

**Inorganic Sorbents for Iodine Removal from Subsurface Plumes – 14347**

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**ABSTRACT**

The radioisotope  $^{129}\text{I}$  is one of the key risk components in the migrating subsurface plumes present in the Hanford site vadose zone due to its long half-life, large inventory, high toxicity, and high mobility in the aquifer. In the subsurface aquatic environment it mainly exists as iodide ( $\text{I}^-$ ), iodate ( $\text{IO}_3^-$ ), and organic derivatives of iodine. Because of different chemical properties of these species and significantly lower concentration than other constituents in the subsurface plumes their removal using commercial ion exchange resins is problematic. Engineered inorganic sorbents with the structure similar to the layered double hydroxides (LDH) or hydrotalcite-like naturally occurring minerals and clays may offer a potential solution. LDH sorbents have been previously demonstrated as promising materials for the removal of hazardous anions. They can be designed to possess superior characteristics including large surface area, high sorption capacity, and good chemical/mechanical/thermal stability and offer a simple, efficient and economic option for the removal of  $\text{I}^-$  and  $\text{IO}_3^-$ . In this paper, we summarize the results of our current research effort focusing on identification and testing the inorganic sorbents selective for these species.

**INTRODUCTION**

Currently, there are no established methods and/or materials, including commercially available ion exchange resins or sorbent materials, for removal of iodine from aqueous media. Removal of radioiodine from groundwater in the 200 Area of the Hanford U.S. DOE site is an essential component for managing the Hanford Site cleanup and protecting the Columbia River. In an effort to address the need for a selective uptake of iodine in the form of iodate ( $\text{IO}_3^-$ ) and iodide ( $\text{I}^-$ ) from the subsurface water, readily available (economic and easy-to-synthesize) inorganic solid-state composite materials have been investigated.

The structure of the tested inorganic materials is similar to the layered double hydroxides (LDH) or hydrotalcite-like naturally occurring minerals and clays. LDH sorbents have been previously demonstrated as promising materials for the removal of harmful oxyanions such as arsenate, chromate, perchlorate, pertechnetate, iodate, and others from contaminated and waste waters [1, and references therein]. These materials typically consist of two-dimensional, nano-structured, divalent cations, octahedrally coordinated by hydroxide ions, where some of the divalent cations are isomorphously replaced by tri- or tetravalent cations. Such a replacement results in charged sheets, where the net positive charge is compensated by anions in the interlayer region.

The LDH materials possess superior characteristics for use as sorbents, including large surface area, high sorption capacity, and good chemical/mechanical/thermal stability and offer a simple,

efficient, and economic option for the removal of harmful anions. The identities of the LDH metal ions can be varied over a wide range, thus giving rise to a large class of isostructural materials with physicochemical properties that can be tailored to achieve high selectivity and capacity for the uptake of an anion of interest [2]. For instance, the uptake selectivity and capacity can be significantly enhanced if it facilitates the rearrangement of the crystal lattice to an energetically more stable form. Furthermore, these materials can be prepared in bulk amounts by efficient and simple single-step synthesis from inexpensive starting reagents, making them promising candidates for the large-scale treatment processes. Since LDH materials are inorganic, they exhibit excellent thermal and chemical stability and can be used in harsh environments, with the exception of concentrated acidic media [3].

Several studies have demonstrated the potential of LDH materials for sorption of iodide and iodate anions from contaminated water samples. Iodine-129 has been immobilized using  $Mg^{2+}/Al^{3+}$  LDH by exchanging the parent  $Cl^-$  anion by  $I^-$  [4]. In another study, calcined  $Mg^{2+}/Al^{3+}/CO_3^{2-}$  material was used to remove iodide from contaminated ground water [5]. Hydrotalcite-type compounds consisting of brucitelike positively charged layers with a  $Mg^{2+}/Al^{3+}/CO_3^{2-}/NO_3^-$  chemical composition showed promise for  $IO_3^-$  uptake [6]. Ternary  $Ni^{2+}/Al^{3+}/Zr^{4+}/NO_3^-$  was successfully utilized as a solid-phase extraction sorbent for the separation and pre-concentration of trace levels of  $IO_3^-$  from environmental and biological samples.

These previous studies prompted this systematic study to evaluate efficiency of the iodate sorption as a function of the chemical composition of the LDH material.

