Optimum pHs for Cr(VI) co-removal with nucleated Cu(II) precipitation in continuous-flow fluidised metal strippers

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Abstract

A compact nucleated precipitation technology using two fluidised sand columns in series was developed to pretreat model metal-plating wastewater containing high concentrations of Cu(II) and Cr(VI). Since either Cu(II) precipitation or Cr(VI) co-removal with Cu(II) precipitation was found to be highly pH dependent in batch tests, the continuous-flow studies were conducted under different pHs. Experimental results show that high pH has no positive influence on either Cr(VI) or Cu(II) removal in the continuous-flow fluidised metal stripper technology. Operation at pH 6.5 in both columns can obtain significantly higher levels of both total Cr(VI) and total Cu(II) removal compared with work at pH 9.5 in both columns and work at pH 6.5 and 9.5 in the 1st and 2nd columns, respectively.

Keywords: nucleated precipitation, continuous-flow fluidised metal stripper, Cr(VI), Cu(II)

Introduction

Many industries, including electroplating, printed circuit, metal finishing, tanneries, photographic, and dye manufacturing, etc., generate wastewater containing variable levels of Cr(VI). Although selective ion-exchange (Segupta, 1986), membrane technology (Ho and Poddar, 2001; Ghosh et al., 2006; Hafez and Manharawy, 2004), adsorption by natural and modified adsorbents (Prasad and Freitas, 2000; Malkoc and Nuhoglu, 2006; Celis et al., 2000; Gode and Pehlivan, 2006), etc., have been successfully demonstrated at laboratory- scale level, they have not been employed in full-scale operation because of high operation costs and generation of pollution. Removal of Cr(VI) by bacterial strain and fungal strain (Shrivastava and Thakur, 2003; Srivastava and Shekhar, 2006) have been investigated in recent years. However, the lower removal efficiency and longer time requirement limit their practical use. Chemical reactions involving reduction of Cr(VI) to Cr(III) by different reducing agents such as $NaHSO_3$, FeS, $FeSO_4$, SO_2, etc., followed by a hydroxide precipitation of Cr(III) (Erdem et al., 2001) have received great attention and were found to operate effectively with higher rate and higher recovery. They are the most widely used methods in full-scale operation over the past decades, especially for high-load (either volume or mass) wastewater streams. However, the methods are restricted due to the cost of the chemicals used and the quality and amount of the sludge produced. Finding cost-effective and space-saving methods for Cr(VI) elimination suitable for practical use and large-scale operation are attractive and important work.

On the basis of heterogeneous precipitation, a single-step compact method was developed by Huang and co-workers to remove such heavy metals as Cu(II), Ni(II), and Zn(II) from industrial wastewaters, including electroplating, printed circuit and metal finishing, etc. The new method uses a fluidised sand column to serve as a metal stripper. Unexpectedly, a large amount of aqueous Cr(VI) was co-removed from the plating wastewater containing Cu(II), Ni(II), Zn(II), and Cr(VI) under an operation at pH 9.5 (Zhou et al., 1999).

Cr(VI) exists mainly in soluble forms of $HCrO_4^-$, $Cr_2O_7^{2-}$ and CrO_4^{2-} in the aqueous environment. They cannot form any precipitate in reaction with either CO_3^{2-} or OH^- ions, unless they are first reduced to Cr(III). Therefore, the mechanisms involved in co-removal of Cr(VI) with the precipitation of other heavy metals were further examined through a series of batch studies. Co-precipitation involving the formation of copper-chromate precipitates and adsorption of Cr(VI) onto the freshly formed copper-carbonate precipitates, both being highly pH dependent, were the main mechanisms responsible for Cr(VI) co-removal (Sun et al., 2003). The maximum co-removal of Cr(VI) with Cu(II) and close to 100% Cu(II) removal was observed at a pH of around 6.5 instead of 9.2 under drip-feed Na_2CO_3 dosing (Sun et al., 2003). Based on the results of the batch tests, a series of continuous-flow nucleated precipitation studies using fluidised sand strippers was further conducted under different pH and dosing techniques to confirm the optimum operating conditions for both Cr(VI) and Cu(II) removal in the continuous-flow system.

