Co-removal of hexavalent chromium through adsorption during copper precipitation

J.M. Sun* and J.C. Huang**

* Associate Professor of Environmental Engineering and Science, Tianjin University, Tianjin 300072, P.R.China. (E-mail: *tju_jmsun@hotmail.com*)

** Professor of Civil Engineering, Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong. (E-mail: *cehoward@ust.hk*)

Abstract A systematic study was conducted to assess the mechanisms involved in the co-removal of hexavalent chromium during chemical precipitation of divalent copper. Batch tests were used to assess the precipitation phenomena in both pure copper solutions and also mixed copper-Cr(VI) solutions with progressive addition of sodium carbonate to increase pH and induce precipitation. It was found that the co-removal of Cr(VI) was caused by two distinct mechanisms: coprecipitation of copper with Cr(VI) at pH 5.0 to 5.2, leading to the formation of $CuCrO_4$ precipitates. Once the fine crystallites of $CuCrO_4$ were formed, the test solution became heterogeneous and this accelerated the production of copper-carbonate precipitates, mainly in the form of $CuCO_3 \cdot Cu(OH)_2$, at pH 5.2 to 6.2. The latter precipitates were negatively charged at pH below 7.5, and thus they were able to adsorb a considerable amount of the remaining chromate ions [$HCrO_4^-$ and CrO_4^{2-}]. The extent of adsorption depended on both pH and surface loading. Besides electrostatic attraction, ligand exchange was also found to play some role. Maximum adsorption occurred at pH 6.5. When pH was raised to 10.0, approximately 25–30% of the adsorbed chromium could become desorbed due to a surface charge reversal on the adsorbent.

Keywords Co-removal of hexavalent chromium; copper precipitation; coprecipitation; electrostatic adsorption; ligand exchange; mechanisms

Introduction

Cr(VI) exists in the soluble forms of $HCrO_4^-$ and CrO_4^{2-}, with the former being predominant at pH below 6.5. Neither can react with either carbonate or hydroxide ions to form a precipitate unless it is first reduced to trivalent form (Cr^{3+} ions). Thus, reduction of Cr(VI) to Cr(III) and then using hydroxide to precipitate Cr(III) has been the most common method for Cr(VI) removal from metal plating industrial wastewater.

Some studies had been attempts made in the past decades to achieve direct Cr(VI) removal by adsorption on oxide surfaces such as pure and peroxide-modified TiO_2 (anatase) (Vasileva *et al*., 1994; Weng *et al*., 1997) and amorphous aluminium hydroxide or iron oxyhydroxide (ferrihydrite) (Benjamin and Bloom, 1981; Zachara *et al*., 1987; Dzombak and Morel, 1990; Mesuere and Fish, 1992). However, all of these processes required large quantities of adsorbents, which also resulted in a large production of sludge residues. Besides adsorption, some other methods, such as selective ion-exchange (Segupta, 1986), membrane technology (Winston and Poddar, 2001), and liquid-liquid extraction (Painter and Yarbrough, 1991) had also been studied for Cr(VI) removal, but none of these would appear suitable for treating industrial wastewater containing high Cr(VI) concentrations due to both high costs and the need for further dealing with the separated concentrated chromium stream.

In recent years, a single-step and space saving new method for removing such heavy metals as Cu(II), Ni(II) and Zn(II) from plating wastewater has been developed in the authors' laboratory (Zhou and Huang, 1999). The new method uses a fluidized sand column to serve as a metal stripper. In operation, plating wastewater is pumped into the fluidized

bed with a simultaneous injection of sodium carbonate to raise its pH to induce direct metal precipitation on the sand surface, a phenomenon called "nucleated precipitation" or "pellet precipitation".

Through this operation, metals become coated on the sand surface, and as the coated particles become large enough, they are removed from the bottom of the stripping column while new sand is added from the top.

In the field trial of this new method, it was found that about 60% of Cr(VI) in the metal plating wastewater was co-removed with other heavy metals (Sun and Huang, 2002; Sun *et al*., 2003). Thus, a systematic study was initiated to examine the mechanisms which were involved in the chromium's co-removal. In this respect, a series of well-designed batch tests were carried out in both pure copper and mixed Cu-Cr solutions to examine the phenomena of their precipitations. The experimental data suggest that there are two mechanisms involved in the co-removal of Cr(VI) with copper precipitation (Sun, 2003; Sun *et al*., 2003): coprecipitation of Cu(II) with Cr(VI) leading to the formation of $CuCrO_4$ precipitates, and adsorption of Cr(VI) ions by copper carbonate precipitates. In order to evaluate the adsorption characteristics of the freshly produced copper carbonate precipitates and also the significance of adsorption/desorption in contributing to Cr(VI) co-removal, a study was conducted to assess the adsorption and desorption of Cr(VI) onto the basic carbonate precipitates at pH ranging from 6.0 to 10.0.

