Leachate analysis of the tannery sludge amended by zero-valent iron nanoparticles under dynamic condition

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ABSTRACT

This study presents the leaching behaviour of chromium from the raw tannery sludge and the sludge stabilized by zero-valent iron nanoparticles (ZVIN) under dynamic condition. The leachability of chromium from raw tannery sludge was found to be more than that from the treated sludge. The optimized conditions at which the ZVIN particles reduced the leachability of chromium from the tannery sludge were found to be 7, 100 g/kg and 48 hours respectively for pH, adsorbent dosage and time. In dynamic condition, the leachate concentration of chromium from the unamended sludge was found to be 1.174 mg/L at 30^{th} pore volume, whereas the sludge amended by ZVIN attained 0 mg/L leaching at 24^{th} pore volume. The sludge amended by ZVIN particles reduced the leachability of chromium more than the raw tannery sludge. The XRD, FTIR, SEM and EDX analyses also confirmed the binding of chromium ions in the tannery sludge.

KEY WORDS: Tannery sludge, Chromium, Zero valent iron nanoparticles.

1. INTRODUCTION

Heavy metal pollution in the environment has become a serious issue globally. Heavy metals such as cadmium, chromium and lead, have been found to be present in amounts higher than the natural level in the environment due to anthropogenic activities. Those industries which utilize these metals, such as the semiconductors, battery manufacturing, metal plating and paint, significantly contribute to the pollution loading in the environment. The indiscriminate discharge of chromium metals into water resources causes serious health hazards to humans and environment because of their toxicity. Chromium exists in trivalent form and hexavalent form in aqueous systems. Cr (III) ions are non toxic and play an essential role in the metabolism of plants and animals. Though Cr^{3+} is less toxic than Cr^{6+}, a long-term exposure to trivalent chromium causes allergic skin reactions. Chromium is considered to be a powerful carcinogenic agent by IRAC which modifies the DNA transcription process causing chromosome aberrations. Tanneries are considered to be one of the major sources of chromium pollution to the aquatic environment. It contaminates surface water and sediments to an unacceptable level as shown by numerous studies. In India, there are about 3000 tanneries processing 600 million kg of raw skin and hide which generate 50 MPD (Million litres Per Day) of liquid wastes and 305 million kg of solid wastes. Though the liquid wastes from tanneries can be treated through the common effluent treatment plant/effluent treatment plant (CETP/ETP), the solid wastes (sludge) from tanneries and CETP creates major environmental threats. Due to the presence of chromium the sludge is classified as hazardous and hence it should be handled properly before its disposal.

The solid wastes can be widely treated using various techniques such as anaerobic digestion, gasification, pyrolysis etc. One of the most widely used techniques is immobilization of the contaminants. In this study, the zero-valent iron nanoparticles have been utilized for the immobilization of chromium ions present in the tannery sludge. The objective of this study is to evaluate the leaching behaviour of chromium from the raw tannery sludge and also from the sludge amended by ZVIN particles under dynamic condition.

2. MATERIALS AND METHODS:

The zero-valent iron nanoparticles (ZVIN) have been subjected to green synthesis. For the preparation of nanoparticles, the tea waste was washed with ethanol and DIW. Then it was oven-dried at 80°C for 24 h. The sludge was collected from common effluent treatment plant (CETP) near Ranipet. The pH and total chromium concentration of the sludge were found to be 8.4 and 24.2 g/kg respectively. The concentration of trivalent chromium and hexavalent chromium in the sludge was 23.23 g/kg and 0.968 g/kg respectively.

Synthesis of ZVIN Particles: 17 mL of 0.1% SDS solution were mixed with 100 mL of tea waste extract (The tea waste extract was prepared by boiling 2.6 g of tea waste in 100 mL of DIW) and stirred for five minutes. To the above mix, 0.1 N of $FeCl_3$ was added drop-wise till the colour of the solution changed from orange to black. The solution was stirred at a temperature of 60°C for fifteen minutes, and it was then oven-dried at 80°C for 24 hours. The dried particles were washed several times with DIW and ethanol. Finally it was again oven-dried at a temperature of 80°C.