It is not the intention of this study to advocate the use of Cu(II) or other heavy metals as an agent to remove Cr(VI). However, since they coexist in most industrial wastewaters, it is advisable to use the available Cu(II) to maximise the co-removal of Cr(VI) first. The advantage of the technology is that the continuous single-step compact system using fluidised metal strippers allows the precipitates produced to coat on the media surface, in which precipitation of heavy metals, co-removal of Cr(VI), and solid-liquid separation occur. Precipitate dewatering is not required, and metals can be recovered by dissolving the metal-coated sands with acids. Therefore, the technology is simple in operation, space-

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saving and cost-effective in practical application. It is feasible and advisable for the pretreatment of industrial wastewater with high concentration of metals, especially for small-scale industries.

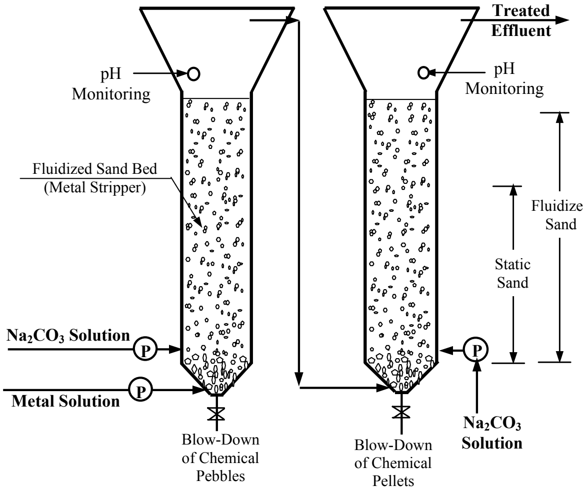
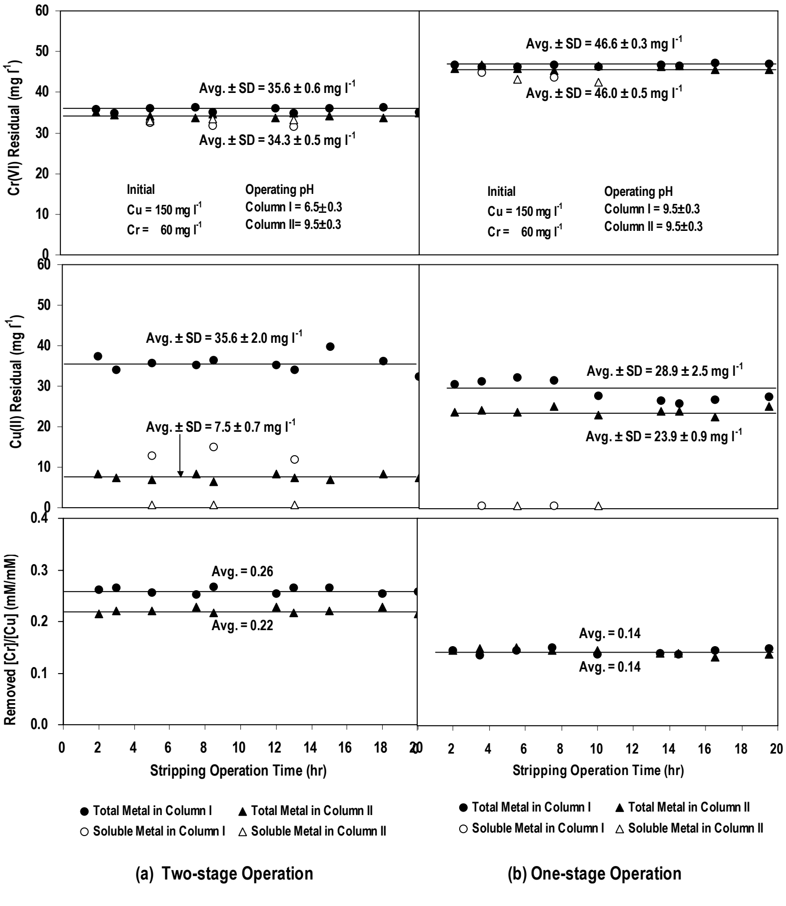


Figure 1
Experimental set-up of the continuous-flow fluidised metal stripper technology



(a) Two-stage Operation **(b) One-stage Operation**

Figure 2
Comparisons of metal residuals in nucleated precipitation systems under different operating pHs

Experimental

Experimental procedures/operation

In batch tests (Sun, 2003), it was found that co-removal of Cr(VI) with drip-feed Na_2CO_3 dosing to a pH of around 10.0 was more than 3 times higher than that with rapid one-shot instantaneous slug Na_2CO_3 dosing to a pH of around 10.0, while only slightly higher than that with two-stage instantaneous slug Na_2CO_3 dosing (e.g. one-shot instantaneous slug dosing to pH of around 6.5 first, after allowing to reach reaction equilibrium, followed by another one-shot instantaneous slug dosing to a pH of around 10.0). In the continuous-flow fluidised metal stripper system, drip-feed dosing to increase pH gradually is not practical. To maximise the co-removal of Cr(VI), two-stage metal stripper system was employed, as shown in Fig. 1 (Sun et al., 2006).

