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Kinetic Study of Redox Processes of Chromium in Natural River Water

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Dedicated to Professor Jan R. Dojlido Head of Department of Environmental Protection on his retirement

Abstract

Chromium contamination in the area of the Radomka river basin in Poland has lead to significant environmental problems. Therefore, chromium redox transformations were investigated in the aquatic environment under conditions as close to natural as possible - at intermediate pH and in the presence of original bottom sediment and dissolved oxygen.

Reduction of Cr(VI) in the Radomka river water occurs at a low rate ($t_{1/2}$ = 19 h). The rate of Cr(VI) reduction increased in the river water spiked by HA ($t_{1/2}$ = 0.5 h), and Fe(II) ($t_{1/2}$ = 2 min). The kinetics of Cr(VI) reduction by Fe(II) was dependent on the evolution of the forms of Cr(VI) and the competing Fe(II) oxidation reaction by dissolved oxygen. The reduction of Cr(VI) by humic acids appeared to be a significantly slower process than Fe(II) oxidation by O_2.

Chromium(III) present in the tanning liquor used and the aged solution of chromium sulphate was less prone to oxidation by MnO_2 than Cr(III) introduced with chromium nitrate and sulphate solutions (7% and 10% conversion over 1 h in comparison with 55% and 32%, respectively). Chromium deposits in bottom sediment turned out to be resistant to oxidation by MnO_2.

Keywords: Chromium; redox transformation; river water.

Introduction

Chromium(VI) is a thermodynamically stable form in aerobic systems while chromium(III) is a stable form in anaerobic systems. The fact that both Cr forms are often found in aerobic and anaerobic environments is due to the slow kinetics of Cr(VI)/Cr(III) redox reactions [1]. Thus, chromium speciation in the environment may reflect the kinetics of its redox transformations and not the equilibrium state. Dramatic differences have been noted in mobility, uptake and toxicity of both chromium oxidation states. The results of such studies have been discussed in a number of reviews [1, 2, 3, 4, 5, 6]. Fe(II) and organic compounds, including humic and fulvic acids, occurring in the aquatic environment, are main reductants of Cr(VI) while Mn(III,IV) oxides are main oxidants of Cr(III) in natural systems [3, 4]. Other naturally-occurring constituents may also participate in chromium redox processes and can significantly affect their rate [2].

Chromium(VI) reduction by iron(II) has recently been studied by Buerge and Hug [7]. In a weakly acidic environment the reaction products are hydroxy com-

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plexes $Fe(OH)_2^+$ and $Cr(OH)_2^+$ while mixed hydroxide with the empirical formula $Fe_{0.25}Cr_{0.75}(OH)_3$ is the product in neutral or weakly basic environments. Reduction rate constants increase with pH - increasing from 1.9 $M^{-1}s^{-1}$ at pH 4.4 to 1700 $M^{-1}s^{-1}$ at pH 7.2.

In natural systems an incomplete reduction of Cr(VI) caused by a parallel reaction of Fe(II) with dissolved oxygen can occur [8]. However, Eary and Rai [9] have observed that the oxidation of Fe(II) by Cr(VI) takes place even in well-aerated solutions at high pH. Buerge and Hug [7] have reported that in a homogeneous system at pH 4 - 8 the oxidation of Fe(II) by Cr(VI) is over 10^3 faster than the oxidation by dissolved oxygen. Fendorf and Li [10] also believe that at pH < 8 micromolar concentrations of Cr(VI) will oxidize Fe(II) faster than dissolved oxygen.

The reduction of chromium(VI) by dissolved organic compounds at pH 4 - 8 is a slow process in a time scale of days at micromolar concentrations and up to months at nanomolar concentrations [11, 12]. However, the synergistic properties of Fe(II) with organic compounds can enhance Cr(VI) reduction. Organic compounds can influence Cr(VI) reduction by Fe(II) by enhanced weathering of Fe-bearing minerals and by Fe(II) complexation [13, 14]. Buerge and Hug [14] have shown that the presence of carboxylates and phenolates can lead to greatly accelerated reduction of Cr(VI) by Fe(II) and to the formation of complexed soluble Cr(III).

