

Removal of Phosphates and Chromates in a Multi-ion System

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Abstract

Because industrialization is increasing the number of manufacturing facilities in traditionally rural agricultural areas globally, ground and surface waters with mixed fertilizer and industry contaminants must be considered. This work characterizes the effect of nitrates, phosphates, and chromates on the removal of phosphates and chromates from contaminated water via ion exchange with calcined hydrotalcite, an inexpensive, synthetic double layer hydroxide. Isotherms for single ion removal are compared with those for multi-ion solutions at contaminant levels typical for contaminated ground and surface waters. In addition, fixed effects statistical analysis of variance, PROC GLM (SAS Version 9) was used to analyze main and interactive effects for target anion removal and Least Significance Difference t-test and Tukey's studentized range honest significant difference at $\alpha = 0.05$ were used a multiple comparison procedures to determine significant mean difference in treatments. It was found that in a binary phosphate-chromate system, phosphate removal was only significantly reduced by higher chromate levels and this effect was magnified at higher phosphate levels. Chromate removal, on the other hand, was reduced at all phosphate levels. For the ternary system, phosphate removal was reduced by chromates, but not nitrates. However, the chromate-nitrate interaction was significant, as was the ternary interaction, particularly at higher phosphate levels. Chromate removal in the ternary system was impacted by the main effects for chromate, phosphate, and nitrate and also by all of the interactive effects. Hence, a multi-step ion exchange process would be required to remove all anions of concern in a mixed contaminant system.

Index terms— ion exchange, phosphate, chromate, nitrate, hydrotalcite, double layer hydroxide.

1 Introduction

As the rate of industrialization increases globally along with suburban growth bringing factories and industry to rural areas, the concern for water contaminated with a mixture of industrial and agricultural wastes is increasing. Many people in these rural areas rely on untreated well water for domestic use. In both the developed and developing worlds, phosphate and nitrate nutrient contamination from agricultural practices have rendered wells unsafe for consumption, primarily because the presence of nitrates above 10 mgL⁻¹ in drinking water can lead to methemoglobinemia, or blue baby syndrome, which affects both humans and farm animals. Nitrates and, particularly, phosphates are both responsible for increased rates of eutrophic waters, which leads to potentially toxic algae blooms and reduced oxygen levels. These greatly reduce the health of aqueous ecosystems, creating dead zones in many waterways globally. Phosphate levels as low as 0.025 mgL⁻¹ can accelerate eutrophication and, because it is the limiting factor for eutrophication, the United States Environmental Protection Agency, USEPA, recommends levels below 0.1 mgL⁻¹ to preserve ecosystem integrity (U.S. E.P. A., 2002). Not just agricultural fertilizers cause eutrophication. Storm runoff, landfill leachate, and domestic and industrial effluents also contribute and have hindered the potential of water reuse (Chang et al., 2010).

3 EXPERIMENTAL PROTOCOLS

In addition to nutrients, many heavy metals may occur naturally in groundwater supplies at levels exceeding maximum values for human health. Heavy metals may also be introduced by anthropogenic activities, such as mining, plating, and tanning industries.