The two-stage metal stripper system comprised two fluidised sand columns in series, each built with a 36-mm (diameter) Plexiglas tube to a total height of 800 mm. Each column was packed with quartz sand to a static height of 450 mm and 25 to 72 mesh (150 to 600 μm) standard quartz sand (BS4550) was used to allow good fluidising and also to provide a large surface area for precipitate coating. The model metal-bearing solution was pumped to the bottom of the 1st column using a peristaltic pump (Cole Palmer, Masterflex, Model 77200-50) at a flow rate of approximately 350 $m\ell \cdot min^{-1}$, which was adequate to fluidise the sands to around 600 mm, i.e. 33% expansion. Na_2CO_3 solution (0.5 N) was injected into each column at a location of 40 mm from the bottom of each column, also using a peristaltic pump (Cole Palmer, Masterflex, Model 77200-50), to increase the operating pH and induce nucleated metal precipitation. A pH controller (JENCO, model 3672) was installed at the top of each column to monitor and control the operating pH within a designed range (pH of 6.5 ± 0.3 or 9.5 ± 0.3). The residence time of the waste stream was approximately 1 min in each column.

In each investigation, around 30 h stripping operation was conducted: during the first 10h no sample was withdrawn in order to achieve a steady state and the subsequent 20 h were for sample taking and observation. Samples withdrawn at different time intervals were either passed through a 0.45 μm membrane filter immediately before acidification for soluble metal determination or acidified with 1+1 HNO_3 before filtration for total metal determination. The filtrates were stored in polypropylene bottles for subsequent metal analysis. As the sand particle-metal precipitate combination becomes large enough, the particles were removed from the bottom of the stripping column while new sand was added from the top.

Model metal solutions and reagents

Model metal solutions used in this study were prepared by dissolving reagent grade $CuCl_2{\cdot}2H_2O$ (Riedel-deHaën) and $K_2Cr_2O_7$ (Nacalai Tesque) into tap water. The solutions contained 150 $mg \cdot \ell^{-1}$ Cu(II) and 60 $mg \cdot \ell^{-1}$ Cr(VI). Their initial pH was adjusted to around 3 with concentrated HNO_3 (70%, Riedel-deHaën) to prevent metal precipitation prior to entering the 1st column. Carbonate solution (0.5 N) was prepared by dissolving industrial grade Na_2CO_3 in tap water.

Analytical methods

Metal concentrations were determined using an atomic absorption spectrophotometer (HITACHI Z-8200 Polarised Zeeman, Japan) in accordance with *Standard Methods* (1998). The particle size distribution of metal precipitates was analysed using an LS laser diffraction particle size analyser (BECKMAN COULTER, LS 13 320 SW, Micro Liquid Module, Single Wavelength) with double-distilled and deionised water as background.

Results and discussion

To make a comparison, two tests under different operating pH were conducted following the procedures described in the section 'Experimental'. In Test I, Na_2CO_3 was pumped to each of the 1st and 2nd strippers to raise their pH to around 6.5 and 9.5, respectively. In Test II, Na_2CO_3 was pumped to only the 1st stripper to raise its pH to around 9.5 while nothing was pumped to the 2nd stripper. The experimental results (averages of three repeated tests) are shown in Figs. 2a and 2b, respectively.