Humic and fulvic acids are organic compounds present in the aquatic environment, which can play an important role as they can act as a significant reservoir of electron donors for Cr(VI) reduction. Wittbrodt and Palmer [12] have reported that the rate of Cr(VI) reduction in the presence of excess fulvic acids decreases in time due to depletion of chromium and decreasing reactivity of the fulvic acids being oxidized. The rate of Cr(VI) reduction (k_{obs}) determined was $4.27 \cdot 10^{-7}$ $M^{-1}s^{-1}$. In another paper Wittbrodt and Palmer [13] suggest for the redox couple Fe(II)/Fe(III) the role of an electron transfer catalyst for the reduction of Cr(VI) by humic acids.

The problem of the effect of solid phase on Cr(VI) reduction by Fe(II) has been comprehensively investigated by Buerge and Hug [15]. The reactivity of the minerals studied decreases in the order of α-FeOOH = λ-FeOOH »montmorillonite > kaolinite = SiO_2 per unit of surface area. However, the differences are relatively small, the respective second order rate coefficients are of the same order of magnitude $2 - 8 \cdot 10^3$ $M^{-1}s^{-1}$.

The effect of the solid phase surface on the rate of Cr(VI) reduction by organic compounds has recently been studied by Deng and Stone [16, 17], who examined Cr(VI) reduction by α-hydroxyl and α-carbonyl carboxylic acids and their esters, dicarboxylic acids and substituted phenols in the presence of TiO_2, FeOOH and γ-Al_2O_3. The adsorbed chromium(VI) undergoes reduction. The adsorption of organic reductants is not a factor limiting the rate of reduction, although it competes with Cr(VI) adsorption. The half-lives of the heterogeneous systems studied ranged from tens to hundreds of hours, whereas in homogeneous systems no measurable decrease of Cr(VI) concentration was found even after 400 days.

In the aquatic environment, both dissolved oxygen and Mn(III,IV) oxides may oxidize Cr(III). However, Cr(III) oxidation by dissolved oxygen is sufficiently slow to be negligible [3]. As a result, Cr(III) oxidation by Mn(IV) oxides is thought to control chromium speciation.

In acidic environments (pH < 5), the reaction between Cr(III) and β-MnO_2 is described by the equation [18,19]:

$$CrOH^{2+} + 1{,}5\ \beta\text{-}MnO_2 = HCrO_4 + 1{,}5Mn^{2+}$$

The confirmation of this stoichiometry by a parallel analysis of the contents of Mn(II) and Cr(VI) has been given by Fendorf and Zasoski [19]. A change in stoichiometry occurs at higher pH (6.3 - 10.1):

$$CrOH^{2+} + 3\beta\text{-}MnO_2 + H_2O = HcrO_4 + 3MnOOH + 3H^+$$

According to that equation only dissolved Cr(III) undergoes oxidation. Ferndorf and Zasoski [19] have calculated that AG of the reaction of solid $Cr(OH)_3$ with MnO_2 at pH > 3 has positive values.

The oxidation of Cr(III) by MnO_2 is characterized by a fast initial stage and subsequent slower rate [8, 18, 19]. Eary and Rai [18] suspect that this is caused by a reduction in the number of active spots on the surface of β-MnO_2 due to insufficient rate of Cr(VI) desorption. In contrast Fendorf and Zasoski [19] explain that this phenomenon is caused by the formation of multinuclear Cr(III) complexes and subsequent surface precipitation of Cr(III) hydroxide.

Chromium(III) oxidation in natural waters has been studied by Schroeder and Lee [8]. Chromium adsorption on MnO_2 as well as adsorption of other water constituents reduced the Cr(III) oxidation rate by 35% in filtered lake water when compared to that in distilled water. Saleh et al. [20] found that $Cr(OH)_3$ was oxidized by β-MnO_2 more readily in rainwater and hardwater than in natural water. Chromium(III) in natural waters had a half-life of 9 years, while in rainwater its $t_{1/2}$ = 2 - 3 years. The process was slowed down further in the presence of suspensions of river bottom sediments and soils.