Globally, abandoned mines have contaminated ground and surface waters and the tanning industry has produced irreversible damage to aquatic environments (Shankar 2008). Chemical spills at industrial sites, improper disposal and storage of wastes, and leaking or abandoned underground storage tanks may all contribute to contamination (USEPA 2002). Studies on urban watersheds in southeast Michigan, United States, for example, showed that current and past land use practices have resulted in groundwater and soil contaminated with chromium, copper, lead, nickel, and zinc (Murray et al. 2006). Hexavalent chromium, in particular, is used in tanning and plating industries, manufacture of dyes and pigments, and in circuit boards. It is on the USEPA list of top twenty total releases and is toxic, carcinogenic, and mutagenic such that the maximum acceptable level in drinking water is 0. In the past decade, the use of naturally occurring or synthetically made clay mineral based layered double hydroxides, LDHs, has been widely investigated as an inexpensive ion exchange media for removal of anions from aqueous solution. This class of materials has become increasingly researched and utilized due to ease of synthesis and low cost compared to resin based ion exchange media. Phosphorus and nitrate removal via super paramagnetic particles modified with LDH was performed by Mandel et al. (2012). Removal of Cr(VI), zinc, and cadmium in a multi-ion solution (Terry et al. 2010) (2009, 2010) and investigates the effect of nitrates, phosphates and chromates on the removal of phosphates and chromates via ion exchange with calcined hydrotalcite, HTC in a multi-ion solution. These three were chosen because of the global concern for nutrient contamination of water and the growing concern that industrialization moving into rural and suburban areas will possibly add industrial waste contamination to the same surface and ground water sources. Because it is toxic, carcinogenic, and mutagenic at very low levels, industrial releases of and water contamination by chromium (VI) is of particular concern. Nitrate removal is not considered in this work because previous work has shown that, while nitrates are removed via ion exchange with hydrotalcite in a single ion solution, removal is significantly diminished in the presence of even low phosphate levels. Phosphate removal, on the other hand, is high in a single ion solution and remains so even when up to 30 mgL⁻¹ nitrate is present.

In this study, first the two ion phosphate-chromate system is characterized including both the effect of chromate on phosphate removal and the effect of phosphate on chromate removal. Next the three ion system is investigated including the effect of chromate and nitrate on phosphate removal and the effect of phosphate and nitrate on chromate removal. In all experiments, concentrations were used that correspond with those typically found in contaminated surface and ground waters, ranging from zero to 6.13 mgL⁻¹ phosphate (2 mgL⁻¹ P), 30 mgL⁻¹ nitrate, and 20 mgL⁻¹ chromate.

2 II.

3 Experimental Protocols

Hydrotalcite,

[Mg₂Al(OH)₆]·2CO₃·3H₂O, ion exchange media used in these experiments was purchased from Sigma-Aldrich chemicals. It was calcined by heating at 450 °C for several hours. Nitrates were added as sodium nitrate, NaNO₃, phosphates as sodium dihydrogen phosphate, NaH₂PO₄, and chromium (VI) as chromium trioxide anhydrous, CrO₃, all research grade from Fisher Chemicals. Nitrate and phosphate levels were measured using a calibrated Shimadzu UV-1601, UV-visible spectrophotometer. An ascorbic acid soluble reactive phosphorus procedure, HACH standard procedure 8048, using HACH Phosver 3 reagent powder was used for phosphate analysis. The test measurement range was 0 to 0.82 mgL⁻¹ P, reported as 0 to 2.52 mgL⁻¹ PO₄³⁻. Chromium (VI) was measured using a Perkin-Elmer 2280 atomic absorbance spectrophotometer.

All experiments were performed in triplicate in batch mode with 100 ml samples in acid washed high density polyethylene bottles. Samples were prepared by adding the appropriate quantity of nitrates, phosphates and chromate, then adding the hydrotalcite. The alkaline nature of the hydrotalcite caused a pH shift from that of deionized water to about 8.2 ± 0.2. Hydrotalcite, HTC, 0.2 gL⁻¹, was added to each solution, which were then shaken for twenty minutes with a NBS gyratory shaker on high speed. Following ion exchange, the HTC was separated from suspension by vacuum filtration through Whatman 0.7 µm glass fiber filters and residual concentrations in the aqueous solution were analyzed.

First, the binary system of chromate-phosphates was characterized. Following the binary system analysis, the ternary system was characterized. between 0 and 6.13 mgL⁻¹ phosphate (1 to 2 mgL⁻¹ P), 0 to 30 mgL⁻¹ nitrate, and 0 to 20 mgL⁻¹ Cr(VI). Both Freundlich and Langmuir isotherms, typically used to model both ion exchange and adsorption processes, were used to characterize the ion exchange effectiveness, assessing by comparison the effect of other anions in a binary or ternary system on ion exchange removal of the target anion. The Freundlich isotherm, $Y = CX^m$,

Where Y = mg of target anion exchanged per unit mass (g) hydrotalcite, X = residual target anion in solution following ion exchange (mgL⁻¹), and C, m = Freundlich model constants is typically used for dilute solutions. The Langmuir isotherm model $Y = bX / (1 + KX)$ Y = mg of target anion exchanged per unit mass (g) hydrotalcite, X = residual target anion in solution following ion exchange (mgL⁻¹), and b, K = Langmuir model constants is more often used and a system is considered favorable when $KX > 1$.