Materials and methods

Experiments were carried out in a series of well-mixed batch reactors containing either pure copper or mixed Cu-Cr solutions to examine the precipitation of each metal at different pH by dosing with Na_2CO_3. In addition, the adsorption of Cr(VI) by freshly produced $Cu-CO_3$ precipitates was also examined. During each precipitation test, a synthetic 150-mg/L copper solution was prepared, and this was dosed with 0.5-N sodium carbonate solution through a burette to increase its pH and induce metal precipitation. The produced precipitates were then collected and washed by double-distilled and deionized water at a similar pH. Some of the precipitates were used to determine their compositions through gravimetric, EDAX and inorganic carbon analyses, and some were used to study their adsorption capacities for hexavalent chromium at different pH. In all cases, the test solutions were prepared from reagent grade chemicals ($CuCl_2.2H_2O$ and $K_2Cr_2O_7$).

Measurements of pH were made using a pH meter (ORION 420-A, USA). Daily calibrations with proper buffer solutions (pH 4.01, 7.00 and 10.01) were performed to ensure its accuracy. Soluble metal concentrations were determined by the Standard Methods 3500 (1995) using an atomic absorption spectrophotometer (HITACHI Z-8200, Japan). The concentrations of soluble copper and chromium in each sample were determined by comparison with the calibration curves developed from a series of standard solutions prior to each analysis. The carbonate content in the copper carbonate precipitates was determined by a total carbon analyzer (Shimadzu TOC, Model-5000A, Japan) following the procedures set forth in the *Standard Methods* 5310 (1995). The morphology and compositions of the metal precipitates were examined spectroscopically using energy dispersive analysis of X-ray (EDAX) (PHILIPS, XL30).

Results and discussion

Pure $CuCO_3$ has not been reported in the literature so far; instead, in nature the copper precipitates exist either as copper carbonate hydroxide or basic copper carbonate [$CuCO_3 \cdot Cu(OH)_2$ or $2CuCO_3 \cdot Cu(OH)_2$]. The formation of the sparingly soluble precipitates is a complex process, and the compositions and properties of the solids formed are greatly dependent on the precipitating conditions, such as metal concentrations, precipitation rate,
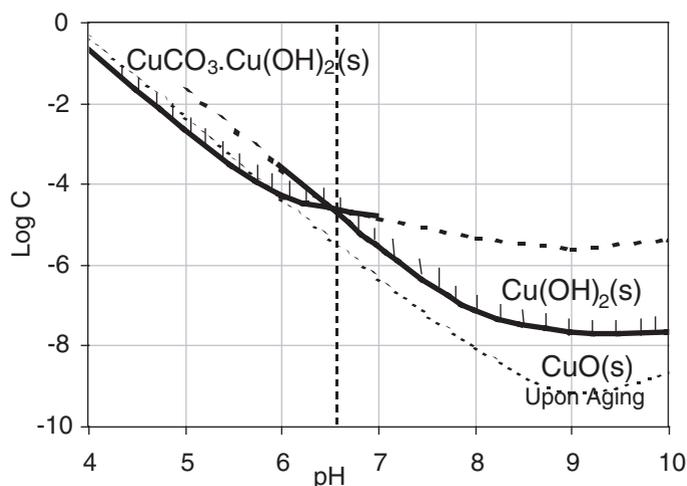
Figure 1 Solubility diagram for copper-carbonate-hydroxide system at different pH ($C_T=10^{-2}$ mol/L)

temperature, and the duration of ageing, etc. (Feitknecht and Schindler, 1963). According to the theoretical solubility diagram describing the copper-carbonate-hydroxide system under a C_T of 10^{-2} mol/L, as shown in Figure 1 (Sun, 2003), the total solubility of Cu(II) is dictated mainly by copper carbonate hydroxide for pH up to 6.6. Beyond this pH, copper hydroxide [$Cu(OH)_2$] is formed, which then governs the total solubility of Cu(II) for a short time. Upon ageing, copper oxide [CuO] will finally be formed and governs the total solubility of Cu(II). Thus, based on our test procedures, the precipitates used for adsorbent tests are mainly in the form of $CuCO_3 \cdot Cu(OH)_2$ or a mixture of $CuCO_3 \cdot Cu(OH)_2$ and $Cu(OH)_2$. These two precipitates are thought to be formed by a gradual reaction of Cu(II) with Na_2CO_3 in a pH range of 5.0 to 10.0. Thus, as the first step of this study, determinations of the adsorbent compositions are important.

