Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Rao, N. N. , Kumar, A. and Kaul, S. N.(2002) 'Chromium exchanged insoluble straw xanthate (ISX-Cr^3) for removal of free cyanide: combined effect of ligand-displacement reaction and sorption', Separation Science and Technology, 37: 9, 2167 — 2182

To link to this Article: DOI: 10.1081/SS-120003507

URL: http://dx.doi.org/10.1081/SS-120003507

SEPARATION SCIENCE AND TECHNOLOGY, 37(9), 2167–2182 (2002)

CHROMIUM EXCHANGED INSOLUBLE STRAW XANTHATE (ISX-Cr^{3+}) FOR REMOVAL OF FREE CYANIDE: COMBINED EFFECT OF LIGAND-DISPLACEMENT REACTION AND SORPTION

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ABSTRACT

The use of chromium exchanged insoluble straw xanthate (ISX-Cr) for cyanide removal from aqueous solutions is reported in this paper. Using a dose of 0.5 g ISX-Cr per 100 mL, about 75–90% of initial CN^- concentration is removed from unbuffered solutions during a contact period of 15 min. Further removal of CN^- is possible by extending the contact period to 24 hr. Interestingly, when the solutions were buffered at pH 9.2 ± 0.01, the CN^- removal rate is considerably reduced, and a contact period of 4 hr is required to achieve 60–75% CN^- removal. The process is found to follow typical pseudo first-order reaction kinetics with respect to initial cyanide concentration. The first order rate constant for CN^- removal from unbuffered solutions is an order of high magnitude ($k = 0.2464\ \text{min}^{-1}$) when compared to that in buffered solutions

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($k = 0.0283\,\mathrm{min}^{-1}$). This difference has been attributed to significant lowering of pH (from pH 9.6 to pH 7.0) found only in the case of unbuffered solutions and to the volatilization of HCN that formed predominantly at pH < 8.0. On the other hand, the net removal of CN^- from the buffered solutions could be assigned to the combined effect of (i) sorption by ISX and (ii) ligand-displacement reaction involving an aqua-hydroxo-chromium complex on the surface of ISX and CN^- as a ligand. The contribution from the ligand-displacement reaction, which is worked out to be 20–25% of net CN^- removed, appears to manifest in the beginning of the CN^- removal process, while sorption prevailed during the complete experimental period. Finally, a representative experiment conducted using bore-well water spiked with 1.0 mg CN^-/L and 0.5 g ISX-Cr per 100 mL dose suggested that CN^- removal efficiency exceeding 90% can be achieved in 24 hr and demonstrated that ISX-Cr^{3+} material can be used to remove cyanide from real water also.

Key Words: Chromium exchanged insoluble straw xanthate; Cyanide; Ligand-displacement reaction; Sorption

INTRODUCTION

Adsorption of metals from water/wastewater using low-cost adsorbents such as starch, straw, sawdust, peat moss, sugar cane pulp, coconut hulls etc., has emerged as a cheaper and an attractive route for heavy metal removal (1,2). A number of studies (3–9) reveal that xanthation of cellulose materials results in the formation of dithiocarbonate groups ($-CH_2OCS_2^-$) that participate in heavy metal removal effectively. Recently, we reported heavy metal removal using alkali-treated and xanthated wheat straw for chromium removal as well as removal of various metal ions simultaneously from mixed metal-ion solutions (10). Our studies on ISX-Cr^{3+} system revealed that xanthate groups bind hexaaqua Cr^{3+} complex, $[Cr(H_2O)_6]^{3+}$, through unidentate monosulfur chelation. But, we found the regenerability of Cr^{3+}-exchanged xanthated straw (ISX-Cr^{3+}) was very low, typically $<20\%$ in 0.1 *N* HCl regenerant. Other regenerants such as sodium salts of ethylenediaminetetraacetic acid [Na_2H_2(edta)], citric acid, and sodium chloride were also tried, but with limited success. The strong binding power of alkoxide and xanthate groups towards metal ions was construed to be the reason for lower regenerability of ISX-Cr^{3+}. Under these circumstances, we started to look for any possible reuse of meal-exchanged ISX. Considering that the coordination sphere around Cr^{3+} linked to ISX consists of aqua and hydroxo ligands, we expected that some ligands stronger than aqua and hydroxo ligands would displace them. Then, we searched for the prospective ligand in the spectrochemical series (11) keeping in view that it should be a common pollutant in water bodies. We found that highly toxic free-cyanide (CN^-) present in some water bodies is a well-known stronger ligand and it is important in pollution context as well. Cyanides are employed in many industrial and manufacturing areas viz. plating industry, heat/surface treatment, and metal ore and smelting, petrochemical, and gold mining. They occur mainly as cyanide ions, hydrogen cyanide, or as complex bound cyanides. The complex bound cyanides are 3–4 orders magnitude less toxic compared to free cyanide (12). A large number of processes of different types are available for treating cyanide-bearing wastewaters: alkali chlorination, electro-chlorination, ozonation, oxidations using "per" compounds, complexation, ion-exchange, adsorption, acid volatilization and combustion, liquid–liquid extraction, and ion-flotation. Recently, Aurelle (12) presented an excellent review on cyanide removal processes. Some biological processes are also known for cyanide destruction (13). The recommended standard values of CN^- in drinking water are: 0.07 mg/L (WHO Guidelines, 1993); 0.05 mg/L (European Community Directive, 1980); 0.20 mg/L (US, EPA, 1992), and 0.05 mg/L (IS 10500, 1983, India).