In addition, fixed effects statistical analysis of variance, PROC GLM (SAS Version 9) was used to analyze main and interactive effects for target anion removal and Least Significance Difference t-test and Tukey's studentized range honest significant difference at $\alpha=0.05$ were used a multiple comparison procedures to determine significant mean difference in treatments. This was performed to analyze any main and interactive effects of, first, phosphate and chromate concentrations on phosphate removal and, second, phosphate and chromate concentrations on chromate removal. The ternary system analysis investigated any main and interactive effects of phosphate, chromate, and nitrate concentrations on first phosphate and then chromate removal.

4 III.

5 Results and Discussion

Results are presented in the form of residual concentrations and isotherms for the target species. For each isotherm, constants for both Freundlich and Langmuir models are presented with R² values showing strength of fit. Also, as described above, fixed effects analysis of variance was used to determine the effect of the target species and non-target species on removal of the target species. a) Binary System First, the effect of Cr(VI) on ion exchange removal of phosphate was measured for low, 0.613 mgL⁻¹, and high, 6.13 mgL⁻¹, phosphate initial concentrations. Cr(VI) ranged from zero to 20 mgL⁻¹. Figure 1 shows residual phosphate as a function of Cr(VI) for both high and low phosphate and Figure ?? gives the comparative isotherms. Langmuir and Freundlich model constants are found in Table 1. Figure 1 shows that at phosphate levels of 0.613 mgL⁻¹, addition of even 1 mgL⁻¹ Cr(VI) resulted in a slightly diminished phosphate removal, from 99.5% to 95.2%, respectively. Increasing Cr(VI) concentration caused a continued reduction of phosphate removal to only 88.9% for 20 mgL⁻¹ Cr(VI). For an initial phosphate of 6.13 mgL⁻¹, the presence of Cr(VI) above 2 mgL⁻¹ affected phosphate residuals, but removal remained high. Percent phosphate removal was 99.5% when no Cr(VI) was present and remained above 98.5% up to 15 mgL⁻¹ Cr(VI). Only at 20 mgL⁻¹ Cr(VI) did phosphate removal decrease to a still high 96.9%. The three isotherms, each measured over a range of zero to 6.13 mgL⁻¹ phosphate, in Figure ?? verify the result. These were obtained at both low, 2 mgL⁻¹ Cr(VI), and high, 20 mgL⁻¹ Cr(VI), and compared to the isotherm for phosphate alone. The isotherms for just phosphate and phosphate with low Cr(VI) show that low Cr(VI) concentrations did not significantly affect phosphate removal. The isotherm for phosphate in the presence of high Cr(VI), on the other hand, showed that higher Cr(VI) levels do impair phosphate removal. Where effect from Cr(VI) ($p < 0.04$), but to a lesser degree, especially for low Cr(VI). The interaction between phosphate and Cr(VI) was also significant ($p < 0.03$), but again less so than the phosphate main effect because only higher Cr(VI) levels affected phosphate removal significantly.