Characterization of copper-carbonate precipitate compositions (adsorbents)

To determine the precipitate compositions, two adsorbent samples (copper-carbonate precipitates) were first produced by dosing with Na_2CO_3 solution (0.5 N) into two 500-mL solutions, each containing 150-mg/L Cu(II), to increase their pH gradually to 6.4 and 8.0, respectively. Each took approximately 10 minutes to reach the target pH, and then an extra 15 min was allowed for the reaction to reach equilibrium. The precipitates were then collected after being subjected to three repeated washings with double-distilled, deionized water (with its pH pre-adjusted to 6.4 or 8.0). The obtained precipitates were oven-dried and weighed gravimetrically before being used for inorganic carbon determination. The vacuum dried $Cu-CO_3$ precipitates were subjected to EDAX analyses.

Gravimetric analysis of precipitates. After the equilibrium precipitation of 150-mg/L Cu(II) solution at pH 6.5 and 8.0, the remaining soluble Cu^{2+} were found to be 29.7 mg/L and 0.5 mg/L, respectively. Thus, through calculations, the amounts of the produced precipitates should be 217.5, 209.3 or 184.7 mg/L at pH 6.4, and 271.2, 260.1 or 229.5 mg/L at pH 8.0, respectively, if the precipitates were purely azurite [$2CuCO_3 \cdot Cu(OH)_2$], malachite [$CuCO_3 \cdot Cu(OH)_2$], or $Cu(OH)_2$. Through gravimetric analysis, the obtained precipitates were 207.0 mg/L at pH 6.5 and 258.0 mg/L at pH 8.0, both being closer to the amounts calculated for malachite [$CuCO_3 \cdot Cu(OH)_2$]. Thus, the adsorbent used for the hexavalent chromium adsorption tests is mainly in the form of $CuCO_3 \cdot Cu(OH)_2$.

EDAX analyses. The EDAX spectrum of the precipitates is shown in Figure 2. From this spectrum, the molar ratio of [Cu]:[O] was 33.18:79.63, which was shown in the direct EDAX printout. This equals a [Cu]:[O] ratio of 1:2.4. This ratio is also close to the value of 1:2.5 calculated for malachite [$CuCO_3 \cdot Cu(OH)_2$]. For comparison, the [Cu]:[O] ratios are 1:2.67 for azurite [$2CuCO_3 \cdot Cu(OH)_2$], and 1:2.0 for $Cu(OH)_2$.

Inorganic carbon in precipitates. The percentage of inorganic carbon in the precipitates was determined by several repeated tests using a total carbon analyzer. The value was found to be between 3.5% and 5.5%, which is also close to the value of 5.4% for malachite [$CuCO_3 \cdot Cu(OH)_2$]. On the other hand, the inorganic carbon percentages are 6.96% for azurite [$2CuCO_3 \cdot Cu(OH)_2$] and 0% for $Cu(OH)_2$.

All of the above data apparently suggested that the major constituent in the adsorbent was $CuCO_3 \cdot Cu(OH)_2$. It was possible that a much smaller percentage of $Cu(OH)_2$ could also be present in the adsorbent solids. To simplify subsequent discussion, the term "Cu-CO_3 precipitates" or "copper-carbonate precipitates" will be used to refer to this type of precipitate.

Adsorption of Cr(VI) onto copper-carbonate precipitates

A series of adsorption tests were first performed at different initial pH using the two Cu-CO_3 precipitates obtained at pH 6.5 and 8.0, respectively. This was to investigate whether the two precipitates obtained at different pH had significant differences in adsorbing Cr(VI). In pursuing this test, Cu-CO_3 precipitates were first prepared by dosing Na_2CO_3 to a 3,000-mL solution [containing 150-mg/L Cu(II)] to raise its pH to 6.5 first. After 15-min equilibrium reaction, half of the completely-mixed mixture was withdrawn, and the precipitates were collected and washed 3 times with double-distilled, deionized water with its pH pre-adjusted to 6.5. Then, the pH of the remaining mixture was further increased to 8.0 with additional Na_2CO_3 dosing. The collected precipitates at this pH were also washed similarly before the adsorption test.