Figure 2a shows that under pH of around 6.5 and 9.5 in the 1st and 2nd columns (Test I), the final total Cr(VI) residual in the treated effluent was approximately 34 mg·ℓ$^{-1}$, that is an approximately 26 mg·ℓ$^{-1}$ (60 - 34 = 26 mg·ℓ$^{-1}$) or 43.3% (26/60 x 100% = 43.3%) removal. For the operation at both pH of around 9.5 in the 1st and 2nd columns (Test II, Fig. 2b), the final total Cr(VI) residual was approximately 46 mg·ℓ$^{-1}$, that is an approximately 14 mg·ℓ$^{-1}$ (60 - 46 = 14 mg·ℓ$^{-1}$) or 23.3% (14/60 x 100% = 23.3%) removal. This is only approximately half of the total Cr(VI) removal in the operation with two-stage pH control, e.g. pH of around 6.5 and 9.5 (Test I). Further, the final residual of total Cu(II) in the treated effluent with two-stage pH control (Test I, Fig. 2a) was approximately 8 mg·ℓ$^{-1}$, while that with one pH operation (Test II, Fig. 2b) was much higher, reaching approximately 23 mg·ℓ$^{-1}$. The observation of final total Cr(VI) and Cu(II) removal confirmed that in the continuous run using fluidised metal stripping technology, the two-stage Na_2CO_3 dosing first to an operating pH of around 6.5 and subsequently to a pH of around 9.5 had much higher levels of total Cr(VI) and total Cu(II) removal compared with one-stage rapid and direct Na_2CO_3 dosing to an operating pH of around 9.5.

For the 1st column operation of the above two tests, the total Cu(II) removal under a pH of around 6.5 and 9.5 was very close, i.e. 113 mg·ℓ$^{-1}$ (150 - 37 = 113 mg·ℓ$^{-1}$) and 120 mg·ℓ$^{-1}$ (150 - 30 = 120 mg·ℓ$^{-1}$), respectively. However, the total Cr(VI) removal under a pH of around 6.5 was approximately 24 mg·ℓ$^{-1}$ (60 - 36 = 24 mg·ℓ$^{-1}$) with a removed total Cr(VI) to total Cu(II) ratio of 0.26 mmol·mmol^{-1} (see Fig. 2a). This is almost double the corresponding total Cr(VI) removal under pH of around 9.5, e.g. only 13 mg·ℓ$^{-1}$ (60 - 47 = 13 mg·ℓ$^{-1}$) with a removed total Cr(VI) to total Cu(II) ratio of 0.14 mmol·mmol^{-1} (see Fig. 2b). The finding confirms that the two-stage technology with the 1st stage at a pH of 6.5 and the 2nd stage at a pH of 9.5 (Test I) had significant improvement of Cr(VI) and Cu(II) removal in the continuous-flow system.

Since high pH has no positive effect on either Cr(VI) or Cu(II) removal in the continuous operation using fluidised metal stripper technology, a similar test under an operating pH of around 6.5 in both the 1st and 2nd columns (as Test III) was conducted, the other conditions and procedures being the same as the previous two tests, to evaluate whether enhancement of Cr(VI) and Cu(II) removal could be obtained. The experimental results (averages of three repeated tests) are shown in Fig. 3.

