ICMIEE20-158

Leaching behavior of chromium from tannery sludge under aerobic condition

Sanjida Kabir, Ismat Zerin, Md. Abul Hashem[*]
Department of Leather Engineering, Khulna University of Engineering & Technology, Khulna-9203, BANGLADESH

ABSTRACT
Tannery solid waste management has become a great challenge for the survival of the leather industry in Bangladesh. The solid waste 'Tannery sludge' is the result of the physicochemical and biological treatment of the discharged liquid wastes through the effluent treatment plant (ETP). The tannery sludge contains heavy metals especially a huge amount of chromium. A trace level of trivalent chromium is essential for certain metabolic functions in the human body. The high concentration of chromium is toxic to human health. In this study, the leaching behavior of chromium was investigated from the tannery sludge using different extractants: rainwater, agricultural fertilizers, and ethylenediamine tetraacetic acid (EDTA) under aerobic conditions. The chromium in the selected tannery sludge was 99.8 mg/kg. About 4 (four) g dried tannery sludge was mixed with 50 mL extractant and the air was purged through an air pump. After a preselected time interval, the suspension was filtered through the filter paper and chromium in the leachate was quantified by the atomic absorption spectroscopy (AAS). Results indicate that rainwater was extracted more chromium than distilled water. The agricultural fertilizers have no significant effect on leach chromium from the tannery sludge. The EDTA could extract more chromium from the tannery sludge among the used extractants. Before dumping the tannery sludge more suitable technique e.g., phytoremediation could be an alternative option to recover the chromium.

Keywords: Tannery sludge, Chromium, Leaching, Extractant, Agricultural fertilizers

1. Introduction

The leather industry is a peristome and emerging role player industry in a developing country like Bangladesh where 90% of raw materials are our own. Tannery waste management has become a great challenge for the survival of the leather industry in Bangladesh. Tannery sludge or sludge is a solid waste which is made from physical-chemical and biological treatment. The solid waste tannery sludge is the result of the physicochemical and biological treatment of the discharged liquid wastes through the effluent treatment plant (ETP). The tannery sludge contains heavy metals especially a huge amount of chromium. A trace level of trivalent chromium is essential for certain metabolic functions in the human body. Hexavalent chromate compounds have high solubility that's why it easily has taken up by organisms. For this reason, the hexavalent form of chromium is more dangerous than the trivalent form. Because of its toxic and carcinogenic properties, it damages the lung, liver, kidney, and causes other health-related complications (Uluozlu et al. 2009; Stout et al. 2009). Thus, chromium leaching from the tannery sludge is an important issue. Till today, several methods have been promoted to leach chromium from tannery sludge. Acid digestion, stirring, airflow is used for leaching of heavy metals.

According to ECR (1997), the discharge level of chromium in the tannery wastewater is 2 mg/L. Hashem et al. (2015) reported that chromium level in the tannery wastewater ranges from 2656-5420 mg/L. Chromium containing wastewater as well as tannery sludge is a great concern for the environment. Chromium from these could enter the human food chain, which is a health concern.

In the tannery, sludge from effluent treatment plant (ETP) management has become an important issue. Tannery sludge contains a high amount of chromium including other heavy metals. Killic et al. (2011) reported that tannery sludge contains chromium 8041 mg/L with various amounts of lead (Pb), nickel (Ni), mercury (Hg), copper (Cu), and cadmium (Cd). Leaching of chromium from the disposing/dumping of tannery sludge could be a potential source to contaminate the groundwater.

The high concentration of chromium is toxic to human health. In this study, the leaching of chromium was investigated from tannery sludge using different extractants: rainwater, agricultural fertilizers, and ethylenediamine tetraacetic acid (EDTA) under aerobic conditions.

In this study, the leaching behavior of chromium was investigated from tannery sludge with different extraction fluid under aerobic conditions. The chromium in the leachate was quantified by atomic absorption spectroscopy.

2. Materials and Methods

2.1 Sampling

Tannery sludge was collected from Riff Leather Ltd. Chattogram, Bangladesh. The sludge was sun-dried and then oven-dried at 105°C for 24 h. The oven-dried sludge was ground through a mechanical grinder and sieve on 80 mesh. The extractant rainwater was collected from the roof after 15 min of starting the rain.

2.2. Chemicals and Reagents

The agricultural fertilizers: triple super phosphate (TSP), muriate of potash (MOP), and urea were collected from a local agricultural dealer, Khulna. The reagents nitric acid (65%, Merck KGaA, Germany), hydrogen peroxide (30%, Merck Specialties private Ltd., India), and ethylenediamine tetraacetic acid (EDTA) were collected from the local scientific store, Khulna.