In each adsorption test, a fixed amount of precipitates [equivalent to that containing 15-mg Cu(II)] was added to a series of 100-mL Cr(VI) solutions, each having 60-mg/L Cr(VI) but with a different pH, to perform the adsorption test. After 1-h reaction, the residual soluble Cr(VI) (in mg/L) in the mixed solution was analyzed and the data are shown in Figure 3. It is clear that the Cu-CO_3 precipitates obtained at pH 6.5 and 8.0 have no significant differences in their adsorption for Cr(VI). The extents of Cr(VI) adsorption are
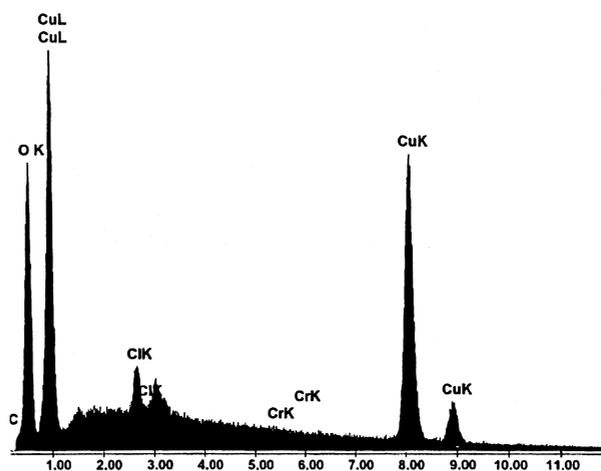

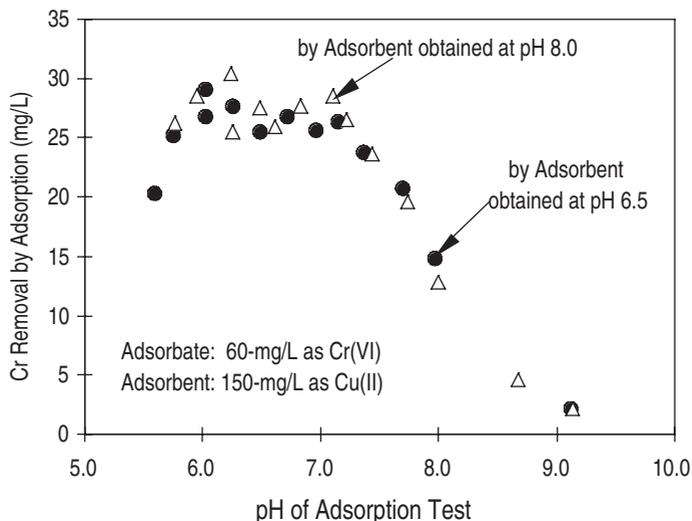**Figure 2** EDAX spectrum of copper-carbonate precipitates

Figure 3 Comparisons of Cr(VI) adsorption by Cu-CO$_3$ precipitates obtained at pH 6.5 and 8.0, respectively

mainly dictated by the initial pH at which adsorption took place. Therefore, the precipitates used in the subsequent adsorption tests were produced at a pH of approximately 8.0.

Rate of adsorption. To assess the rate of adsorption, a 500-mL solution containing 60-mg/L Cr(VI) with an initial pH of 6.5 was prepared. Then a fixed amount of freshly produced Cu-CO$_3$ precipitates containing an equivalent of 75-mg Cu(II) was added. The mixture was continuously mixed, and 10-mL sample was withdrawn, filtrated, and acidified after 1, 3, 5, 15, 30, 60, 120 and 180 min of reaction. The remaining soluble Cr(VI) in each sample was determined and the data are shown in Figure 4. The open and solid data points show the results of duplicate tests.