## **EXPERIMENTAL**

### **Synthesis of the Composite Materials**

The general synthetic procedure included weighing the appropriate starting transition metal salts for the specific LDH synthesis. The compounds then were combined in ~50 mL deionized (DI) water. The solution was stirred for about an hour and the initial pH measured, then 0.5M Na(K)OH was added to solution under stirring until the desired pH was achieved. The mixture was then transferred to a Teflon-lined autoclave for hydrothermal synthesis at 110 °C for 72 hours in a oven to yield the LDH aggregate. The set temperature variation was within  $\pm 5$  °C. The resulting composite was filtered from the solution under gravity and allowed to air dry. The dried compound was then ground into a fine powder with mortar and pestle and rinsed with water until the filtrate ran clear. Then it was allowed to air dry before being ground into a fine powder again.

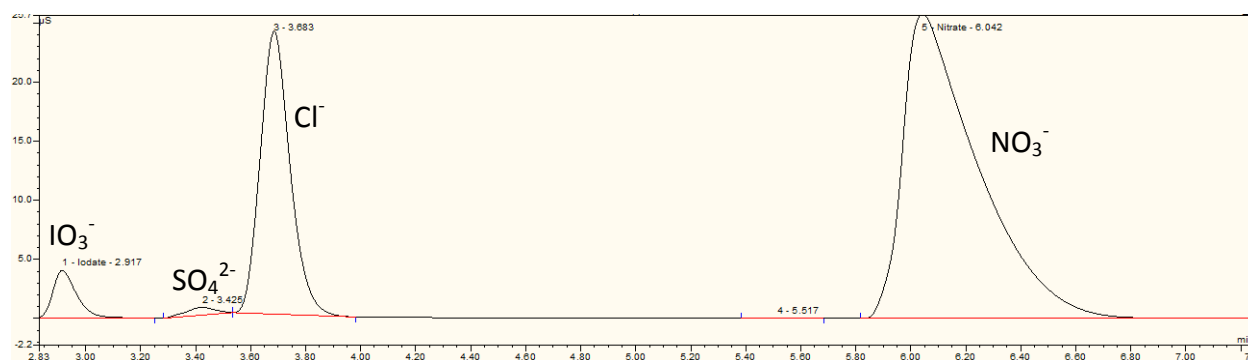
### **Raman Monitoring of $IO_3^-$ Uptake by Composite Materials**

The affinity of the synthesized LDH sorbents for  $IO_3^-$  was initially assessed by monitoring  $IO_3^-$  uptake from DI water using Raman spectroscopy. An InPhotonics Raman system operating with MoleCue software and equipped with 670 nm laser and fiber optic and an InPhotonics Probe was used for the continuous monitoring of  $IO_3^-$  sorption. Typical sample preparation involved

mixing 100 mg of LDH with 1 mL of 0.025M  $\text{KIO}_3$  solution in DI water in a glass vial. The vial was then centrifuged at 4000 rpm for 10–30 min until the sorbent settled at the bottom, leaving a clear solution at the top, which was monitored by Raman spectroscopy. An initial spectrum of the 0.025M  $\text{KIO}_3$  and a spectrum of the water using identical glass vials served as the reference. In a typical experiment, continuous monitoring of the solution was done for 180 acquisitions, each with 10-second integration time, with a 50-second delay between measurements. After 3 hours of monitoring, the solid composite material was re-suspended in the solution and the sample was stirred overnight, and Raman measurements were continued the next day after re-centrifuging the samples. The spectra were baseline-corrected and normalized to the water band. A water spectrum was subtracted from each sample spectrum. The Raman intensity of the  $\text{IO}_3^-$  band at  $801\text{ cm}^{-1}$  was used to quantify the  $\text{IO}_3^-$  uptake by the composite material.

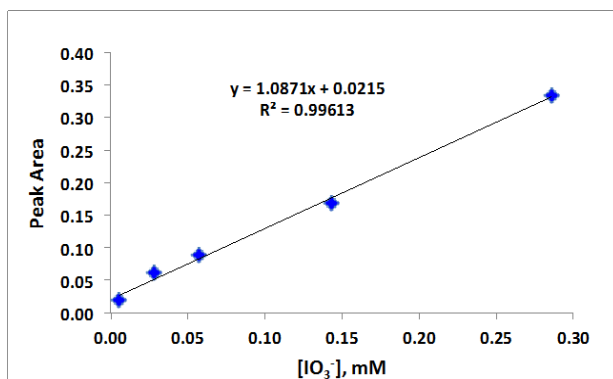
### Ion Chromatography (IC) Method for Determination of $\text{IO}_3^-$