2.3 Acid digestion

The total chromium (Cr) in the tannery sludge was quantified after acid digestion following the method

* Corresponding author. Tel.: +88-01674590373
E-mail addresses: mahashem96@yahoo.com

(EPA3050B). About 2.0 g oven-dried sludge sample was acid digested with nitric acid and hydrogen peroxide. The Cr was quantified of the aliquot by the atomic absorption spectroscopy (AAS).

2.4 Batch leaching test

A batch-wise leaching experiment was performed with different leaching agents: rainwater, TSP, MOP, urea, and EDTA under aerobic conditions. About 4 g dried tannery sludge was mixed into 50 mL leaching fluid and the air was purged from an air pump at the flow rate of 20 mL/min. The experiment was conducted at different time intervals with various concentrations of the leaching agents. The solution was filtered through the filter paper then Cr was quantified in the leachate by the atomic absorption spectroscopy.

2.5 Effect of stirring on Cr leaching

The effect of stirring time on Cr leaching was conducted at different time intervals. About 4 g dried tannery sludge was mixed with 50 mL rainwater and stirred on a magnetic stirrer for different time intervals. Finally, the Cr was quantified in the leachate by atomic absorption spectroscopy (AAS).

3. Results and Discussion

3.1 Tannery sludge characterization

Table 1 depicts the characterization of tannery sludge. The pH, EC, and moisture content of the tannery sludge were 8.8, 6.5 mS, and 13.3%, respectively. The Cr content of the tannery sludge was 99.8 mg/kg. It seems that tannery sludge was contained a higher amount of Cr. The pH of the tannery sludge was within the discharge level (6-9).

Table 1 Characterization of tannery sludge

Parameters	Value	Unit
pH	8.8	-
EC	6.5	mS
Moisture	13.3	%
Cr	99.8	mg/kg

3.2 Effect of rainwater on Cr leaching

The effect of rainwater on Cr leaching from the tannery sludge is shown in **Fig. 1**. The leached amount of Cr by the effect of rainwater at 1, 2, 3, 4, 5, 6, 7, and 8 h was 1.07, 1.09, 1.60, 2.64, 2.25, 1.63, 1.48, 1.57 mg/L, respectively. For a time the leaching amount of Cr was gradually increased until 4 h then gradually decreased.

According to ECR (1997), Cr level more than 2 mg/L in the wastewater is not dischargeable. It seems that the highest amount of Cr was leached at 4 h (2.64 mg/L). After 4 h, steadily Cr leaching was decreased. A plausible reason is that after 4 h of leaching, Cr was readsorbed from solution on the tannery sludge surface. During leaching, the solution pH was almost constant and it was 8.5.

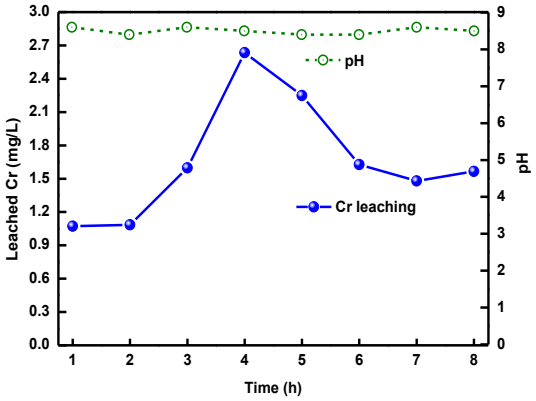

Fig. 1 Effect of rainwater on Cr leaching from tannery sludge under aerobic condition

3.3 Effect of TSP on Cr leaching

Figure 2 depicts the Cr leaching by the effect of TSP from the tannery sludge. It is clear that with increasing the TSP dose, the leached amount of Cr was gradually decreased. TSP dose at 0.5 g for 4 g tannery sludge, leached Cr was 1.139 mg/L. At TSP dose 2 g for 4 g tannery sludge, leachable Cr was only 0.002 mg/L. The Cr might form a complex with the TSP as an insoluble substance. Therefore, although TSP was increased the leached Cr in the aqueous was decreased. Of course, the solution pH was decreased with increasing the TSP dose.