The data of Figure 4 seem to coincide with the commonly observed relationship for most adsorption that the quantity adsorbed varies with t$^{1/2}$ rather than with t (Weber and Morris, 1963). It appeared that Cr(VI) adsorption by Cu-CO$_3$ precipitates followed a two-phase theory. The first was a linear, rapid adsorption phase, which was attributed to the instantaneous utilization of the most readily available adsorbing sites on the adsorbent surface. The
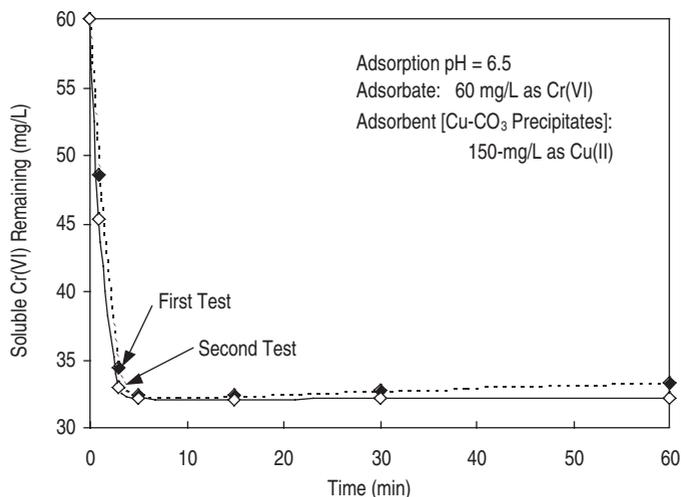

Figure 4 Rate of Cr(VI) adsorption by Cu-CO$_3$ precipitates

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second was a quasi-stationary phase, which was attributed to a slow diffusion of chromium ions (either $HCrO_4^-$ or CrO_4^{2-}) from the liquid film into the internal voids of the adsorbent, or the least accessible sites of adsorption. The first phase took place within 3 min, during which approximately 90% of the total adsorption capacity was reached. Beyond that, the second phase of adsorption took place and was completed in the next two min. There was very little further adsorption thereafter. Thus, in all of our adsorption tests, a reaction time of 1 h was allowed to ensure the attainment of equilibrium adsorption.

Factors affecting adsorption. Most adsorption reactions can be affected by temperature, solution pH, surface loading and ionic strength. In our study, it is known that temperature may have a bearing on the type of precipitates produced and its surface structure, and it can also affect the adsorption rate and capacity. However, the wastewater temperature in Hong Kong lies in a narrow range of 23 to 30°C most of the time. Thus, we conducted all experimental tests at a fixed room temperature of 23°C. The emphasis of the study was to examine the effects of other factors, such as pH, surface loading and adsorbent concentration, on the Cr(VI) adsorption.

The effect of pH was examined by conducting the adsorption tests at two different initial pH: 6.5 and 10.0. As in other adsorption tests, repeated experiments were performed by adding different amounts of adsorbent ($Cu-CO_3$ precipitates) to two sets of 60-mg/L Cr(VI) solution. The first set had a pH of 6.5, and the second set had a pH of 10.0. The extents of Cr(VI) adsorption were determined after 1-h reaction time, and the data are shown in Figure 5 by the solid circular and solid triangular points, respectively. Then, upon the initial adsorption at pH around 6.5 (first set), the solution pH was then increased to 10.0 to evaluate the extent of Cr(VI) desorption. The data are shown in the same figure by the open circular points. A blank test with the use of only double-distilled, deionized water (with prior pH adjustments) instead of the Cr(VI) solution was also conducted to determine whether there was any copper leaching from the adsorbent at pH 6.5 and 10.0. Since no copper leaching was observed in the blank test at these two different pH, any change in the soluble Cr(VI) level in each test solution was attributed to adsorption and/or desorption.

The test results of Figure 5 clearly reflected that the extent of Cr(VI) adsorption was much greater at acidic pH (e.g. pH 6.5) than that at alkaline pH (e.g. pH 10.0). Also, a portion of the initial adsorption at the acidic pH could be subsequently desorbed when the solution pH was increased to the alkaline range. When pH was increased from 6.5 to 10.0, approximately 25–30% of the initially adsorbed Cr(VI) could become desorbed. For
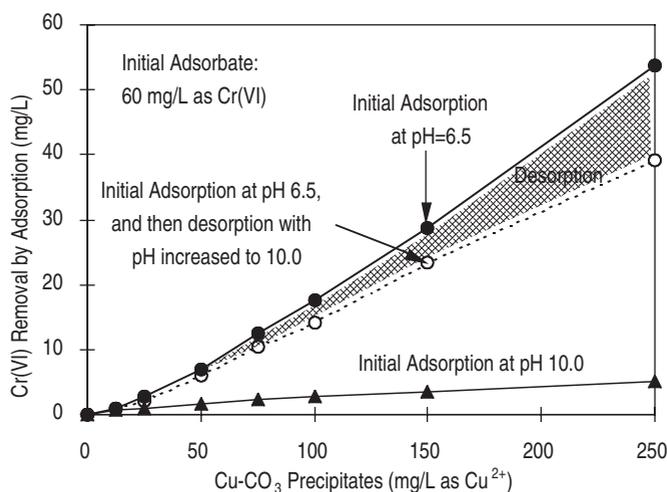