This work describes redox chromium transformations in river water contaminated with tannery effluents. The oxidation rates of anthropogenic Cr(III) by MnO_2 and the reduction of Cr(VI) by Fe(II) and humic acids were assessed, with care to maintain realistic environmental conditions. The aim of the study was to facilitate forecasting the fate of chromium discharged into the environment by tanneries located in the Radomka River basin. Earlier field studies made it possible to determine the occurrence and speciation of anthropogenic chromium [21]. Chromium forms which can be extracted with hydroxyamine hydrochloride solution and acidified hydrogen peroxide solution predominate in sediments. The presence of soluble organic complexes of Cr(III) and Cr(VI) (extraction with sodium pyrophosphate solution and NaOH solution, respectively) was also detected.

Experimental Procedures

Reagents and Materials

Analytical-grade reagents were used throughout. Chromium nitrate, $Cr(NO_3)_3$ (POCH Gliwice, Poland), chromium sulphate, $Cr_2(SO_4)_3$ (Reachim, SU) and potassium dichromate, $K_2Cr_2O_7$ (POCH Gliwice, Poland) were used as sources of Cr(III) and Cr(VI), respectively. The stock solutions (1 mg/cm^3) of chromium(III), chromium(VI), sodium humate salt, (HA, Sigma-Aldrich), Mohr's salt, $Fe(NH4)_2(SO_4)_2$ (POCH Gliwice, Poland), were prepared in ~ 18 MΩ • cm water. Manganese(IV) oxide, activated 5 micron, ca. 85% (Sigma-Aldrich) was used as an oxidizing agent. Diphenylcarbazide (Reachim SU), phosphoric acid 85% (POCH Gliwice Poland), and ethanol were used for Cr(VI) determination by the spectrophotometric method.

Filtered Radomka River water (pH - 7.6, COD - 38 mg/dm^3, ammonia - 7.8 mg/dm^3, nitrate - 4.6 mg/dm^3, sulphate - 75 mg/dm^3, phosphate - 4.8 mg/dm^3, iron - 80 µg/dm^3, chromium - 2 µg/dm^3) and air-dried and sieved Radomka River bottom sediment containing: Cr - 40.4 mg/kg, Fe -1460 mg/kg, Mn - 21.5 mg/kg, Zn - 32 mg/kg, Ca - 358 mg/kg, Mg - 103 mg/kg, were used in the experiments.

Procedures

The kinetic studies were carried out in a system similar to the one described by Patric et al. [22]. After placing in the system 100 cm^3 river water, 30 g air-dried sediment and eventually de-aeration by sparging with N_2, the mixture was conditioned at fixed pH for 18 h. In the study of reduction, after setting Cr(VI) concentration at 0.5 mg/dm^3 by means of potassium dichromate solution, 0.05 cm^3 of solution Mohr's salt (p = 1 mg/cm^3 Fe(II)) or 1 cm^3 and 0.25 cm^3 HA solution (p = 1 mg/cm^3). Also, the control tests of Cr(VI) reduction without the addition of any Fe(II) or HA were performed. The studies of Cr(III) oxidation were also carried out in river water and distilled water without bottom river sediments. After adding a measured amount of MnO_2 (25 or 10 mg) the suspension was mixed for 2 h, and then measured amounts of chromium(III) nitrate solution (0.05 cm^3) or used tanning liquor or fresh or aged (boiled for 2 h) solution of chromium sulphate (0.05 cm^3) were added, depending on the type of investigation. Required pH was maintained by automatic addition of 0.01 M HNO_3 or 0.01 M NaOH from a pH-stat-controlled burette. The experiments were carried out at 20° ± 0.1°C in the dark. Two cm^3 samples were periodically withdrawn with a syringe and filtered through a Millex-HV_{13} unit with pore size of 0.4 µm (Millipore). The concentration of Cr(VI) was determined immediately after sampling by using the spectrophotometric method with diphenylcarbazide described by Fendorf and Zasoski [19].

Results and Discussion

Reduction of Chromium(VI) by Fe(II)

The study of Cr(VI) reduction was performed under conditions similar to those found in natural aquatic environments. Reactant (HA, Fe(II)) concentrations were maintained at a level commonly found in surface waters in the presence of oxygen and the original bottom sediment, with pH near neutral. This complexity may change Cr(VI) reduction relative to that predicted in model kinetic studies [7, 10, 15].