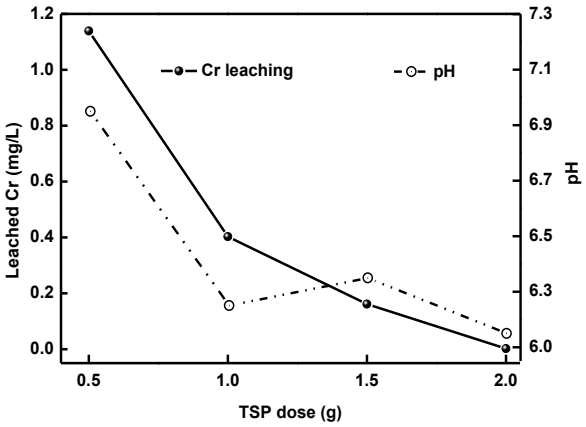

Fig. 2 Effect of TSP on Cr leaching from tannery sludge under aerobic condition

3.4 Effect of urea on Cr leaching

Fig. 3 shows the leaching behavior of Cr by the effect of urea from the tannery sludge. The Cr was leached by effect urea dose 0.5, 1.0, 1.5, 2.0 g for 4 g tannery sludge was 1.65, 1.60, 1.31, and 1.28 mg/L, respectively. It is clear that with increasing the urea dose in the suspension leached amount of Cr was declined.

The solution pH was increased with increasing urea dose. For example, at 0.5 g urea dose, pH was 7.7 but in the case of 2.0 g urea dose where pH was 8.4. pH between the ranges 6.5-8.5, Cr(III) form insoluble

chromic hydroxide (Byrne et al. 2016). Therefore, the leached amount of Cr was gradually decreased with increasing the urea dose in the suspension. It appears that urea has no significant effect on Cr leaching from the tannery sludge.

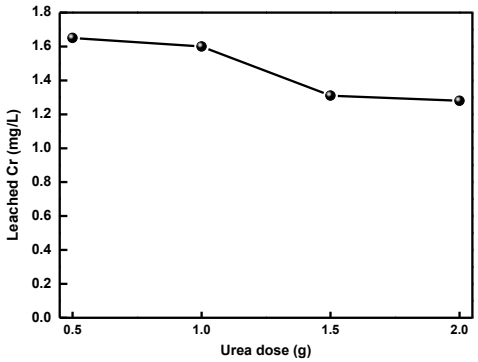

Fig. 3 Effect of urea on Cr leaching from tannery sludge under aerobic condition

3.5 Effect of MOP on Cr leaching

Fig. 4 shows the effect of MOP on Cr leaching from the tannery sludge under aerobic conditions. It is clear that with increasing the MOP dose Cr leaching was gradually increased. At 0.5 g MOP dose for 4 g tannery sludge, leached Cr was 1.201 mg/L. On 2 g MOP dose for 4 g tannery sludge, leached Cr was 1.232 mg/L. It seems that the difference between the MOP doses of 0.5 g and 2 g for 4 g tannery sludge was 0.031 mg/L, which implies that the correlation of dose and leached Cr is not significant. The pH of the suspension was between the ranges of 8.4-8.5. However, it is clear MOP can leach only a small amount of Cr from the tannery sludge.

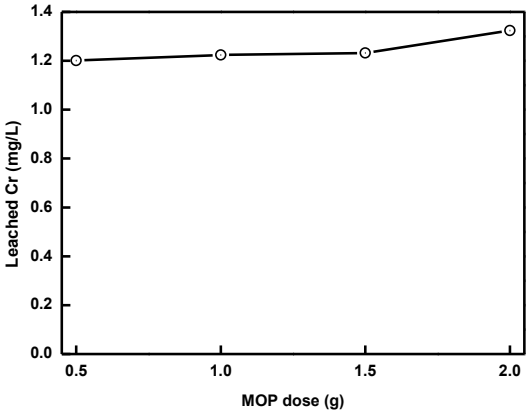

Fig. 4 Effect of MOP on Cr leaching from tannery sludge under aerobic condition

3.6 Effect of EDTA on Cr leaching

Cr leaching from the tannery sludge by the effect of EDTA is shown in **Fig 5**. EDTA mixed tannery sludge suspension was stirred on magnetic stirred for 8 h. The quantified leached Cr was 2.247, 2.559, 3.444, and 4.390 mg/L by the effect of EDTA dose 0.1, 0.15, 0.2, and 0.25 M, respectively.

It is clear from Fig. 4 that with increasing the EDTA dose in the suspension leached amount of Cr was increased. Wang et al. (2007) studied to leach various metals (Cu, Zn, Cd, and Pb) from the contaminated soil EDTA as a chelating agent. EDTA forms a chelate complex with Cr, which keeps these Cr ions in a soluble form. Hence, the leached amount of Cr was increased in the suspension.