In this paper, we report the removal of free cyanide from aqueous solution using ISX-Cr^{3+}. The effectiveness of ISX-Cr, initially demonstrated using somewhat higher initial concentration of CN^- (2–22 mg/L) in deionized water, was finally extended to a real-water sample fortified with approximately 1.0 mg CN^-/L. The findings of this work are important because this is the first ever attempt to make use of metal-exchanged insoluble straw xanthate (ISX) for removal of toxic pollutant, such as cyanide from water. It may be noted that several synthetic polymeric ligands have been devised in the past to abstract heavy metal ions, but a similar development for anion uptake is unknown.

EXPERIMENTAL

Materials

Insoluble straw xanthate was prepared according to a reported procedure (10,14). Chromium-loaded ISX was obtained by bulk adsorption of Cr^{3+} on the surface of ISX. Chromium nitrate, $Cr(NO_3)_3$ was used to prepare stock solutions of Cr^{3+} of varying concentrations in the range 10–50 mg/L. A 25-g of ISX was added to 500 mL of 10 mg/L solution of Cr^{3+}. The admixture was stirred for 90 min, filtered, and washed with deionized water. The material was then dried at room temperature. Similarly 10 g of ISX was used for individual cases of Cr^{3+} concentration ranging from 20 to 50 mg/L to get ISX loaded with Cr^{3+}. This material is recognized as ISX-Cr^{3+}, henceforth. All the metal salts and solvents were of analytical or reagent grade.

Stock solution of cyanide (1000 mg CN^-/L) was prepared by dissolving 2.5 g KCN in 1 L of 1 *M* sodium hydroxide solution. All working solutions were prepared by diluting the stock solution with deionized water.

Cyanide Removal Experiments

Batch experiments for cyanide removal were conducted using 0.5 g of ISX-Cr^{3+} per 100 mL solution of appropriate concentration of cyanide, chosen in the range 2.0–22.0 mg/L. Generally, ISX-Cr^{3+} with loaded Cr^{3+} concentration of 10.63 mg Cr^{3+}/g ISX was used throughout the studies unless otherwise stated. These experiments were carried out at 25 ± 1°C and the solutions were shaken at 30 rpm using a shaker cum controlled-temperature water bath (Gallenkamp, England, UK). Initially, some experiments were conducted using as-prepared cyanide solutions without pH adjustment. In order to assess the effect of pH on cyanide removal, some experiments were also conducted in cyanide solutions whose pH is adjusted to 8.00, 9.10, and 10.20 using either 0.1 *N* HCl or NaOH. At the end of each experiment, the reaction mixture was decanted and analyzed for pH (final) and final cyanide concentration. Subsequently, experiments were conducted in cyanide solutions that were buffered to pH 9.2 ± 0.01. For all the kinetic studies, the initial cyanide concentration was varied in the range 2.0–22.0 mg/L in buffered aqueous solutions and the changes in the cyanide concentration for each case were monitored as a function of contact time. In experiments to assess the effect of ISX-Cr^{3+} doses, the dose of ISX-Cr^{3+} was varied from 0.2 to 1.0 g per 100 mL. Some control experiments were also performed for checking the removal of cyanide by ISX without any Cr loading. The analytes were also checked for residual chromium. Further, the feasibility of cyanide removal from real-water samples was examined using bore-well water spiked with 1.0 mg CN^-/L and 0.5 g ISX-Cr per 100 mL dose. The initial pH of bore-well water was around 7.8. This was adjusted to pH 9.0–9.1 using 0.01 *N* NaOH prior to cyanide removal experiments.