A rapid drop in Cr(VI) concentration was observed under anaerobic conditions at pH 7.2 - over 80% of Cr(VI) underwent reduction within several minutes. In the presence of oxygen, the degree of reduction was - 10% lower due to competing oxidation of Fe(II) by dissolved oxygen. At pH 8.8 the reduction of Cr(VI) proceeded much more slowly, and was markedly affected by oxygen (Fig. 1).

Cr(VI) reduction by Fe(II) is described using the second-order kinetic equation [7, 15]. A sufficiently good fit of experimental results was obtained at pH 8.8 (Fig. 2). The second-order rate coefficients k_{obs} determined in this way for experiments conducted at pH 7.2 should be treated only as estimated values because the reduction rate is too high. All the second-order rate coefficients are given in Table 1. Cr(VI) reduction rate constants at pH 7.2 both in anaerobic environments and in aerated sol-

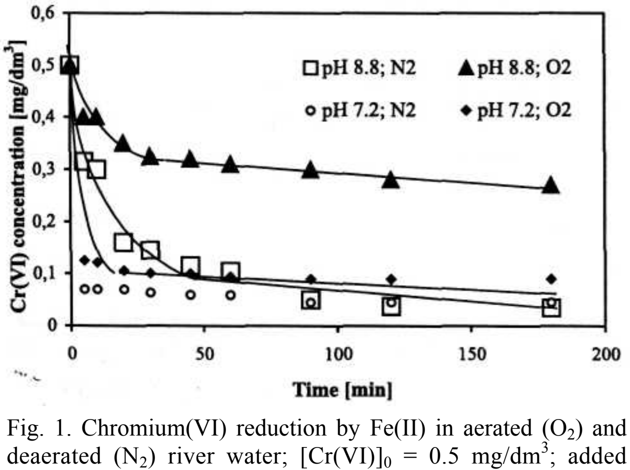

Fig. 1. Chromium(VI) reduction by Fe(II) in aerated (O_2) and deaerated (N_2) river water; $[Cr(VI)]_0$ = 0.5 mg/dm^3; added [Fe(II)] = 1.5 mg/dm^3; pH 7.2 and 8.8; t = 20°C.

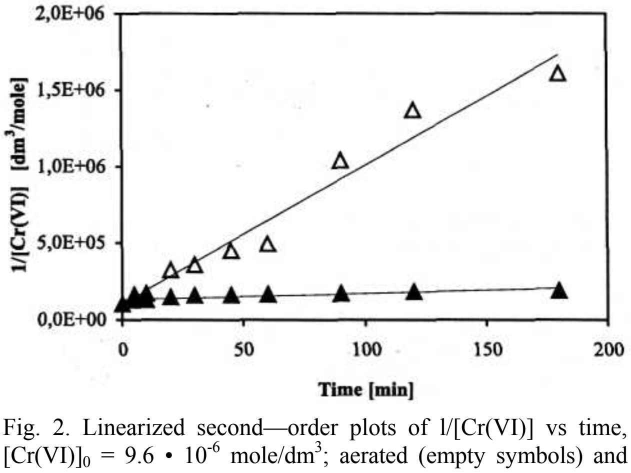

Fig. 2. Linearized second—order plots of l/[Cr(VI)] vs time, $[Cr(VI)]_0 = 9.6 \cdot 10^{-6}$ mole/dm^3; aerated (empty symbols) and deaerated (filled symbols) river water; pH = 8.8; t = 20°C.

Table 1. Second-order rate coefficients of Cr(VI) reduction by Fe(II) in river water.

Conditions	k_{obs} [$mole^{-1} \cdot dm^3 \cdot s^{-1}$]	$t_{1/2}$ [min]
pH 7.2; N_2	$2 \cdot 10^3$	1
pH 7.2; O_2	$1 \cdot 10^3$	2
pH 8.8; N_2	$1.5 \cdot 10^2$	12
pH 8.8; O_2	6	290

utions appeared to be of the same order as the rate coefficient of Cr(VI) reduction by Fe(II) determined for model conditions - $1.7 \cdot 10^3$ $mole^{-1} \cdot dm^3 \cdot s^{-1}$ (distilled water, de-aerated homogeneous system, stoichiometric amounts of reactants) [7].