Next the effect of phosphate on the removal of Cr(VI) was measured for low, 2 mgL⁻¹, and high, 20 mgL⁻¹, Cr(VI) with phosphate varied from zero to 6.13 mgL⁻¹. Figure ?? has residual Cr(VI) as a function of phosphate and Figure 4 shows the Cr(VI) isotherms with low, 0.613 mgL⁻¹, and high, 6.13 mgL⁻¹, phosphate compared to single ion Cr(VI) ion exchange isotherm. Both Freundlich and Langmuir model constants are presented in Table 2. Figure ?? shows that for both 2 mgL⁻¹ and 20 mgL⁻¹ initial Cr(VI), Cr(VI) removal via ion exchange is significantly reduced compared to single ion removal by the presence of even low phosphate levels. Ion exchange removal of Cr(VI) in a single ion solution was 95% for both high and low initial Cr(VI), but in a binary solution with 0.31 mgL⁻¹ phosphate, removal of 2 mgL⁻¹ Cr(VI) was reduced to 63.5% and that of 20 mgL⁻¹ Cr(VI) was reduced to 69%. For 2 mgL⁻¹ initial Cr(VI), percent removal decreased to about 54% at 0.613 mgL⁻¹ phosphate and remained at that level for higher phosphate concentrations. At 20 mgL⁻¹ initial Cr(VI), removal continued to decrease to only 37% at an initial phosphate concentration of 6.13 mgL⁻¹. The isotherm in Figure 4 also verifies this result. At even low phosphate levels, Cr(VI) ion exchange was reduced greatly across the spectrum of Cr(VI) initial values. This effect was magnified at higher phosphate levels. Fixed effects analysis of variance, the Least Significant Difference t-test, and Tukey's studentized range honest significant difference at $\alpha = 0.05$ showed the main effect from Cr(VI) was significant ($p < 0.02$) as was the main effect from phosphate ($p < 0.01$). The interaction between phosphate and Cr(VI) was also significant ($p < 0.01$), again showing that both Cr(VI) and phosphate initial concentrations significantly reduce Cr(VI) removal.

6 b) Ternary System

Once the effects of phosphate and Cr(VI) on each one's respective removal in a binary system was characterized, the ternary system of phosphate, nitrate and chromate was investigated. First, the interactive effect of nitrate, phosphate and Cr(VI) on phosphate removal was determined, then the effect of nitrate, phosphate, and Cr(VI) on Cr(VI) removal was tested. Nitrate removal, as stated, was not considered because previous experiments showed that even low levels of phosphate result in significantly reduced nitrate removal. Nitrate was included in the ternary systems, however, because it is usually present in ground and surface waters contaminated with phosphate and, therefore, may participate in interactive effects.

Figure ?? shows residual phosphate as a function of initial phosphate, Cr(VI), and nitrates. Initial phosphate concentrations ranged between zero and 6.13 mgL⁻¹. Low and high Cr(VI) levels were 2 mgL⁻¹ and 20 mgL⁻¹ and low and high nitrates were 3 mgL⁻¹ and 30 mgL⁻¹. As the figure displays, phosphate removal was affected by the presence of both Cr(VI) and nitrate, with the effect increasing at higher initial phosphate levels. There was no significant difference between the reduction in phosphate removal when both low Cr(VI) and either low

or high nitrates were present, leading to the observation that nitrates, when Cr (VI) was low did not significantly affect phosphate removal. In both cases, phosphate removal decreased from over 99% for the single ion phosphate system to a minimum of 93.1% for 6.13 mgL⁻¹ initial phosphate, 2 mgL⁻¹ Cr (VI) and both 3 and 30 mgL⁻¹ nitrate. As would be expected from the binary system results, for the ternary system of phosphate with 20 mgL⁻¹ Cr(VI) and both 3 mgL⁻¹ and 30 mgL⁻¹ nitrate, there was a greater reduction in phosphate removal. This effect was amplified at 30 mgL⁻¹ nitrate compared to 3 mgL⁻¹ nitrate, showing a greater interactive effect. For the high Cr (VI), low nitrate system, phosphate removal decreased from 95.2% to 85.2% with increasing initial phosphate, while for the high Cr (VI), high nitrate system, it decreased from 92.3% to 75% with increasing initial phosphate. The isotherms for this system, shown in Figure ??, and the isotherm model constants in Table 3 confirm this result. Greatest phosphate removal occurred in the single ion system, after which it decreased a small amount with addition of 2 mgL⁻¹ Cr (VI) at both high and low nitrate levels. For these latter two, the isotherms are identical. Declining isotherms for high Cr (VI) and either low or high nitrate show the worst phosphate removal was observed at both high Cr (VI) and high nitrate. Fixed effects analysis of variance, the Least Significant Difference t-test, and Tukey's studentized range honest significant difference at $\alpha = 0.05$ showed the main effect from Cr(VI) was significant ($p < 0.02$) as was the main effect from phosphate ($p < 0.01$), but the main effect from nitrate was not significant ($p < 0.08$). As was observed in the binary system, the interaction between phosphate and Cr (VI) was also significant ($p < 0.01$), again showing that both Cr (VI) and phosphate initial concentrations significantly reduce phosphate removal. The interaction between Cr(VI) and nitrate was also significant ($p < 0.03$), as is observed by a reduction in phosphate removal between the high Cr (VI) and low nitrate system compared to the high Cr (VI) and high nitrate system. Finally, the interaction between Cr (VI), nitrate and phosphate was determined to be significant ($p < 0.03$) as would be expected from the binary interactions.