Analytical Procedures

An atomic absorption spectrophotometer (GRC 904 AA, Dadoneng, Australia) with oxygen–acetylene flame was used to analyze the initial and final concentrations of Cr^{3+} in test samples. The detection level for Cr is 0.006 mg/L. A water quality analyzer (ELICO PE 136, Hyderabad, India) equipped with combination pH electrode was used to measure pH of all solutions. The accuracy of measurement is ±0.01 pH. Microprocessor-controlled pH Ion Meter (PMX

3000/Ion, WTW, Wilheim, Germany) with a silver–silver chloride reference electrode and a cyanide electrode (CN-500, WTW, Wilheim, Germany) was used to determine concentration of cyanide. The minimum detection level for cyanide is 0.03 mg/L. Prior to analysis, the instrument was subjected to double-point calibration on each day using 1- and 10-mg CN^-/L standard solutions. A slope between 58 and 62 mV is regarded as suitable for proceeding with analysis for cyanide. Both reference and cyanide electrodes were wrapped with "gauge cloth" to prevent direct contact of ISX fibers with the electrode membrane, which otherwise resulted in fluctuations in readings. In general, each data point reported is representative of at least duplicate tests, the error of determination in cyanide being about 2% at >1.0 mg CN^-/L and about 5% at <1 mg CN^-/L.

RESULTS AND DISCUSSION

Loading of Cr^{3+} on to Insoluble Straw Xanthate

The extent of chromium loading per gram of ISX by bulk adsorption from different concentrations of Cr^{3+} solutions is given in Table 1. The data indicated that an average saturation loading of 24.5 mg Cr^{3+}/g ISX could be obtained. The desired loading of 30, 40, and 50 mg Cr^{3+}/g ISX could not be achieved.

Cyanide Removal Process—pH Dependence and Manifestation of Equilibrium Between Free Cyanide and Hydrocyanic Acid

During the preliminary batch experiments for cyanide removal using as-prepared cyanide solutions (without pH adjustment) and ISX-Cr^{3+}, it is found

Table 1. Desired and Actual Loading of Cr^{3+} per g of ISX

Sr. No.	Desired (mg Cr^{3+}/g ISX)	Actual (mg Cr^{3+}/g ISX)
1	5	4.85
2	8	8.34
3	10	10.63
4	20	20.31
5	30	22.73
6	40	24.10
7	50	26.81

that significant quantity (75–90%) of cyanide is removed during the initial 15-min contact period (Fig. 1). This is accompanied by a drop in pH from 9.0–9.6 to 7.1–7.5. On the other hand, the cyanide removal was found to be considerably slower in buffered solutions (Fig. 2). A contact period of about 4 hr is required to achieve 60–75% CN^- removal. The residual CN^- concentration and percent CN^- removals at different initial CN^- concentrations and at different contact periods are given in Table. 2. The final pH remained very close to the buffered pH of 9.2 ± 0.01. The concentration of chromium in the test solutions was below detectable limit. The initial rates of cyanide removal at different concentrations of cyanide were estimated from the slopes of the 5-min sections of plots shown in Figs. 1 and 2. The dependence of initial rate of removal of cyanide from unbuffered and buffered solutions upon the initial concentration of CN^- is shown in

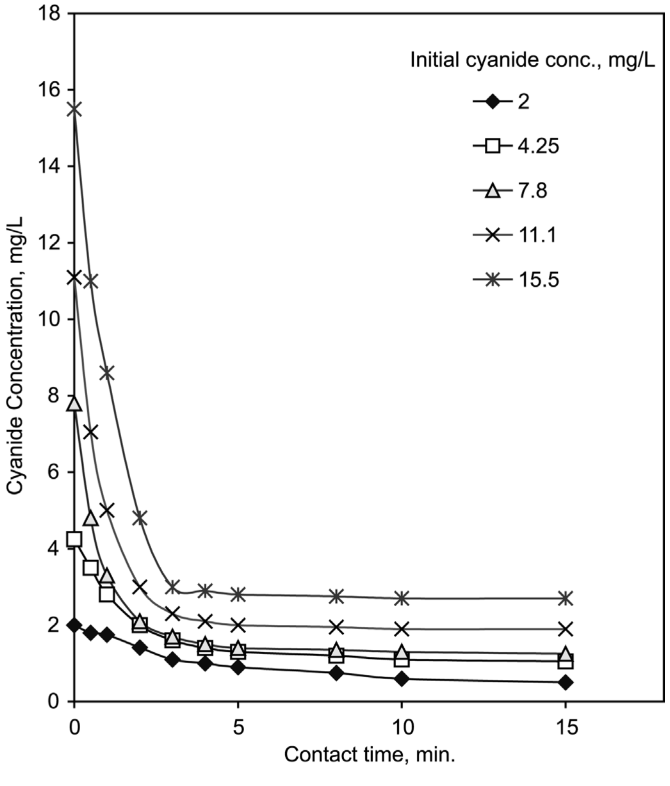


Figure 1. Cyanide removal from unbuffered cyanide solutions using ISX-Cr^{3+} as a function of contact time; dose = 0.5 g ISX-Cr per 100 mL; initial pH = 9.0–9.6.