The respective k_{obs} values in model heterogeneous systems (FeOOH, SiO_2) at pH 4.9 are in the range of 2 - 8 • 10^3 $mole^{-1} \cdot dm^3 \cdot s^{-1}$ [15]. The results from this study are also comparable to the kinetic data on Cr(VI) reduction by Fe(II) in an aerated model system described by Schroeder and Lee [8], with a $t_{1/2}$ = 1.5 min at pH 7.1 and a tic = 6 min at pH 7.5. Minor differences in the rate of Cr(VI) reduction at pH 7.2 in the presence or absence of dissolved oxygen indicates oxygen's minimal effect on this process. Cr(VI) reduction slows down significantly in the presence of oxygen at pH 8.8, with a $t_{1/2}$ = 290 min due to increased competition by dissolved oxygen for Fe(II). At pH 8.8 the Cr(VI) reduction proceeds at a rate over 10 times more slowly even in the absence of dissolved oxygen. Such a significant decrease in the rate of Cr(VI) reduction may have been caused by a change in Cr(VI) forms present in the heterogeneous system studied: water - sediment grains coated by hydrous ferric oxide.

The extent of chromium(VI) adsorption in the presence of a suspension of hydrous ferric oxide has been determined using surface complexation modeling. The following surface reactions were considered:

$$\equiv FeOH_2^+ = \equiv FeOH^\circ + H^+ \qquad pK_1^{int} = 7.29$$
$$\equiv FeOH^\circ = FeO^- + H^+ \qquad pK_2^{int} = 8.93$$
$$\equiv FeOH^\circ + H^+ + CrO_4^{2-} = \equiv FeCrCO_4^- + H_2O \qquad pK_3^{int} = 10.67$$

Model calculations assumed the following: ionic strength μ = 0.01 mole/dm^3 and coulombic correction factor logP = -1.85, -0.84 and 0.65 at pH = 6, 7.2, and 8.8, respectively; the numerical values for intrinsic constants and coulombic correction factors were taken from Morel and Hering [23]. The calculations apply to an idealized system in which iron(III) oxides are the only adsorbents, adsorption is reversible and there are no competing sorption processes. The calculation results are given in Table 2.

Table 2. Chromium(VI) speciation in the presence of suspension of hydrous ferric oxide.

pH	Percent species [%]		
	$HCrO_4^-$	CrO_4^{2-}	$\equiv FeCrO_4^-$
6.0	0.5	0.2	99.3
7.2	3.6	24.0	72.4
8.8	0.4	99.4	0.2

Surface complexation modeling indicates that at pH 6, Cr(VI) is present primarily in the adsorbed form as $\equiv FeCrO_4^-$ while at pH 7.2 the sorption decreases to 72.4%, and the amount of the dissolved chromates increases to: CrO_4^{2-} - 24.0% and $HCrO_4^-$ - 3.6%. When pH reaches 8.8, nearly all chromium(VI) is in solution.

The pronounced change in the content of adsorbed Cr(VI) occurring when pH changes from 7.2 to 8.8 cannot be ignored when considering the reasons for a decrease in the rate of Cr(VI) reduction.

Chromium(VI) Reduction in the Presence of Humic Acids

The results of chromium(VI) reduction by humic acids is described in Fig. 3. In river water spiked with HA the reduction proceeded in two steps, with an initial fast step and a slow sustained process. The kinetics of the slow step of reduction was similar to the kinetics of Cr(VI) reduction in river water (control test). The kinetic plots for Cr(VI) reduction in water spiked with humic acids remained almost parallel. This behaviour suggests that a fast initial decrease in Cr(VI) concentration caused by oxidation of the most reactive HA groups is followed by oxidation of groups exhibiting similar rates of reaction with Cr(VI). Thus, in this reaction HA should be treated as a finite set of functional organic groups that react at different rates. Such a possibility was earlier suggested by Wittbrodt and Palmer [12]. The dependence of the rate of reduction on the initial concentration of the reductant is reflected in the lack of a sufficient excess of HA in relation to Cr(VI). In the systems studied HA concentrations were specifically selected to match the contents commonly found in surface waters [24]. Taking into account the average molecular mass Aldrich HA 14-20 kD [25], at an unknown number of reducible groups per 1 molecule of HA, the amount of Aldrich HA used could not constitute a sufficient excess to establish

