7.5. The floatability of charcoal was not affected by changing the temperature in this range. Unless otherwise stated, all experiments were carried out at room temperature, ~25 °C.

Effect of Ionic Strength: To study the effect of the ionic strength on the flotation efficiency of Cr(VI) or Cr(III), different flotation experiments were conducted under the optimum conditions. The experiments took into account the effect of salt and charge variation. The obtained data are listed in Table 1. As can be seen, the flotation efficiency of both ions are slightly varient over a wide increase in the ionic strength.

Table 1. Effect of Ionic Strength on the Floatability of 5.0 mg dm^{-3} of Each of Cr(III) at pH 2 and Cr(III) at pH 7.5 using 1×10^{-4} mol dm^{-3} HOL and 2.0 mg dm^{-3} PACh

Ionic Strength	Salt	Floatability/%	
mol dm^{-3}		Cr(VI)	Cr(III)
0.01	NaCl	100.0	100.0
	Na_2SO_4	99.5	99.0
	$CaCl_2$	99.0	98.9
	$MgCl_2$	99.0	99.0
0.1	NaCl	99.9	99.9
	Na_2SO_4	99.5	99.0
	$CaCl_2$	99.0	98.8
	$MgCl_2$	98.8	98.7
0.5	NaCl	99.5	98.9
	Na_2SO_4	99.4	98.8
	$CaCl_2$	98.5	98.5
	$MgCl_2$	98.4	98.3

Effect of Foreign Ions: By following the proposed procedure, the effect of various ions on the separation of Cr(VI) or Cr(III) from aqueous solutions was investigated under the optimum conditions. It has been found that the following cations and anions (present in a 20-fold concentration of the chromium ion) have no effect on the flotation efficiency: Hg^{2+}, Cu^{2+}, Fe^{2+}, Fe^{3+}, Ca^{2+}, Mg^{2+}, Sb^{3+}, Ni^{2+}, Cd^{2+}, Bi^{3+}, Zr^{4+}, Th^{4+}, Co^{2+}, Pb^{2+}, Cl^-, I^-, SO_4^{2-}, PO_4^{3-} or MoO_4^{2-}. Only Ti^{3+} and SiO_3^{2-} have an adverse effect on the separation process.

Selective Separation of Cr(VI) from Cr(III) in Admixture: A trial was made to apply the above procedure for the selective separation of Cr(VI) from Cr(III), since the system Cr(VI)/Cr(III) is toxic and occurs in industrial effluents and some surface water. The two ions were separated selectively and quantitatively from mixtures containing 5 mg dm^{-3} Cr(VI) and different concentrations of Cr(III) using the previous procedure at pH 2 in the presence of 2 mg dm^{-3} PACh and 1×10^{-4} mol dm^{-3} HOL. The results are presented in Fig. 6. Practically no influence was found, even when 80 mg dm^{-3} of Cr(III), 16-times more than Cr(VI), was present. Moreover, the total chromium could be removed by carrying out experiments at pH 2 for Cr(VI) flotation, raising the pH of the residual solution (containing only Cr(III)) to pH 7.5 and floating for removing Cr(III). Therefore, this investigation presents a simple flotation procedure for the removal of Cr(VI) and Cr(III) from aqueous solutions and having an analytical application for speciation studies.

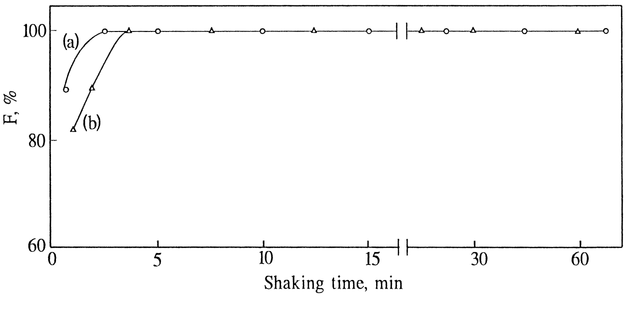

Fig. 5. Floatability of Cr(VI) and Cr(III) vs shaking time. Cr(VI) and Cr(III), 5.0 mg dm^{-3}, each; HOL, 1×10^{-4} mol dm^{-3}; PACh, 2.0 mg dm^{-3}; (a) Cr(VI) at pH 2; (b) Cr(III) at pH 7.5.