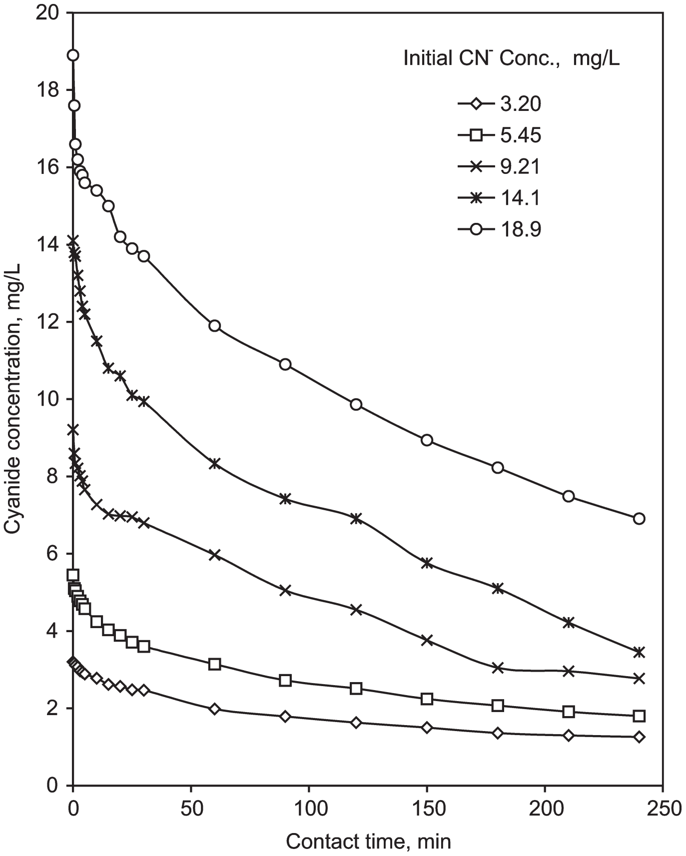


Figure 2. Cyanide removal from buffered cyanide solutions (pH 9.20 ± 0.01) using ISX-Cr^{3+} as a function of contact time; dose = 0.5 g ISX-Cr per 100 mL.

Fig. 3. A straight-line graph suggested that the rate of cyanide removal is approximately proportional to cyanide concentration and the reaction of cyanide removal follows typical pseudo first-order rate equation with respect to cyanide. The first-order rate constant, as deduced from the initial linear section of the curve representing the case of unbuffered solutions is $0.2464\,\text{min}^{-1}$. The first-order rate constant for cyanide removal from buffered solutions is estimated to be $0.0283\,\text{min}^{-1}$ from the slope of the corresponding straight-line graph in Fig. 3. Thus, the first-order rate constant for cyanide removal from unbuffered solutions is 10-fold high when compared to that in buffered solutions.

Table 2. Residual Cyanide Concentration and Percent Cyanide Removals at Different Initial Cyanide Concentrations and Different Intervals Obtained Using 0.5 g ISX-Cr^{3+} per 100 mL in Buffered Solutions (pH 9.20 ± 0.01)

Initial CN Concentration (mg/L)	20 min		2 hr		4 hr	
	Residual CN (mg/L)	% R	Residual CN (mg/L)	% R	Residual CN (mg/L)	% R
3.2	2.57	20.0	1.63	49.0	1.26	60.6
5.45	3.89	28.6	2.51	54.0	1.8	67.0
9.21	6.98	24.2	4.55	50.6	2.77	70.0
14.1	10.6	24.8	6.91	51.0	3.45	75.5
18.9	14.2	24.8	9.86	47.8	6.91	63.5

The extent of cyanide removals at different adjusted pH values viz. 8.00, 9.10, and 10.20 and the final pH values attained in each case are presented in Table 3. The highest removal efficiency for cyanide is obtained at pH 9.0. On the other hand, the removal efficiency decreased by 5–6 times at pH 10.2. Experiments could not be performed at pH 8 as the solutions had only 30% of free CN^- and 70% of HCN (12).