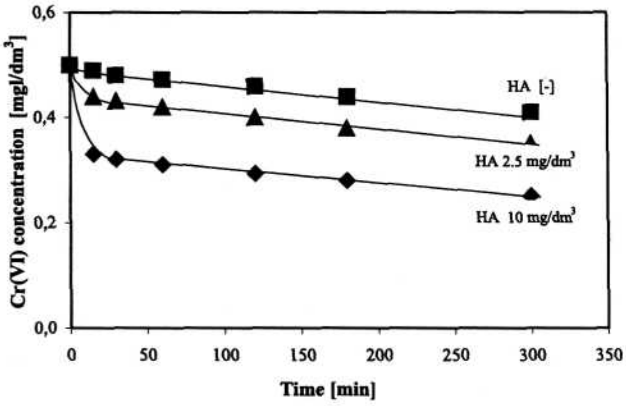

Fig. 3. Chromium(VI) reduction in river water spiked with HA, (added [HA] are in the figure); $[Cr(VI)]_0$ = 0.5 mg/dm^3; pH = 7.2; t = 20°C.

Table 3. Kinetic parameters of Cr(VI) reduction by HA in river water.

Spiking [HA] [mg/dm^3]	Fast step k$_{obs}$ [mole^{-1} · dm^3 · s^{-1}]	Fast step t$_{1/2}$ [h]	Slow step k$_{obs}$ [mole^{-1} · dm^3 · s^{-1}]	Slow step t$_{1/2}$ [h]
–	1.5	19	1.5	19
2.5	16	1.8	1.8	16
10	59	0.5	2.9	10

pseudo-zeroth-order conditions with respect to HA concentration, especially when considering the groups participating in the initial fast step.

The little known structure of humic acids allows only for empirical approach to the kinetic equation of Cr(VI) reduction by HA. The equation for the second-order kinetics was used, obtaining good fit of experimental data for the slow step of reduction (Fig. 4). Rate constants (k_{obs}) and their corresponding half-lives are presented in Table 3.

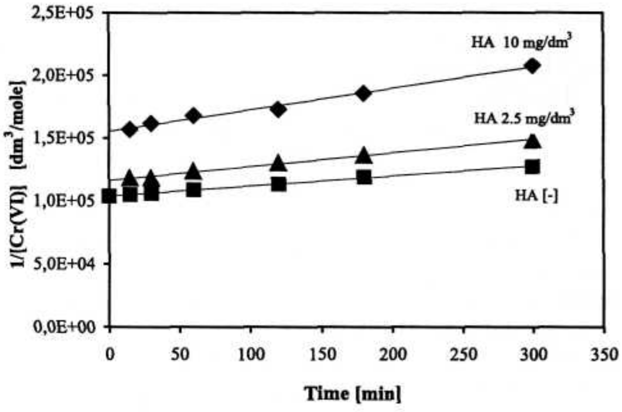

Fig. 4. Linearized second—order plots of l/[Cr(VI) vs time; $[Cr(VI)]_0 = 9.6 \cdot 10^{-6}$ mole/dm^3; pH = 7.2; t = 20°C; added [HA] are in the figure.

Because of the low degree of reaction and fast Cr(VI) reduction in the initial step, the quantities found are approximate for the slow step and only tentative for the fast step. Under experimental conditions Cr(VI) reduction by HA was characterized in the initial phase by the rates that were more than an order of magnitude higher than those in the slow step.