Quantification of  $\text{IO}_3^-$  was conducted using an Ion Chromatograph (Dionex) equipped with Dionex IonPac AS16 high-capacity column optimized for the determination of polarizable anions and a suppressed conductivity detector. An isocratic elution method using 50 mM NaOH at 1 mL/min was applied. This method allows for simultaneous determination of target  $\text{IO}_3^-$  and  $\text{I}^-$  in the presence of  $\text{Cl}^-$ ,  $\text{NO}_3^-$ , and  $\text{SO}_4^{2-}$  anions in the sample. The respective retention time for these anions was found to be 2.9, 24.5, 3.6, 6.0, and 3.4 min. Since  $\text{SO}_4^{2-}$  is present in the groundwater at a significantly smaller concentration than  $\text{Cl}^-$ , it does not interfere with the  $\text{Cl}^-$  determination. It was observed that the ground water collected from the well 299-W19-36 can be analyzed for these anions without pretreatment. The chromatogram of the well 299-W19-36 groundwater containing 50 ppm added  $\text{IO}_3^-$  is shown in Figure 1.



**Figure 1.** The chromatogram of the well 299-W19-36 groundwater containing 50 ppm  $\text{IO}_3^-$ . The part of the chromatogram where iodide comes off is not shown. No  $\text{I}^-$  was detected in the sample.

As seen in Figure 1, the  $\text{IO}_3^-$  peak is sufficiently separated from the peaks due to sulfate, chloride, and nitrate present in the ground water for easy quantitation. The IC calibration plot for  $\text{IO}_3^-$  in the groundwater is shown in Figure 2.



**Figure 2.** IC calibration plot for  $\text{IO}_3^-$  in the well 299-W19-36 groundwater.

The detection limit for  $\text{IO}_3^-$  in the well 299-W19-36 groundwater was calculated to be 0.013 mM (2.27 ppm) using Eq. (1):

$$\text{DL} = 2 \cdot S_B / m \quad (1)$$

where DL is the detection limit for  $\text{IO}_3^-$ ,  $S_B$  is the standard deviation of the blank, and  $m$  is the calibration slope [7].

## RESULTS AND DISCUSSION

As it is evident from Figure 3, the  $\text{IO}_3^-$  uptake can be quantified based on the Raman measurements. Table 1 compares the 24 hr  $\text{IO}_3^-$  sorption performance of the tested LDH composite materials. It should be noted that since no stirring was applied during the first few hours of contact, the  $\text{IO}_3^-$  uptake was diffusion-limited. Examination of the  $\text{IO}_3^-$  sorption results reported in Table 1 revealed a few interesting trends. Most notably it was observed that Cr(III)-containing composites exhibited nearly quantitative uptake of  $\text{IO}_3^-$  (Sample 1, 2, and 5) with exception of Mn(IV)-Cr(III) composite (Sample 14), which performed only modestly. Further, the kinetics of this uptake was fast (Figure 3).

The second observation is that among LDH materials containing no Cr(III), the quaternary Ni(II)-Sn(II)-Al(III)-Zr(IV) composite (Sample 4) exhibited superior  $\text{IO}_3^-$  sorption. The  $\text{IO}_3^-$  uptake was only slightly reduced by the ternary composite Ni(II)-Sn(II)-Al(III) (Sample 6). When Zr(IV) was replaced with Mn(IV) (Sample 14), sorption efficiency significantly decreased. Elimination of Sn(II) from the LDH composition reduced  $\text{IO}_3^-$  uptake by approximately 20% (Sample 7). Based on these results, Ni(II)-Sn(II)-Al(III)-Zr(IV) LDH was tested for the  $\text{IO}_3^-$  uptake in the column configuration as described below.