Column Studies: The leachate analysis of the treated sludge was studied under continuous flow of DIW. Totally, 8 g of amended and non-amended sludge were packed in the glass column of inner diameter 2 cm and height 7 cm. The schematic sketch of the column used in this study was given in Figure 1. Three layers of glass wool were placed in the column to avoid the disturbance of the influent flow and the sludge surface. The amended and non-amended sludge columns were saturated with DIW to reach field-holding capacity prior to leaching. The amount of water required for one pore volume was found to be 8.6 mL for unamended sludge and sludge amended by ZVIN nanoparticles. The time required to collect one pore volume of leachate was found to be 27 h for unamended sludge and sludge amended by ZVIN nanoparticles.

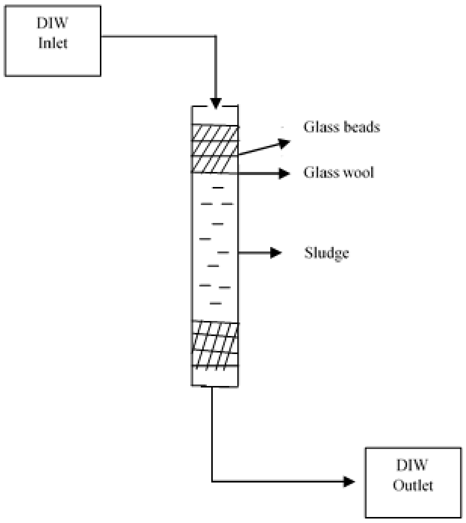


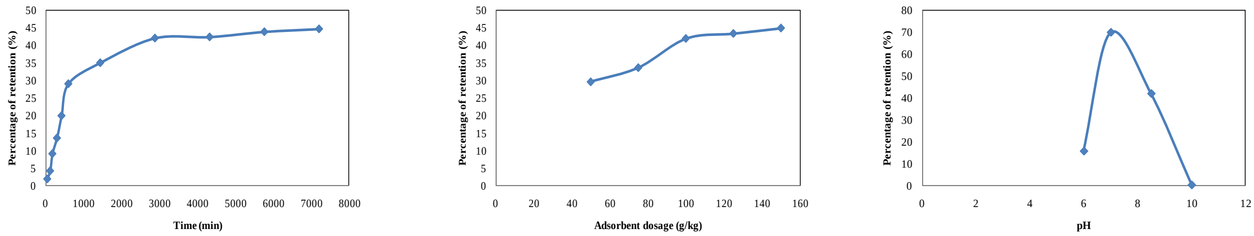
Figure.1. Schematic representation of Column (not to scale)

The DIW was applied to the top of each column at a rate of 0.5 mL/min every 27 h for unamended sludge and sludge amended by ZVIN nanoparticles. This leaching was continued up to 30 pore volumes. The leachate samples were collected and filtered through a 0.42 μm Whatman filter paper for the analysis of chromium concentration in atomic adsorption spectroscopy.

Instrumentation Analysis: The tannery sludge before and after the treatment was analysed using XRD, FTIR and SEM. FEI Quanta FEG 200 scanning electron microscopy was used for scanning the surface and analysing the composition of the S/S matrices. The samples were sprinkled onto adhesive carbon tapes supported on metallic disks, and their images and elemental contents were recorded at different magnifications. For FTIR analysis, the samples were made as pellets with KBr and they were then ground in an agate mortar. Shimadzu-IR-AFFINITY-1 spectrometer in the range of 500-4000 cm^{-1} was used for identifying functional groups in the samples. The BRUKER's D8 advance instrument was used for XRD analysis. The source consisted of Cu Ka radiation (λ=1.54187Ǻ). Each sample was scanned in the 2θ range of 10 -80°. The heavy metal concentration in the sample was analyzed using Varian-AA240 atomic adsorption spectroscopy.