All the values appear to be much higher than those quoted by Wittbrodt and Palmer [13], who studied Cr(VI) reduction by HA in a homogeneous system using an excess (100-fold w/w) of HA. The authors determined $t_{1/2}$ of about 50 h at pH 2 and nearly 5 months at pH 6. Cr(VI) reduction was accelerated in the presence of Fe(III). The 2 µM concentration of Fe(III) was enough to shorten $t_{1/2}$ to less than 17 h. In this study Cr(VI) reduction by HA was carried out in a system with solid phase - river bottom sediment containing over 1 g/kg Fe. In a control sample without Cr(VI) the presence of 10 mg/dm^3 HA increased the aqueous Fe concentration by 1 mg/dm^3 Hence, it is probable that Fe oxides in bottom sediment are a source of a much more reactive reducing agent, such as Fe(II) or its complexes with HA [26, 27]. This increased Fe(II) concentration may explain the sudden decrease in Cr(VI) concentration in the initial step of Cr(VI) reduction. Thus, it is possible that Fe(II) released while conditioning the river water - bottom sediment - HA system reduced the added Cr(VI) at a considerable rate.

Oxidation of Chromium(III)

No measurable amounts of Cr(VI) were detected after 60 min. in a control experiment (river water + bottom sediment + MnO_2). The anthropogenic chromium present in the bottom sediment turned out to be resistant to the oxidative behaviour of MnO_2. Under those conditions Cr(III) added to the river waters was oxidized by MnO_2. Courses of Cr(III) oxidation were similar. The initial fast step was followed in a relatively short time (15-30 min) by complete inhibition of the oxidation process. The initial rate of Cr(III) oxidation and conversion degree were affected considerably by aqueous and solid composition (Fig. 5). The highest degree of Cr(III) transformation to Cr(VI) was found in distilled water (92%); a lower degree in river water (74%) probably resulted from partial blocking of the MnO_2 surface due to adsorption of water constituents. Sorption of Cr(III) species on the surface sediment further decreased the oxidationate up to 55% in the system containing bottom sediment. System pH also influenced the kinetics of chromium(III)

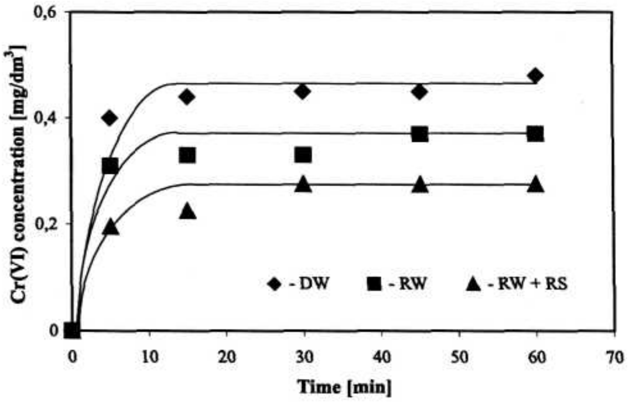

Fig. 5. Chromium(III) oxidation by MnO_2 in distilled water (DW), river water (RW), river water containing bottom sediment (RW + RS); $[Cr(III)]o = 0.5$ mg/dm^3; $[MnO_2] = 250$ mg/dm^3; pH = 6.9; t = 20°C.

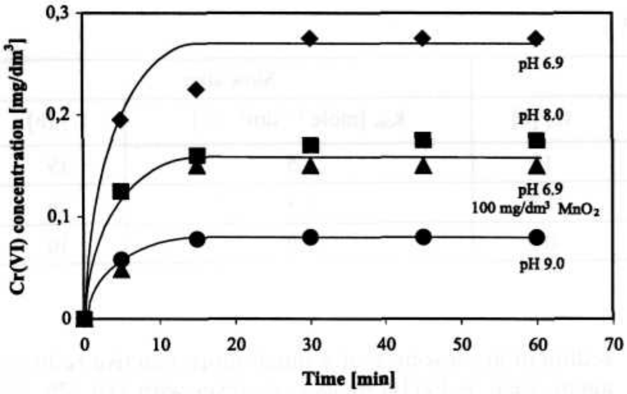

Fig. 6. Chromium(III) oxidation by MnO_2 in river water containing bottom sediment, at various pH 6.9, 8.0, 9.0; $[Cr(III)]_0$ = 0.5 mg/dm^3; [MnO_2] = 250 mg/dm^3 and 100 mg/dm^3; t = 20°C.

oxidation by MnO_2 in the presence of sediment (Fig. 6). Net oxidation over 60 minutes decreased from 55% at pH 6.9 to 15% at pH 9.0. The decrease in conversion with increasing pH may be associated with conversion of dissolved Cr(III) species into hydroxides, which are more difficult to oxidize. The transformation of Cr(III) to Cr(VI) is also dependent on MnO_2 content; lowering the content of the oxidizing agent from 250 mg/dm^3 to 100 mg/dm^3 at pH 6.9 resulted in a decrease of conversion to 29%.