The results, particularly the 10-fold higher magnitude of rate constant found in unbuffered solutions can be attributed to significant lowering of pH that accompanied CN removal in this case. It is known that cyanide and hydrocyanic acid exist in pH- and temperature-dependent equilibrium as shown below.

$$[CN^-]_{aq} \leftrightarrow [HCN]_{aq} \rightarrow [HCN]_g \uparrow \quad \text{at pH} < 8.0$$

The equilibrium shifts towards the right at $pH < 8.0$, thereby producing hydrocyanic acid. The hydrocyanic acid easily volatilizes. It is found that the

Table 3. Effect of pH on the Percent Removal of Cyanide. Contact Time = 30 min; ISX-Cr^{3+} = 0.5 g per 100 mL

Sr. No.	pH		% CN^- Removed
	Adjusted	Final	
1	8.0	—	—
2	9.1	7.1	69.9
3	10.2	9.6	10.5

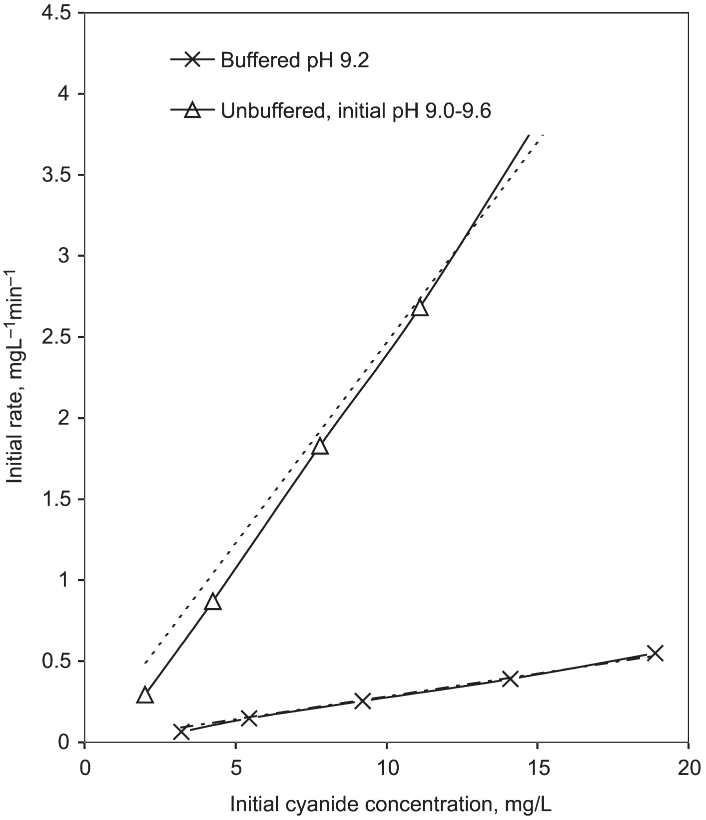


Figure 3. Dependence of initial cyanide removal rate on the initial concentrations of cyanide; dose = 0.5 g ISX-Cr per 100 mL.

above-mentioned equilibrium, persistent in unbuffered solutions, contributes to cyanide removal in the form of volatile HCN. The above-mentioned equilibrium is exploited for destroying cyanides using Cyan-Cat™ process, which is essentially acidification of cyanide wastes to pH 2.5, followed by air stripping of HCN and its combustion in a catalytic furnace (12,14).

It was mentioned earlier that a contact period of about 4 hr is required to achieve 60–75% CN^- removal using 0.5 g ISX-Cr^{3+} per 100 mL. The longer contact period and lower efficiency are typical of slow complexation and sorption process. Thus, it would require 37 kg ISX-Cr^{3+} for removing 1 kg CN^-, at 75% removal efficiency. In contrast, chemical oxidation processes, such as ozonation and alkaline-chlorination oxidize cyanide into cyanate efficiently in shorter contact periods. For example, about 1.85–2.8 kg O_3/kg CN^- and a contact time of 10–15 min is adequate for oxidizing CN^- into cyanate completely (12).

Effect of the Dose of ISX-Cr^{3+} on Cyanide Removal

Table 4 presents the percent cyanide removed for a range of ISX-Cr^{3+} doses between 0.2 and 1.0 g. The CN^- removal efficiency increased from 63.0 to 89.6% when the dose is increased from 0.2 to 0.5 g. Thereafter, the cyanide removal efficiency remained almost constant (89–90%) up to a maximum applied dose of 1.0 g.