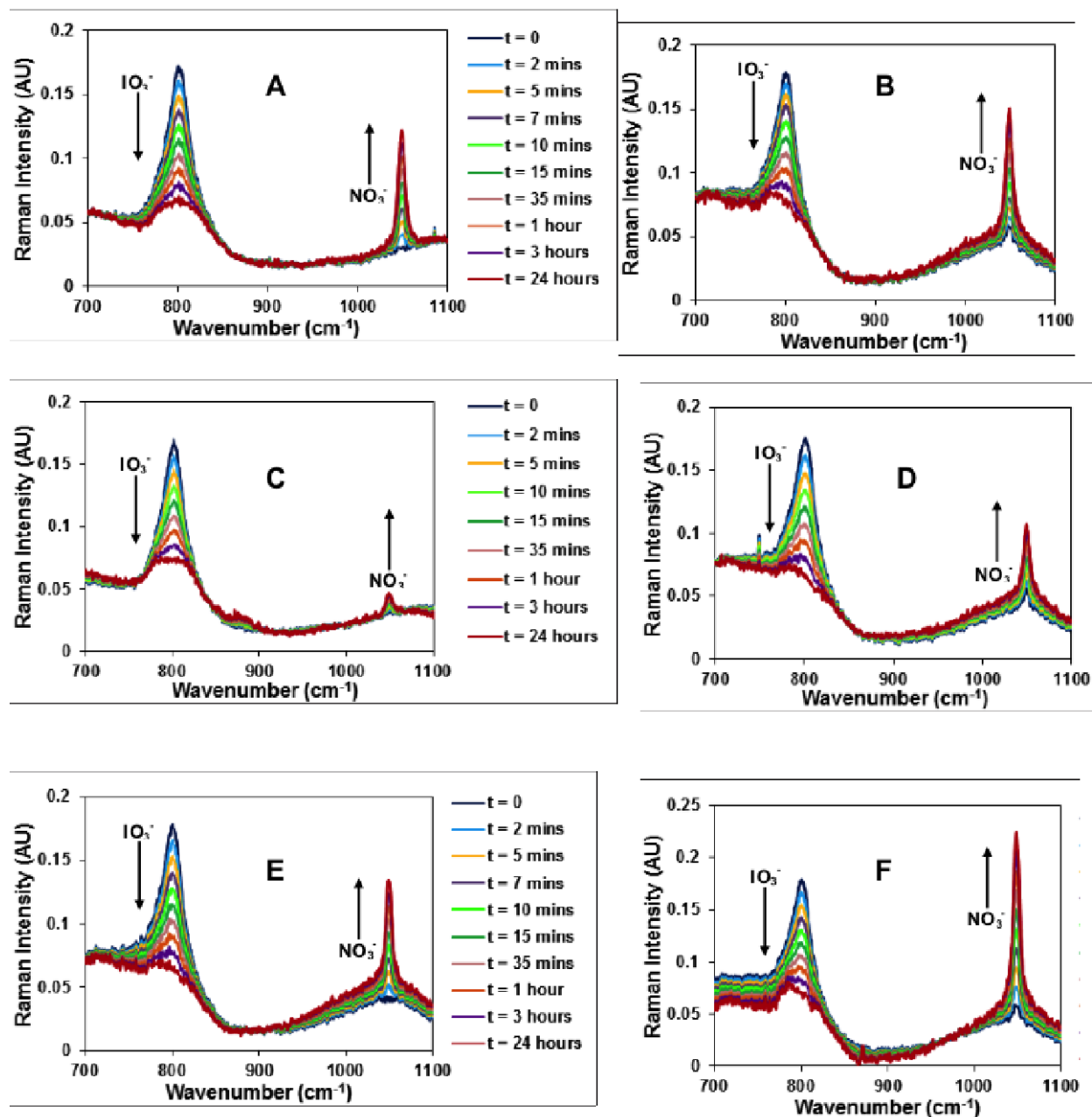
**Table 1.** Preliminary evaluation of  $\text{IO}_3^-$  uptake by the synthesized composite materials using Raman spectroscopy. Reported values correspond to 24 hr uptake.

Sample ID	Composite material	Percent $\text{IO}_3^-$ Sorption from	
		DI Water	Groundwater
1	Ni(II)-Cr(III)	100 <sup>(a)</sup>	91
2	Cu(II)-Cr(III)	98 <sup>(a)</sup>	
3	Zn(II)-Al(III)-Zr(IV)	97 <sup>(b)</sup>	
4	Ni(II)-Sn(II)-Al(III)-Zr(IV)	95 <sup>(a)</sup>	97
5	Co(II)-Cr(III)	89 <sup>(a)</sup>	95
6	Ni(II)-Sn(II)-Al(III)	83 <sup>(a)</sup>	
7	Ni(II)-Al(III)-Zr(IV)	76	
8	Ni(II)-Fe(III)-Mn(IV)	74	
9	Ni(II)-Fe(III)	50	
10	Ni(II)-Fe(III)-PEG <sup>(c)</sup>	44	
11	Ni(II)-Al(III)-PEG <sup>(c)</sup>	39	
12	Ni(II)-Sn(II)-Al(III)-Mn(IV)	35	
13	Sn(II)-Al(III)-Zr(IV)	35	
14	Mn(IV)-Cr(III)	33	
15	Ni(II)-Fe(III)-Zr(IV)	30	
16	Sn(II)-Hydroxyapatite	26	
17	Ni(II)-Al(III)	22	
18	Bonechar	16	
19	Sn(II)-Bonechar	13	
20	Zn(II)-Fe(III)-Zr(IV)	13	
21	Co(II)-Al(III)-PEG <sup>(c)</sup>	13	
22	Zn(II)-Al(III)-Mn(IV)	11	
23	Sn(II)-Al(III)	8	
24	Zn(II)-Al(III)	8	
25	$\text{MnO}_2$	6	
26	Sn(II)-Fe(III)-Zr(IV)	5	
27	Cu(II)-Al(III)-PEG <sup>(c)</sup>	4	
28	Sn(II)-Fe(III)	3	
29	Zn(II)-Fe(III)	1	
30	Sn(II)-Al(III)- $\text{PO}_4$	0	