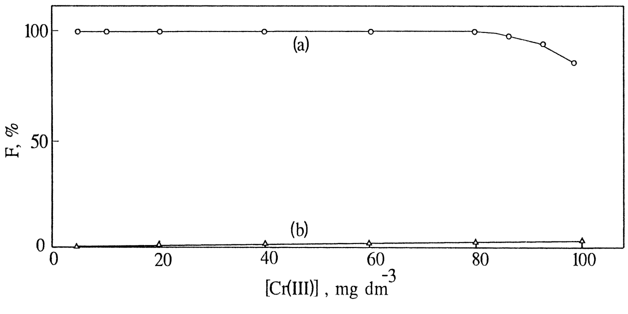

Fig. 6. Floatability of Cr(VI) vs Cr(III) concentration. Cr(VI), 5.0 mg dm^{-3}; HOL, 1×10^{-4} mol dm^{-3}; PACh, 2.0 mg dm^{-3} at pH 2; (a) Cr(VI); (b) Cr(III).

Table 2. Recovery of Cr(VI) at pH 2 and Cr(III) at pH 7.5 Added to 1 dm^3 Tap and Natural Water Samples Using 3.0 mg dm^{-3} PACh and 10 cm^3 of 1×10^{-3} mol dm^{-3} HOL

Sample (location)	Added	Cr(VI)		Cr(III)	
	mg	Re/%	RSD[a)]/%	Re/%	RSD[a)]/%
Tap water	5	99.8	1.5	99.9	1.3
(our Laboratory)	10	100.0	1.3	100.0	1.1
Nile water	5	99.7	1.8	99.9	1.6
(Giza City)	10	99.9	1.4	99.9	1.5
Sea water	5	99.5	1.6	99.7	1.6
(Alexandria)	10	99.6	1.5	99.9	1.4

a) Calculated for five replicate analyses.

Table 3. Removel of Cr(VI) at pH 2 and Cr(III) at pH 7.5 from Leathers Tanning Baths using 3.0 mg dm^{-3} PACh and 10 cm^3 of 1×10^{-4} mol dm^{-3} HOL

Bath Number	Cr(VI)			Cr(III)		
	Present[a)]	Residual[b)]	F[c)]	Present[a)]	Residual[b)]	F[c)]
	mg dm^{-3}	mg dm^{-3}	%	mg dm^{-3}	mg dm^{-3}	%
1	3.2	0.04	98.75	4.5	0.09	98.0
2	1.2	0.02	98.3	10	0.03	99.7

a) The amount of ions present in the bath after tanning process.

b) The amount of ions present after flotation process.

c) The mean value of three measurements.

Application: In order to investigate the applicability of the recommended procedure, two series of experiments were conducted under the optimum conditions.

The first series was applied to recover known amounts of Cr(VI) or Cr(III), added to tap and natural water samples. The flotation experiments were carried out, using a flotation cell (b), on 1 dm^3 aliquots of filtered clear, uncontaminated samples, after adjusting the pH with H_2SO_4, immediately after sampling. The results are presented in Table 2.

The second series was applied to remove Cr(VI) and Cr(III) from leather tanning baths by floating these ions from 1 dm^3 of filtered waste, after adjusting the pH firstly to 2 for Cr(VI) and then to 7.5 for Cr(III) measurements. Table 3 lists the obtained data. The data, shown in Table 2 and Table 3, indicate that the recommended procedure gives satisfactory results for the flotation of Cr(VI) and Cr(III) from real samples.

Flotation Mechanism: The flotation mechanism may be suggested according to the following bases: i) most carbon surfaces are negatively charged;[10] ii) activated carbons are characterized by the presence of oxo groups C_xO and C_xO_2,[11] carboxylic and phenolic hydroxyl groups,[23] which are confirmed experimentally by the appearance of two bands in the IR spectra of PACh at 1550 and 3444 cm^{-1}, respectively; iii) in aqueous solutions Cr(VI) may have the species $HCrO_4^-$, CrO_4^{2-}, CrO_7^{2-}, depending on the solution pH.[21] $HCrO_4^-$ was the dominant species in this investigation at the recommended pH; iv) as a function of pH[2,27] Cr(III) may have the species Cr^{3+}, $Cr(OH)^{2+}$, $Cr(OH)_2^+$ and $Cr(OH)_4^-$ and v) oleic acid begins to dissociate at pH ≥ 5.2.[20]

Therefore, hexavalent chromium as $HCrO_4^-$ formed at pH 2 may be adsorbed onto PACh via a chemical reaction, and combines with undissociated HOL through hydrogen bonding. Trivalent chromium (in the absence of PACh) as $Cr(OH)_3$, positively charged, combines electrostatically at pH 7.5 with oleate ions. In the presence of PACh, trivalent chromium as $Cr(OH)^{2+}$, $Cr(OH)_2^+$ and $Cr(OH)_3$ may be adsorbed onto charcoal and combines electrostatically with oleate ions or through hydrogen bonding with undissociated HOL. Oleic acid surfactant makes the above aggregates hydrophobic and capable of flotation.

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