3. RESULT AND DISCUSSIONS

Sludge Treatment: The individual variables such as time, adsorbent dosage and pH were investigated on the immobilization of chromium in the tannery sludge. The optimization of the independent variables was done by varying the adsorbent dosage (50-150 g/kg), pH (6-11) and time (45 minutes - 120 hours). The shaking speed and temperature were maintained at 120 rpm and 30°C respectively. The optimization of time was done by maintaining the adsorbent dosage and pH at 100 g/kg and 8.5 respectively as constants. The plot depicts that all the adsorbents attained the equilibrium at 48 hours. The maximum chromium retaining efficiency at equilibrium time was found to be 42% for ZVIN particles (Figure 2a). The optimization of adsorbent dosage was carried out at normal sludge pH (8.5) and equilibrium time (48 hours). At 100g/kg, the maximum retaining efficiency was found to be 42% for ZVIN (Figure 2b). The optimization of pH was done by maintaining equilibrium time and adsorbent dosage at 48 hours and 100 g/kg respectively. The percentage of retention was found to be 69.9% for ZVIN particles (Figure 2c) at pH 7.



a b c

Figure.2. Immobilization of chromium in tannery sludge with various parameters (a) Time (b) adsorbent dosage and (c) pH

Leachate analysis under dynamic condition: The mobility of chromium from the unamended sludge and the sludge amended by ZVIN was studied in the downward movement. Figure 3 shows that the highest chromium concentration occurred in the first leaching event for all the samples. The highest amount of leaching was observed in all leaching experiments for the unamended sludge. At the first pore volume, the chromium concentration was found to be 2.506

and 0.768 mg/L, respectively for the unamended sludge and sludge amended by ZVIN. At the 30th pore volume, the leachate concentration of chromium from the unamended sludge was found to be 1.174 mg/L. The sludge amended by ZVIN attained 0 mg/L leaching at 24 pore volumes. Thus, the results show that, with increase in pore volume, the sludge amended by ZVIN significantly reduced the concentration of chromium in the leachate.

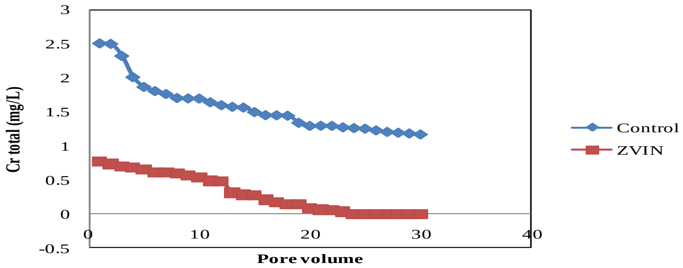


Figure.3. Leachability of chromium from unamended sludge and sludge amended by ZVIN under dynamic condition

Instrumentation analysis: The XRD analysis confirmed the presence of trivalent chromium in the tannery sludge. The trivalent chromium ions found in the sludge are chromium nitrate hydrate ($Cr(NO_3)\cdot 9H_2O$), chromium chloride ($CrCl_3$), chromium oxide hydroxide ($CrOOH$), chromium hydroxide hydrate ($Cr(OH)_3\cdot 3H_2O$) and chromium sulfate ($Cr_2(SO_4)_3$). The data show the presence of traceable amounts of hexavalent chromium ions such as chromium carbonyl (C_6CrO_6) and ammonium chromium oxide ($(NH_4)2Cr_2O_7$) in the unamended sludge and sludge amended by ZVIN. The formation of iron chromium oxide hydrate ($Fe_2Cr_4O_{15}\cdot 4H_2O$) observed in the sludge amended by ZVIN is due to the reaction between iron and chromium compounds. The EDX analysis showed the presence of oxygen, calcium, carbon, chromium, chloride, sodium, sulphur, aluminium, magnesium, silicon and iron in the unamended sludge/control and sludge amended by ZVIN. The SEM image showed that the sludge amended by ZVIN was found to be more agglomerated than the unamended sludge. This may be due to the binding of chromium ions on the surfaces of nanoparticles and nanobiocomposites. The FTIR analysis confirmed the presence of amine groups, carboxylic groups etc. in the treated tannery sludge and the involvement of these functional groups in the retention of chromium ions.

4. CONCLUSION

The leachability of chromium from the raw tannery sludge and sludge amended by ZVIN was evaluated in this study. The results suggest that the leachability of chromium from the tannery sludge with ZVIN was found to decrease with increase in time and pore volumes. The sludge amended by ZVIN particles attained 0 mg/L leaching at 24th pore volume whereas the unamended sludge continued leaching even after 24th pore volume and at 30th pore volume, the leachability of chromium from unamended sludge was found to be 1.174 mg/L. The XRD, FTIR and SEM analyses confirmed the retention of chromium ions by the ZVIN particles, attributed to the minimal leaching of chromium ions from the tannery sludge.

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