(a) The reported value is the average of two independent experimental results.

(b) The value corresponds to the  $\text{IO}_3^-$  uptake measured 7 days after the initial contact.

(c) The composite material contained 5–10 wt% of poly(ethylene glycol) with average molecular weight of 1500.



**Figure 3.** Time dependent IO<sub>3</sub><sup>-</sup> uptake by the representative composite materials monitored by the intensity of Raman 801 nm iodate band. Spectrum taken at t = 0 corresponds to 25 mM IO<sub>3</sub><sup>-</sup> solution before the addition of LDH material. The broad spectral feature observed in the 770–830 cm<sup>-1</sup> range is due to the glass absorption. (A) Cu(II)-Cr(III) LDH in DI water, (B) Cu(II)-Cr(III) LDH in ground water, (C) Co(II)-Cr(III) LDH in DI water, (D) Co(II)-Cr(III) LDH in ground water, (E) Ni(II)-Sn(II)-Al(III)-Zr(IV) LDH in DI water, (F) Ni(II)-Sn(II)-Al(III)-Zr(IV) LDH in ground water.

Overall it can be concluded that among divalent transition metals, Ni(II) favors the  $\text{IO}_3^-$  uptake (Samples 4–12) while Zn(II) exhibits the opposite effect (Samples 20, 22, 24, 29). It is also suggested that Sn(II) enhances  $\text{IO}_3^-$  uptake by Ni(II)-containing materials (Samples 4, 6, 12). Comparison of the behavior of LDH materials containing Al(III) and Fe(III) indicated that Al(III) enhanced  $\text{IO}_3^-$  sorption, particularly in combination with Ni(II) and Zr(IV) (Samples 4, 6, 7). A similar trend was observed for Zr(IV) and Mn(IV). Structural studies of the obtained LDH materials are warranted to elucidate mechanism of the  $\text{IO}_3^-$  uptake.

The Raman monitoring of  $\text{IO}_3^-$  uptake using the three most efficient sorbents was conducted using 0.025M  $\text{KIO}_3$  solution prepared using well 299-W19-36 groundwater obtained from the Hanford Site. The observed sorption efficiency was very similar to the  $\text{IO}_3^-$  uptake from the DI water. For all three tested sorbents, the concomitant nitrate release was greater for the groundwater in comparison with the DI water (Figure 3). It can be attributed to the simultaneous sorption of other anions present in the ground water. This increase was especially pronounced for the Co(II)-Cr(III) LDH, possibly suggesting a different sorption mechanism for this composite.

To test the performance of the selected composite materials for  $\text{IO}_3^-$  removal from the solutions containing potentially interfering constituents, groundwater from the well 299-W19-36 obtained from the Hanford Site was used. The major inorganic constituents present in the groundwater are listed in Table 2.

**Table 2.** Concentrations of the selected specified constituents in 299-W19-36 source water (taken from Mattigod et al. 2010 [8]).

Constituent	Concentration		
	( $\square$ g/L)	Molar Mass	Molarity
Barium	113	137.3270	8.23E-07
Calcium	122000	40.0780	3.04E-03
Chloride	181000	35.4515	5.11E-03
Total Cr	17.3	51.9961	3.33E-07
Cr(VI)	0.05	51.9961	9.62E-10
Magnesium	36400	24.3050	1.50E-03
Molybdenum	65.9	95.9400	6.87E-07
Nitrate	317000	62.0049	5.11E-03
Potassium	7010	39.0983	1.79E-04
Sodium	118000	22.9898	5.13E-03
Sulfate	50000	96.0600	5.21E-04
Strontium	618	87.6200	7.05E-06
Tin	216	118.7100	1.82E-06
Alkalinity ( $\text{CaCO}_3$ )	116000	100.0869	1.16E-03
Uranium	174	238.0289	7.31E-07

Batch sorption experiments were conducted using measured quantities of a composite material and volumes of the well water. Two composite materials were tested, including Co(II)-Cr(III) and Ni(II)-Cr(III). The samples were placed in the centrifugation tubes, agitated for 17 hr at room temperature, and centrifuged. The contact solutions were separated from the composite material and subjected to the IC analysis to determine  $\text{IO}_3^-$  concentration.