Cyanide Removal: ISX vs. ISX-Cr^{3+}

The comparison of ISX and ISX-Cr^{3+} for their effectiveness to remove cyanide is shown in Fig. 4. It is found that ISX also removes cyanide, although to a lesser extent, about 24% of CN^- can be removed in a 2-hr contact period. In contrast, about 60–65% CN^- is removed using ISX-Cr^{3+} in the same contact period. The curve relevant to ISX-Cr^{3+} exhibited two distinct regions (unlike that of ISX): region I showing much faster CN^- removal initially within a 15–20-min period and region II showing gradual removal of CN^- similar to that found with ISX. About 25% of initial CN^- concentration is removed in region I, and the remaining is removed gradually. The gradual removal of cyanide by ISX can be

Table 4. Dependence of Percent Cyanide Removals on the Dose of ISX-Cr^{3+}. Initial Cyanide Concentration = 30 mg/L; pH = 9.20 ± 0.01; Contact Time = 24 hr

Sr. No.	Dose of ISX-Cr^{3+} (g/100 mL)	% Cyanide Removal
1	0.2	63.0
2	0.3	75.5
3	0.4	84.6
4	0.5	89.6
5	0.6	89.7
6	0.8	89.0
7	1.0	90.0

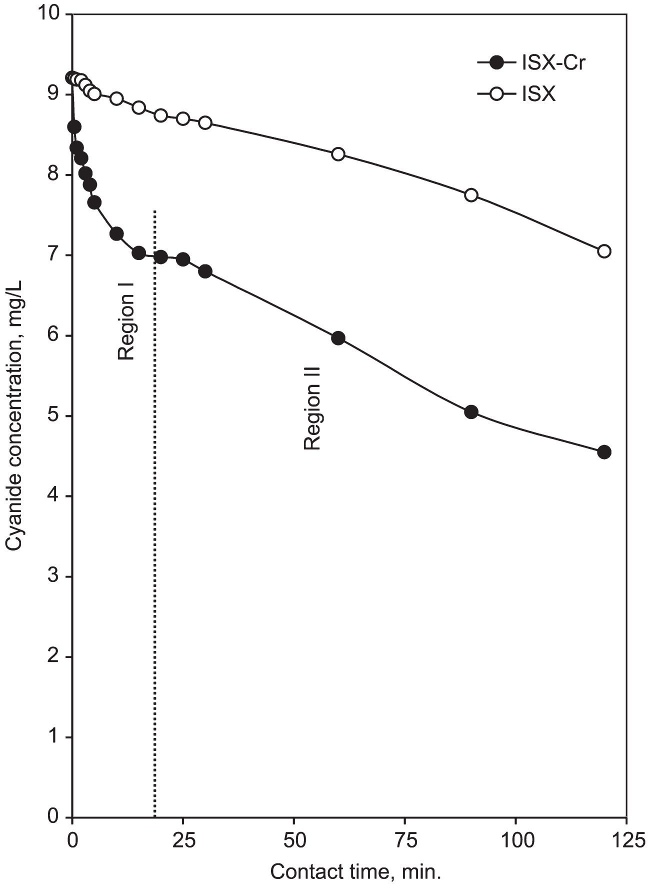


Figure 4. Comparison of ISX and ISX-Cr for their effectiveness in cyanide removal; initial cyanide concentration = 9.21 mg/L; pH = 9.2 ± 0.01; dose = 0.5 g ISX-Cr per 100 mL or 0.5 g ISX per 100 mL.

attributed to slow sorption. On the other hand, a considerably faster CN^- removal process preceded sorption removal when ISX-Cr^{3+} is used.

Influence of Loaded Cr^{3+} Concentration on CN^- Removal

The influence of loaded Cr^{3+} concentration on the efficiency of cyanide removal is shown in Fig. 5. It is found that the quantity of cyanide removed