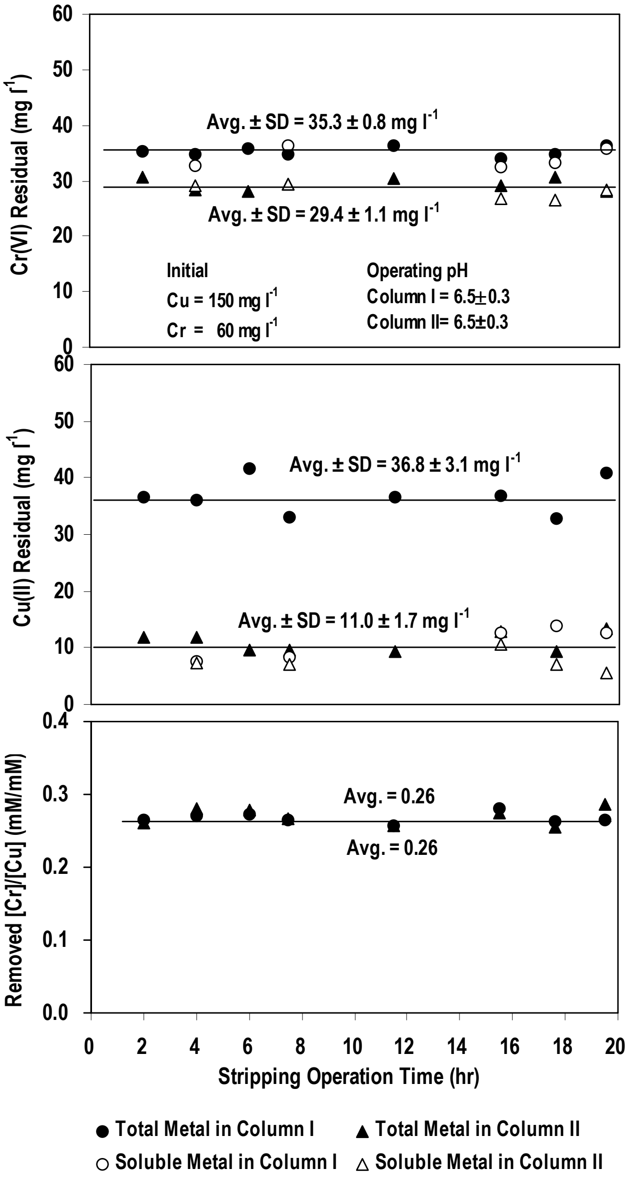


Figure 3
Nucleated precipitation under operating pH of around 6.5 in both columns

Figure 3 shows clearly that the 1st column was able to reduce the total Cr(VI) from 60 to around 36 mg·ℓ$^{-1}$ (24 mg·ℓ$^{-1}$ or 40.0% removal) and the total Cu(II) from 150 to around 37 mg·ℓ$^{-1}$ (113 mg·ℓ$^{-1}$ or 75.3% removal), the same as those observed in the two-stage pH control system (Test I, Fig. 2a). This was expected since the 1st columns were operated under the same pH conditions in both tests. After passing through the 2nd column, the final total Cu(II) further decreased to around 10 mg·ℓ$^{-1}$, still at a level close to the two-stage pH control system (i.e. 8 mg·ℓ$^{-1}$, Test I); while the final total Cr(VI) further decreased to approximately 29 mg·ℓ$^{-1}$ (31 mg·ℓ$^{-1}$ or 51.7% removal) with a molar ratio of 0.26 mmol·mmol^{-1} of the finally removed total Cr(VI) to total Cu(II). This is higher than the corresponding total Cr(VI) removal of 26 mg·ℓ$^{-1}$ or 43.3% and molar ratio of 0.22 mmol·mmol^{-1} in the two-stage pH control system (Test I, Fig. 2a).

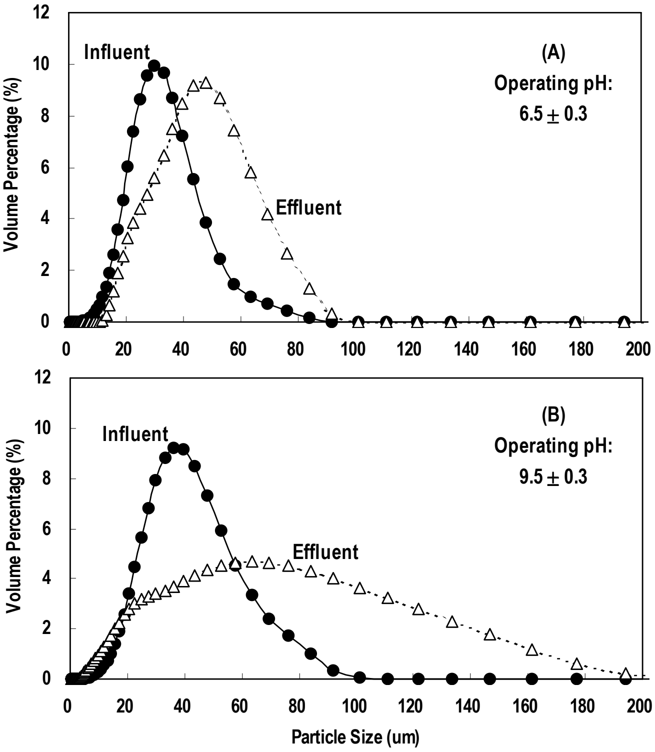


Figure 4
Comparisons of particle size distributions under different operating pHs

The above findings indicate that an operating pH of around 6.5 is more favourable for the co-removal of Cr(VI) with Cu(II) precipitation than work at pH of around 9.5 in the continuous-flow fluidised metal stripper technology. Further, an operation at pH of around 6.5 is more economical due to lower Na$_2$CO$_3$ dosage compared to an operation at pH of around 9.5 and also saving on acid usage to neutralise the treated effluent to satisfy the pH requirement for discharge.