The  $\text{IO}_3^-$  batch sorption results are summarized in Table 3. The Co(II)-Cr(III) composite exhibited selective and efficient sorption of  $\text{IO}_3^-$ . It was observed that the concentration of nitrate and chloride significantly increased in the contact solutions upon  $\text{IO}_3^-$  uptake, suggesting an ion exchange mechanism of the sorption and/or removal of the corresponding sodium salt. The increase of the nitrate concentration was approximately similar for all contact solutions. The chloride concentration in the post-contact solutions increased along with the weight of the Co(II)-Cr(III) composite, suggesting release of NaCl trapped in the composite during its preparation. Therefore, a more thorough post-synthetic procedure to wash Co(II)-Cr(III) composite should be implemented. Despite the significantly larger concentrations of the chloride and nitrate contact solutions, these anions did not interfere with the  $\text{IO}_3^-$  uptake.

**Table 3.**  $\text{IO}_3^-$  sorption isotherm data for Ni(II)-Cr(III) and Co(II)-Cr(III) composite materials.

LDH weight (g)	Solution volume (mL)	$\text{IO}_3^-$ concentration (ppm)		$\text{Cl}^-$ concentration (ppm)		$\text{NO}_3^-$ concentration (ppm)	
		initial	final	initial	final	initial	final
Co(II)-Cr(III)							
0.0272	12	31.3	25.0	181	355	317	433
0.0480	12	31.3	19.7	181	493	317	460
0.1010	12	31.3	1.94	181	816	317	454
0.1511	12	31.3	BD <sup>a)</sup>	181	808	317	401
Ni(II)-Cr(III)							
0.05723	25	31.3	27.3	181	138	317	576
0.1012	25	31.3	14.5	181	74	317	652
0.1529	25	31.3	6.73	181	61	317	729
0.1592	12	31.3	BD	181	57	317	873
0.1483	6	31.3	BD	181	56	317	864

(a) BD is below detection.

The Ni(II)-Cr(III) composite exhibited effective sorption of  $\text{IO}_3^-$ , although slightly less so than that of Co(II)-Cr(III) material (Table 3). This effect was attributed to the competitive sorption of  $\text{Cl}^-$ . Chloride concentration in the contact solutions gradually decreased as the weight of the Ni(II)-Cr(III) composite in the sample increased. Interestingly, despite  $\text{Cl}^-$  sorption, efficient removal of  $\text{IO}_3^-$  by this material was observed; this suggests greater affinity for  $\text{IO}_3^-$  than for  $\text{Cl}^-$ .



## CONCLUSIONS

Several inorganic composite materials possessing a clay-like structure were synthesized and screened for iodate uptake from deionized water by Raman spectroscopy. It was determined that the Cr(III)-containing materials and the Ni(II)-Sn(II)-Al(III)-Zr(IV) composite exhibited superior performance.

The  $\text{IO}_3^-$  sorption performance of the Co(II)-Cr(III) and Ni(II)-Cr(III) materials was further evaluated using the well 299-W19-36 groundwater in which the  $\text{IO}_3^-$  concentration adjusted to 31.3 ppm. The ion chromatography method was developed and used to quantify  $\text{IO}_3^-$  uptake. It was found that Co(II)-Cr(III) composite is selective for  $\text{IO}_3^-$  over both chloride and nitrate, which are present in the groundwater at 181 and 317 ppm, respectively.  $\text{IO}_3^-$  uptake efficiency by Ni(II)-Cr(III) was slightly reduced by the competitive sorption of chloride.

It was concluded that both Co(II)-Cr(III) and Ni(II)-Cr(III) composite materials are promising for the  $\text{IO}_3^-$  removal from groundwater containing high nitrate concentrations. Follow-on column testing is warranted to determine sorption kinetics, capacity, and breakthrough behavior of the Co(II)-Cr(III) inorganic material. Structural characterization of this material is needed to elucidate the mechanism of the  $\text{IO}_3^-$  sorption.

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