Figure 7 shows residual Cr (VI) as a function of initial phosphate, Cr (VI), and nitrates. Initial Cr (VI) concentrations ranged between zero and 20 mgL⁻¹. Low and high phosphate levels were 0.613 mgL⁻¹ and 6.13 mgL⁻¹ and low and high nitrates were 3 mgL⁻¹ and 30 mgL⁻¹. As the figure displays, Cr (VI) removal was affected by the presence of both phosphate and nitrate, with the effect increasing at higher initial Cr (VI) levels. In a single ion system, Cr (VI) removal was above 95% for all initial Cr (VI) concentrations. As with the binary Cr (VI) and phosphate system, even low phosphate levels reduced Cr (VI) removal and this effect was amplified at higher phosphate levels. For the low phosphate and low nitrate system, Cr (VI) removal fell from a maximum of 85% at 1 mgL⁻¹ initial Cr (VI) to only 46% for 20 mgL⁻¹ initial Cr (VI) and for the high phosphate-low nitrate system, this was reduced further to only 60% and 35% for initial Cr (VI) concentrations of 1 and 20 mgL⁻¹, respectively. The presence of nitrate also interacted to reduce Cr (VI) ion exchange. For the high phosphate-high nitrate system, Cr (VI) removal fell from only 40% for 1 mgL⁻¹ initial Cr (VI) to 20% for 20 mgL⁻¹ initial Cr (VI). The isotherms, presented in Figure 8 and the model constants, given in Table 4, reinforce this result. The isotherm for the single ion system shows significantly greater removal than the isotherms for any of the ternary systems. Increasing either phosphate or nitrate results in a diminished isotherm. Fixed effects analysis of variance, the Least Significant Difference t-test, and Tukey's studentized range honest significant difference at $\alpha = 0.05$ showed the main effect from Cr(VI) was significant ($p < 0.01$) as was the main effect from phosphate ($p < 0.01$) and the main effect from nitrate ($p < 0.02$). As was observed in the binary system, the interaction between phosphate and Cr (VI) was also significant ($p < 0.01$), again showing that both Cr (VI) and phosphate initial concentrations significantly reduce Cr (VI) removal. The interaction between Cr (VI) and nitrate was also significant ($p < 0.02$), as is observed by a reduction in Cr (VI) removal between the high phosphate-low nitrate system compared to the high phosphate-high nitrate system. Also, the interaction between phosphate and nitrate was significant, resulting in the lowest Cr (VI) removal under high phosphate-high nitrate conditions. Finally, the interaction between Cr(VI), nitrate and phosphate was determined to be significant ($p < 0.02$) as would be expected from the binary interactions and the lowest measured Cr(VI) removal at high initial concentrations of all three.

IV.

7 Summary

Experiments were performed to determine the effect of nitrates, chromates (Cr (VI)), and phosphates on the removal of either chromates or phosphates in multi-ion solutions via ion exchange with calcined hydrotalcite, a synthetically made double layer hydroxide. Levels of each anion associated with contaminated ground or surface waters were considered. Both Langmuir and Freundlich isotherm models were applied to characterize and compare each system. Fixed effects analysis of variance was used to analyze both main and interactive effects and the Least Significant Difference t-test and Tukey's studentized range honest significant difference at $\alpha = 0.05$ were used as multiple comparison procedures to determine significant mean difference in treatments.