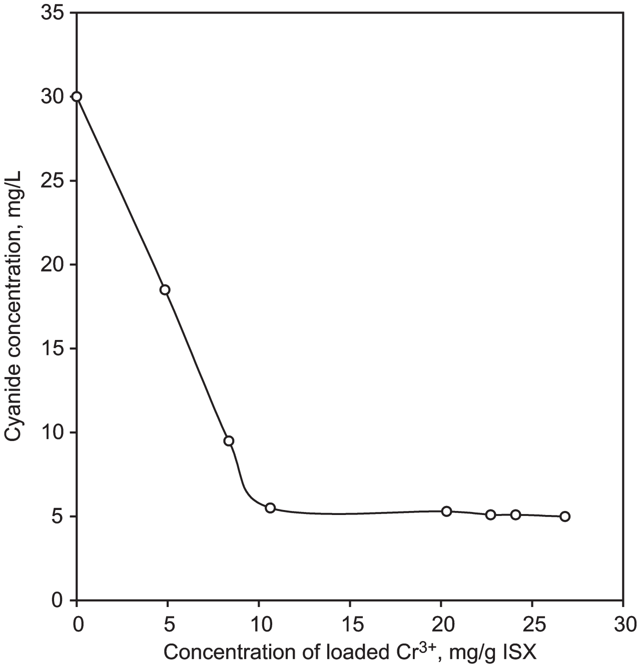


Figure 5. Influence of concentration of loaded Cr^{3+} on the cyanide removal; dose = 0.5 g ISX-Cr per 100 mL; contact time = 4 hr; pH = 9.2 ± 0.01.

gradually increased with increase in the Cr^{3+} loading up to 10 mg/g ISX. Thus, a saturation removal efficiency of about 81.6% of initial cyanide concentration could be attained. Further increase in loaded Cr^{3+} concentration did not prove to be useful in enhancing the quantity of cyanide removed.

Cyanide Removal from Real-Water Sample

The feasibility of cyanide removal from bore-well water using 0.5 g ISX-Cr per 100 mL dose is shown in Fig. 6. It can be seen that U.S. EPA (1982) recommended standard for CN^- in drinking water (0.20 mg/L) may be achieved within a 16-hr contact period. Further stringent guidelines of WHO (0.07 mg/L), European Community (0.05 mg/L), and IS 10500-1983 (0.05 mg/L) may also be achieved in about 24 hr. The rate of CN^- removal is relatively slow (initial rate 0.02 mg/L/min) as expected from the first-order rate dependence in CN^-.

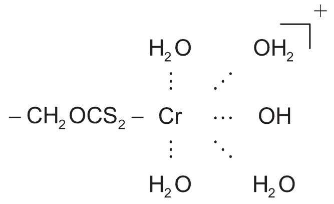
Mechanism of Cyanide Removal Using ISX-Cr^{3+}—Combined Effect of Ligand-Displacement Reaction and Absorption

The results presented thus far suggest that the net removal of CN^- from aqueous buffered solutions can be assigned to the combined effect of (i) sorption by ISX bulk material and (ii) reaction of CN^- with Cr^{3+} species on the surface of ISX. The participation of Cr^{3+} on the surface of ISX is suggested based on the results shown in Figs. 4 and 5. The facts that ISX-Cr^{3+} exhibited quite faster CN^- removal initially when compared to that of ISX alone and cyanide removal showed dependence on the loaded concentration of Cr^{3+}, support Cr^{3+} participation in cyanide removal.

It has been shown earlier (10) that the surface of ISX exhibits polyfunctionality, comprising groups such as $-CH_2OH$, $-CH_2O^-Na^+$ and $-CH_2OCSS^-Na^+$. Since the bulk adsorption of Cr^{3+} was carried out using $Cr(NO_3)_3$ solution having a natural pH of about 3.6, the $[Cr(H_2O)_6]^{3+}$ species is expected to participate in adsorption-exchange reaction with ISX. It was also confirmed earlier by us that xanthate groups bind Cr^{3+} aqua complex through unidentate monosulfur chelation as shown below.

$$-CH_2OCSS^-Na^+ + [Cr(H_2O)_6]^{3+} \rightarrow -CH_2OCSS\,Cr(H_2O)_5^{2+} + Na^+ + H_2O \qquad (1)$$

Since cyanide removal experiments in the present study were conducted at buffered pH 9.2, it is expected that one or more aqua ligands (H_2O) are replaced by OH^- ligands. The resultant Cr^{3+} bound to ISX could be viewed as below.



$$\left.\begin{array}{cccc} & H_2O & & OH_2 \\ & \vdots & \cdot^{\cdot^{\cdot}} & \\ -CH_2OCS_2- & Cr & \cdots & OH \\ & \vdots & \ddots & \\ & H_2O & & H_2O \end{array}\right]^{+}$$

When ISX-Cr^{3+} with above description is exposed to CN^-, the H_2O/OH^- ligands may be displaced by CN^- ions, since the latter is a stronger ligand/nucleophile (11). Thus, the initial activity of ISX-Cr^{3+} in cyanide removal may be assigned to the ligand-displacement reaction [Eq. (2)]. The reaction is shown to follow first-order kinetics with respect to cyanide concentration as per the rate law, $-d[CN^-]/dt = k[CN^-]$, where $k =$ rate constant of the reaction