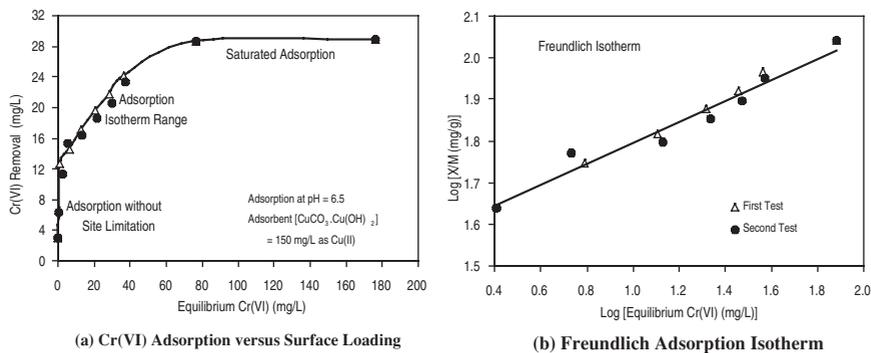**Figure 5** Adsorption of Cr(VI) by Cu-CO$_3$ precipitates at various pH

Figure 6 Adsorption of Cr(VI) by Cu-CO$_3$ precipitates at different surface loading rates

example, at an adsorbent level containing an equivalent of 250-mgL Cu(II), the initial Cr(VI) adsorption was 53 mg/L at pH 6.5, which was subsequently reduced to 39 mg/L when the pH was raised to 10.0. The portion of desorbed Cr(VI) (53–39 = 14 mg/L) represented a "reversible" reaction, which was originally caused by "electrostatic adsorption". On the other hand, the non-desorbed portion was originally caused by "ligand exchange" in the original adsorption process (Sun *et al*., 2003). All of these reflected that Cr(VI) adsorption was strongly pH-dependent.

The effect of surface loading was examined by dosing a fixed amount of Cu-CO$_3$ precipitates (containing an equivalent of 15-mg Cu) into a series of 100-mL solutions, each of which contained a different concentration of Cr(VI). In this phase of the study, the adsorption pH was controlled at the optimum level of 6.5. After 1-h adsorption, the equilibrium Cr(VI) remaining in each test solution was determined, and the data are shown in Figure 6.

Figure 6a shows clearly that surface loading affected Cr(VI) adsorption in three different patterns. At a very low loading level (about 0 to 15-mg Cr/150-mg adsorbent expressed as Cu equivalent), chromium ions were adsorbed onto the surface of Cu-CO$_3$ precipitates without a site limitation, thereby most of the adsorbate being adsorbed completely. At a medium level of surface loading (about 15 to 60-mg Cr/150-mg adsorbent as Cu), the specific quantity of Cr(VI) adsorbed was a function of the surface loading. Thus, its equilibrium isotherm followed the Freundlich-type relationship, as shown in Figure 6b. At a higher surface loading, then the specific Cr(VI) adsorption reached a saturated level. In this case, all of the adsorption sites had been occupied and any further increase in surface loading would not lead to a further increase of chromium adsorption.

Conclusions

The main constituent of the precipitates obtained from the reaction of CuCl$_2$ and Na$_2$CO$_3$ is CuCO$_3$·Cu(OH)$_2$. Depending on the rate of precipitation and the reaction pH, a minor amount of Cu(OH)$_2$ may be present. The extent of Cr(VI) adsorption by such precipitates is mainly dictated by the adsorption pH, rather than by the pH at which the adsorbents are produced. More Cr(VI) adsorption occurs at an acidic pH than at an alkaline pH. Approximately 25–30% of the initially adsorbed Cr(VI) at pH 6.5 can be subsequently desorbed when the solution pH is increased to 10.0. This portion of original adsorption is caused by electrostatic attraction between the adsorbent and the adsorbate. The non-desorbed portion is originally caused by ligand exchange. The specific quantity of Cr(VI) adsorption depends strongly on the surface loading. At a loading of 15- to 60-mg Cr/150-mg adsorbent expressed as Cu equivalent, and the equilibrium adsorption isotherm follows the Freundlich-type model.

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