First, the binary chromate-phosphate system was characterized. It was found that while low Cr (VI) concentrations did not significantly affect phosphate removal, higher Cr (VI) levels did have a negative impact, especially at higher phosphate initial concentrations. The main effects for initial phosphate and Cr (VI) and the phosphate-Cr (VI) interaction were all found to be significant ($\alpha < 0.05$). On the other hand, Cr (VI) ion exchange was significantly reduced by phosphate at both high and low phosphate levels. Both the main effect for

Cr (VI) initial concentration and phosphate were significant as was the interaction between the two. At higher Cr (VI) levels, the negative effect of phosphate became intensified.

Characterization of the ternary system showed that the main effects for phosphate initial concentration and Cr(VI) did affect phosphate removal, while the nitrate main effect did not. Isotherms show that phosphate exchange did decrease with increasing Cr (VI), but the effect was greater at higher Cr (VI) initial concentration. The interactions between Cr (VI)phosphate and Cr (VI)-nitrate were also significant, as can be observed by a lowered isotherm capacity as Cr (VI) and nitrates both increased. The lowest phosphate removal isotherm capacity was recorded for the high nitrate-high Cr (VI) case. The ternary interaction was also significant. Finally, Cr (VI) ion exchange was negatively impacted by the presence of phosphates and nitrates to a greater degree than phosphates were affected in the ternary system. The main effects of Cr (VI), phosphate and nitrate and the interactive effects of Cr (VI)phosphate, Cr (VI)-nitrate, nitrate-phosphate, and Cr (VI)-phosphate-nitrate were all significant. Even small quantities of phosphate or nitrate greatly reduced Cr (VI) removal, with the lowest removal capacity occurring at the highest concentrations of the three anions.

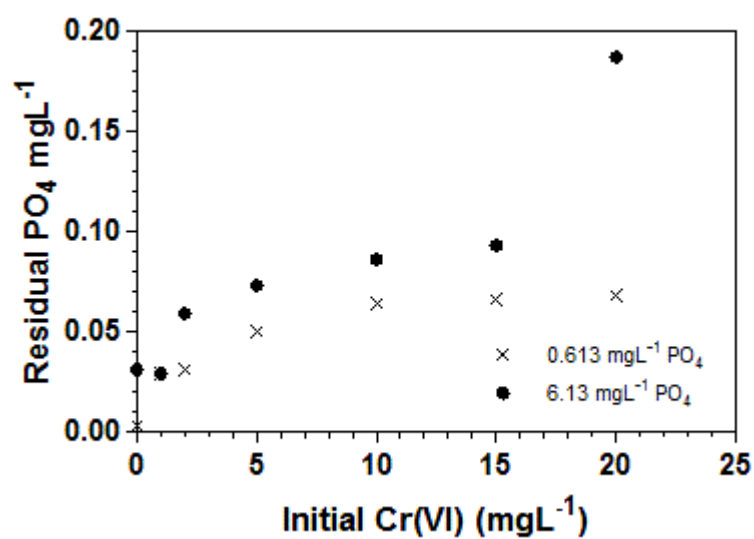
As industrial effluents begin to be introduced into rural areas that already experience nutrient contamination of surface and ground waters, removal of anions in aqueous solution via ion exchange should consider the effect of non-target anions competing for exchange sites with the target anion. Presence of even small amounts of some competing species may significantly reduce the effectiveness of removing target contaminants. In these cases, if it is desired to remove all contaminants, multi-step separation processes removing the most competitive anions first and the least competitive anion last may be required.