In the above Tests I, II and III, the final residuals of total Cu(II) in the treated effluent was as high as 8 mg·ℓ$^{-1}$, 23 mg·ℓ$^{-1}$ and 10 mg·ℓ$^{-1}$, respectively. Such high total Cu(II) residuals were unexpected. To establish whether the high total Cu(II) residual was due to the insufficient metal precipitation or due to discrete metal precipitation and the coated/adsorbed precipitates being released off the sand particle surface area into the liquid, soluble metal residuals in the effluents of the 1st and 2nd columns in each test were measured and are shown in Figs. 2a, 2b and 3, respectively (see open points).

In the 1st column with an operation at pH of around 6.5 (Tests I and III), Cu(II) was reduced from 150 mg·ℓ$^{-1}$ to approximately 37 mg·ℓ$^{-1}$ (with approximately 10 mg·ℓ$^{-1}$ Cu(II) residual in its soluble forms). After the 2nd column with an operation at pH of around 6.5 (Test III), Cu(II) residual was further reduced to 10 mg·ℓ$^{-1}$ (with almost all in soluble form). This indicates that under the operation at pH of around 6.5, around 27 mg·ℓ$^{-1}$ insoluble Cu(II) leakage from the 1st column was probably because the 1st column alone did not provide a sufficient surface area or retention time to allow all Cu(II) precipitates to be effectively plated out. Some of the metal precipitates entered the 2nd column and were plated out there. However, around 10 mg·ℓ$^{-1}$ Cu(II) residual (almost all in soluble form) in the 2nd column was due to insufficient metal precipitation at pH of around 6.5 instead of the limitation of surface area or retention time.

In the 2nd column under an operation at pH of around 9.5 (Tests I and II), soluble Cu(II) concentrations were close to zero while the corresponding total values were still as high as 8 mg·ℓ$^{-1}$ or 23 mg·ℓ$^{-1}$, respectively. That is also to say the decreased levels of Cu(II) in the 2nd column were not as high as the corresponding levels in the 1st column. This indicates that the high total Cu(II) residuals in the treated effluent were not due to insufficient metal precipitation and the limitation of surface area or retention time. They were most probably due to less heterogeneous deposition (because of lower soluble metals) and more difficult for small particles/fines adsorption on the surface of sand or metal precipitate-sand combination (because of lower energy). The surface of metal precipitates consists of a wide distribution of surface-site types and surface energy (Leckie et al., 1980), thus has various coating properties. The portion, which is easier to coat the virgin sand or metal precipitate-sand combination, may have been removed as more as possible in the 1st column. Therefore in the 2nd column, even though similar conditions and surface sites were provided, only limited remaining precipitates coat the sands. Further, crystal ageing or agglomeration through secondary nucleation in liquid phase may enhance the conversion of small particles into larger size precipitates. Smaller particles have relatively higher surface energy and are easier to coat onto the larger ones or other solids (Snoeyink et al., 1980; Henisch, 1991), while the aged precipitates or larger size precipitates may not have as good coating properties as that of freshly formed precipitates or smaller size precipitates.

To test this assumption, particle size distributions in the effluents of the 1st columns in the aforementioned Tests I and II were measured and are shown in Fig. 4, see open triangular points. For comparison, particle size distributions in batch tests with instantaneous slug Na$_2$CO$_3$ dosing to the target pH are also shown in Fig. 4; see solid circular points.

Figure 4a shows that the precipitate sizes lay between 10 to 90 µm, with the prevalent size at around 30 µm after instantaneous Na$_2$CO$_3$ dosing to a pH of 6.5. However, after passing through the 1st column under a pH of around 6.5 (Test I), even though the particle sizes still lay between 10 to 90 µm, the prevalent size shifted to around 50 µm. Figure 4b shows that the precipitate sizes lay between 10 to 100 µm, with the prevalent size at around 35 µm after instantaneous Na$_2$CO$_3$ dosing to a pH of 9.5. However, after passing through the 1st column under a pH of around 9.5 (Test II), the particle sizes lay between 10 to 200 µm, with the prevalent size at around 70 µm. The observation confirms the aforementioned assumption.

Conclusions

pH affects Cu(II) precipitation, Cr(VI) co-removal with Cu(II) precipitation and secondary nucleation or metal-precipitate coating onto the sand surface. High pH has no positive influence on either Cr(VI) or Cu(II) removal in the continuous-flow fluidised metal stripper technology. Under an operation at pH 6.5 in both columns, significantly higher removal levels of both total Cr(VI) and total Cu(II) were obtained compared with work at pH of 9.5 in both columns and work at pH of 6.5 and 9.5 in the 1st and 2nd columns, respectively.

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