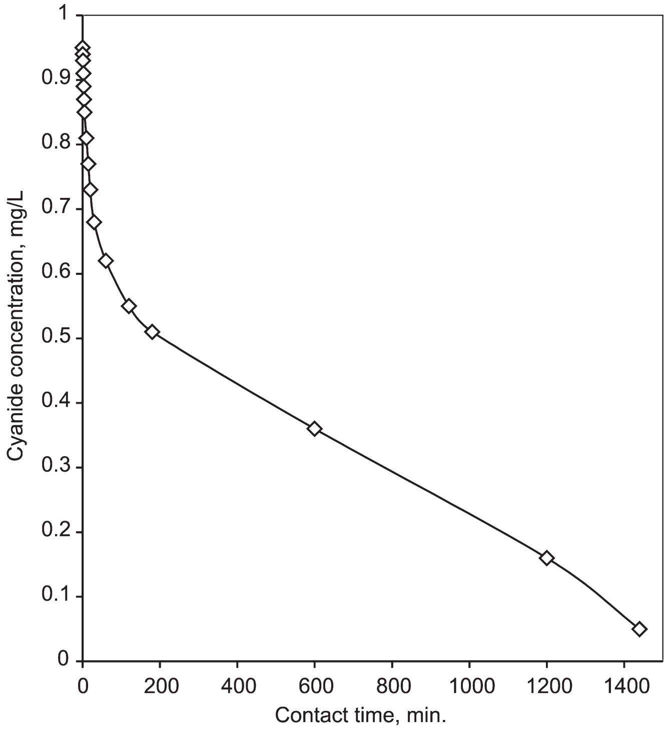
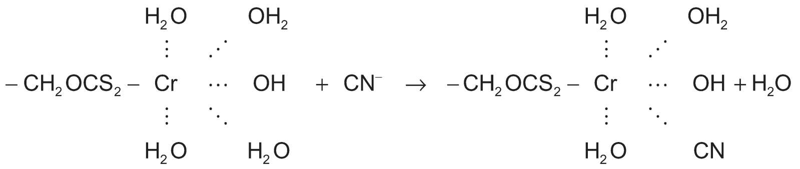


Figure 6. Cyanide removal from bore-well water spiked with 0.95 mg CN^-/L; dose = 0.5 g ISX-Cr per 100 mL; pH 9.0–9.1.

which is found to be 0.0283 min^{-1}.



$$\begin{array}{ccccccccc} & H_2O & & OH_2 & & & & H_2O & & OH_2 \\ & \vdots & & \cdot^{\cdot^{\cdot}} & & & & \vdots & & \cdot^{\cdot^{\cdot}} \\ -CH_2OCS_2- & Cr & \cdots & OH & + CN^- \rightarrow & -CH_2OCS_2- & Cr & \cdots & OH + H_2O \\ & \vdots & & \ddots & & & & \vdots & & \ddots \\ & H_2O & & H_2O & & & & H_2O & & CN \end{array} \quad (2)$$

Generally, two types of mechanisms for ligand-displacement reaction are possible (4). Firstly, the complex may dissociate, losing a water molecule to generate a five-coordinate complex, and the vacancy in the coordination shell is then taken by CN^- ligand. Secondly, the CN^- attacks the surface chromium complex directly to form a seven-coordinate activated complex, which then expels a water molecule. However, it is not possible to identify the exact mechanistic route based on the present results.

CONCLUSIONS

The ISX-Cr^{3+} material can be used to remove highly toxic pollutants such as cyanide from water with high removal efficiency. The net removal of CN^- is due to simultaneous action of sorption and ligand-displacement reaction involving surface bound aqua-hydroxo-chromium octahedral complex and strongly nucleophilic CN^- ligand. The ligand-displacement reaction contributes to 20–28% of net cyanide removed during the initial 15–20-min period and further cyanide removal becomes possible through sorption by bulk ISX material. Due to first-order dependence of initial rates of cyanide removal on the initial cyanide concentration, removal of cyanide from feebly contaminated waters might require longer contact periods. The ISX-Cr^{3+}, or some suitable polymer-bound chromium complex that may be tailor-made, may find application in water treatment in reference to abatement of cyanide pollution. However, the problem of regeneration of used ISX-Cr is very important as is very common with many other newly developed low-cost adsorbents and ion-exchangers too. It is necessary to study this aspect separately in detail.

ACKNOWLEDGMENTS

The authors are thankful to Dr. R. N. Singh, Director, NEERI for granting permission to publish this work.

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Received January 2001
Revised September 2001