Figure 1: Figure 1 :

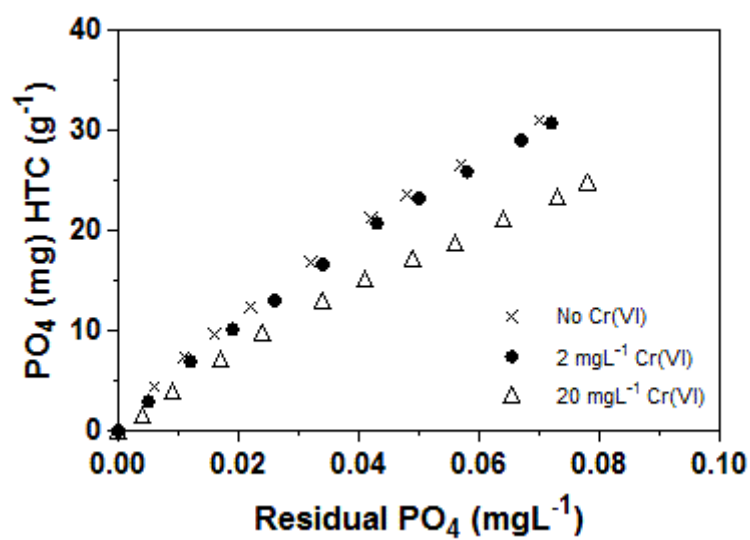
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²Removal of Phosphates and Chromates in a Multi-ion System



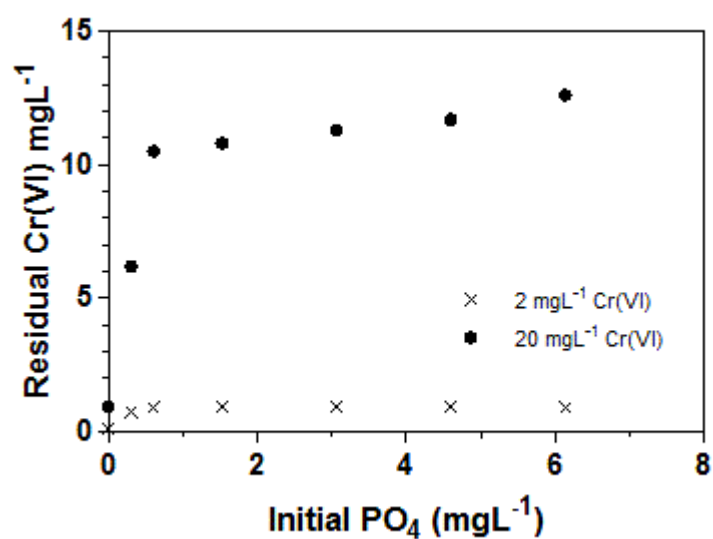
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Figure 2: Figure 2 :Figure 3 :



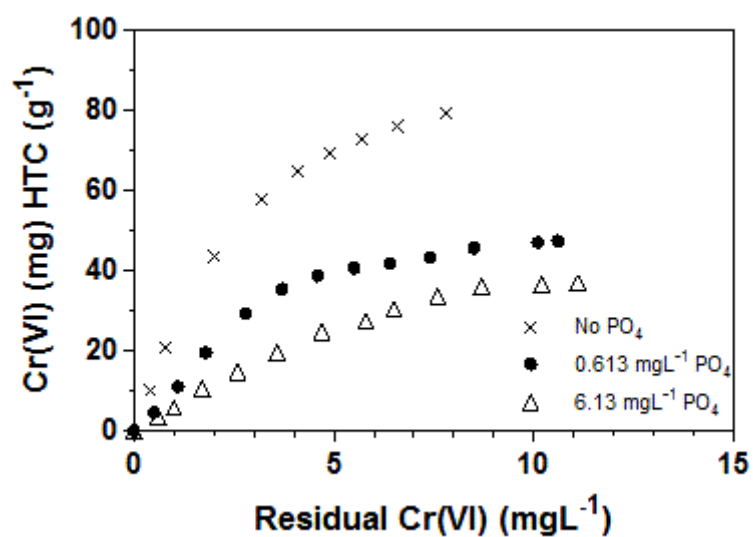
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Figure 3: Figure 4 :