The most easily oxidizable chromium compound was $Cr(NO_3)_3$ (55% conversion over 1 hr). Chromium introduced as freshly prepared $Cr_2(SO_4)_3$ solution was oxidized 32% over the same period. Chromium from used tanning liquor and in aged $Cr_2(SO_4)_3$ solution was the most difficult to oxidize (Fig. 7). The fact that chromium contained in used tanning liquor was oxidized to a somewhat larger extent than the one in aged $Cr_2(SO_4)_3$ probably results from the presence of not only sulphato-Cr(III) and oligomeric-Cr(III) species but also soluble, at intermediate pH, organic chromium complexes [28, 29, 30, 31].

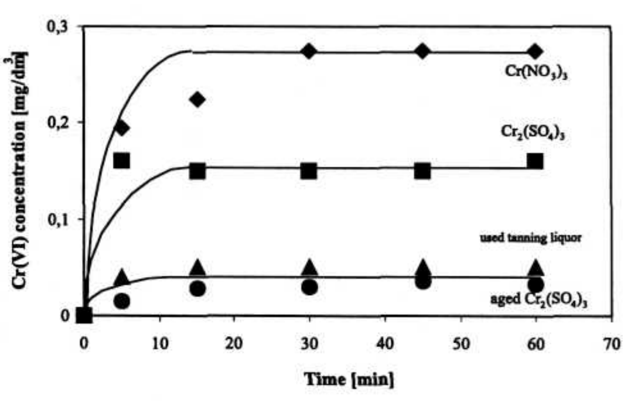

Fig. 7. Oxidizability of varies Cr(III) forms by MnO_2 in the river water containing bottom sediment; $[Cr(III)]_0$ = 0.5 mg/dm^3; [MnOJ = 250 mg/dm^3; pH = 6.9; t = 20°C.

Conclusions

The aim of this study was to facilitate forecasting the fate of chromium discharged into the environment by the tanning industry located in the Radomka River basin in Poland. Cr(VI) may be present in the polluted environment only in low concentrations originating from impurities of mineral tanning agents and as a result of Cr(III) oxidation. The results indicate potential instability of chromium(VI) in the environment studied. Cr(VI) undergoes a reduction at a low rate ($t_{1/2}$ = 19 h) in the Radomka River water. This natural Cr(VI) reduction process to some extent participated in the reduction observed in river water spiked by HA and Fe(II); however, Cr(VI) reduction by HA may be ignored due to a considerable half-time of this reduction.

An increase in the HA content increases the rate, particularly in the initial step ($t_{1/2}$ = 0.5 h). It is highly probable that also in this case the Fe(III)/Fe(II) redox couple appears to act as an electron transfer catalyst for the reduction of Cr(VI) [13]. Micromolar concentrations of Fe(II) significantly speed up the reduction of Cr(VI) ($t_{1/2}$ = 2 min). In a weakly alkaline environment the rate of Cr(VI) reduction decreases due to competing oxidation of Fe(II) by dissolved oxygen ($t_{1/2}$ = 5 h) and a change in Cr(VI) speciation.

The rate constants determined are appropriate only for the conditions in the investigated environmental system. However, such an approach is useful when determining the interrelation between various chromium species in the environment.

The appearance of MnO_2 in river water polluted by chromium(III) may result in its oxidation to chromium (VI). Chromium present in used tanning liquor is less oxidizable by MnO_2 than Cr(III) in solutions of chromium nitrates and sulphates. Also, a change in pH towards alkaline decreases the rate of Cr(III) to Cr(VI) transformation. Chromium deposits in bottom sediment are resistant to the oxidative action of MnO_2 under those conditions. Thus, the speciation and solid-phase partitioning of Cr(III) must be considered to accurately determine chromium redox chemistry.

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