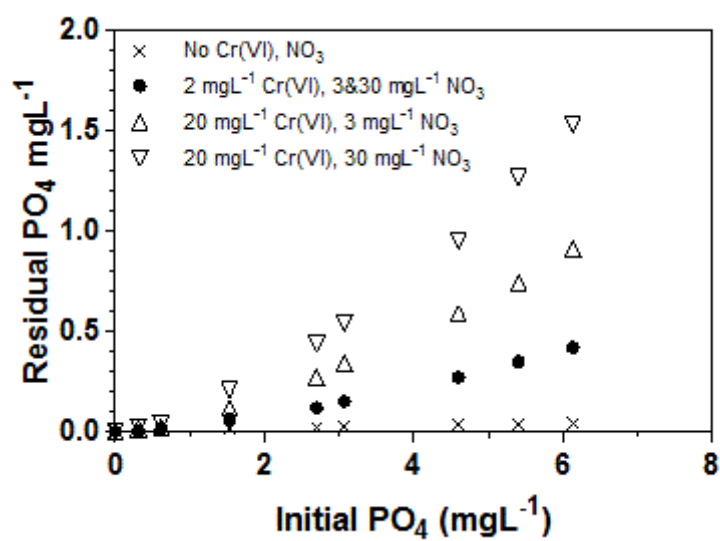
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Figure 4: Figure 5 :Figure 6 :



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Figure 5: Figure 7 :



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Figure 6: Figure 8 :

of 6. At concentrations below 1.6 mgL^{-1} , it may also appear as bichromate (HCrO_4^-).

Much work has focused on removal of anions from aqueous solution, usually as single ions, co-removal of nutrients, or co-removal of heavy metals.

Recent methods to remove phosphates include adsorption onto a zirconium sulfate surfactant micelle mesostructure (Pitakteeratham et al. 2013), recovery by a continuous struvite reaction crystallization process (Hutnik et al. 2013), immobilization using natural calcium rich sepiolite (Yin et al. 2013), adsorption onto biochar/MgAl-LDH ultra-fine composites (Zhang et al. 2013), and enhanced biological removal (Mielczarek et al. 2013).

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above a pH of 8 and as dichromate ($\text{Cr}_2\text{O}_7^{2-}$) below a pH

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Figure 7:

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Removal of Phosphates and Chromates in a Multi-ion System

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Cr (VI)	Freundlich			Langmuir		Global Journal of Re-
mg L ⁻¹	C	m	R ²	b	K	searches in Engineering
0	253.2	0.7868	0.9996	665.6	7.395	R ²
2	279	0.8352	0.9993	578.2	4.987	
20	197.6	0.8123	0.9985	451.7	5.615	

Figure 8: Table 1 :

2

PO ₄ ³⁻	Freundlich			Langmuir		
mg L ⁻¹	C	m	R ²	b	K	R ²
0	28.28	0.5366	0.9783	34.54	0.2999	0.9983
0.613	15.84	0.499	0.9478	17.18	0.257	0.9858
6.13	8.194	0.6626	0.9795	7.675	0.1075	0.9936

Figure 9: Table 2 :

3

and nitrate on phosphate ion exchange							
Cr	NO ₃	Freundlich			Langmuir		
(v1)	-						
mg L ⁻¹	mg L ⁻¹	C	m	R ²	b	K	R ²
1	-1						
0	0	253.2	0.7868	0.9996	665.6	7.395	0.9990
2	3	255.9	0.8096	0.9981	601.2	6.22	0.9996
2	30	259.8	0.8145	0.9981	599.2	6.138	0.9998
20	3	243.9	0.9044	0.9992	359.0	1.997	0.9985
20	30	260.8	0.9849	0.9999	277.1	0.286	0.9999

Figure 10: Table 3 :

4

and nitrate on Cr (v1) ion exchange							
PO 4 3-	NO 3	Freundlich		Langmuir			
mg L -1	mg L -1	C	m	R 2	b	K	R 2
0	0	28.6	0.5313	0.9709	35.52	0.3098	0.9946
0.613	3	14.7	0.533	0.9613	15.86	0.229	0.9904
0.613	3	14.58	0.536	0.9615	15.69	0.226	0.9903
6.13	30	7.689	0.6786	0.981	7.12	0.0969	0.9936
6.13	30	6.371	0.6763	0.9651	5.714	0.0882	0.9832

Figure 11: Table 4 :

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