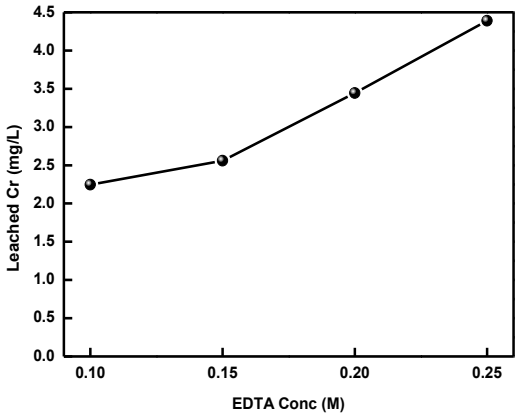

Fig. 5 Effect of EDTA on Cr leaching from tannery sludge under aerobic conditions for 8 h stirring

3.7 Effect of stirring time on Cr leaching

Stirring time is one of the factors to leach Cr from the tannery sludge. **Fig. 6** depicts the batch-wise leaching of Cr from the tannery sludge by the effect of rainwater at 2, 4, 6, 8, 10, 12, 14, 16, 18, 20, 22, and 24 hours under aerobic conditions.

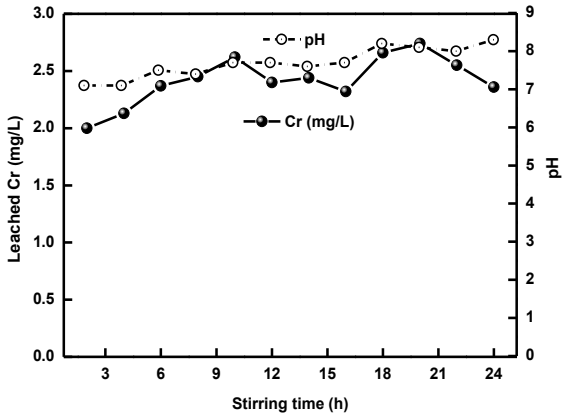

Fig. 6 Effect of stirring time on Cr leaching from tannery sludge under aerobic conditions

It appears that Cr leaching at stirring time 2 h was 2.0 mg/L and maximum leaching was observed 2.66 mg/L for 18 h stirring time. It is noticeable that Cr leaching was range 2.0-2.66 mg/L and there is no significant effect of stirring time on Cr leaching from the tannery sludge. The leached amount of Cr has exceeded the discharge level of ECR (1997).

In comparison among the leaching extractants, rainwater can leach Cr from the tannery sludge under the aerobic condition at a certain time (4 h), which exceeds the ECR (1997) guideline. The agricultural fertilizers (TSP, MOP, urea) have no significant effect on Cr leaching from the tannery sludge. There is a moderate effect of stirring time on Cr when rainwater was used as extractant fluid. The chelating agent EDTA could extract more Cr than other chemical agents e.g. TSP, MOP, and urea.

4. Conclusion

In this study, the leaching behavior of chromium from tannery sludge with different extractants: rainwater, TSP, MOP, urea, and EDTA was investigated. The agricultural fertilizers have no significant effect on chromium leaching under aerobic conditions. Rainwear has a moderate effect on chromium leaching from the tannery sludge. The effect of stirring time on chromium leaching from the tannery sludge in rainwater has a positive impact. Chromium could leach slowly from the disposing of high chromium containing tannery sludge. Tannery authority should not dump or dispose of tannery sludge anywhere without decontamination to save the environment.

5. References

[1] K Uluozlu, OD., Tuzen, M., Mendil, D., Kahveci, B. Saylak, M., 3-Ethyl-4-(p-chlorobenzylidenamino-4,5-dihydro-1H-1, 2, 4-triazol-5-one (EPHBAT) as precipitant for carrier element free coprecipitation and speciation of chromium (III) and chromium (VI), *Journal of Hazardous Materials*, vol. 172, pp. 395-399, 2009.

[2] Stout MD, Herbert RA, Kissling GE, Collins BJ, Travlos GS., Witt KL., Melnick RL., Abdo KM., Malarkey DE., Hooth MJ., Hexavalent chromium is carcinogenic to F344/N rats and B6C3F1 mice after chronic oral exposure, *Environmental Health Perspectives*, vol. 117, pp. 716-722, 2009.

[3] Environment Conservation Rules (ECR), Ministry of Environment & Forests (MoEF), Government of the People's Republic of Bangladesh, 1997.

[4] EPA method 3050B: Acid digestion of sediments, sludges, and soils.

[5] Hashem MA., Islam A., Mohsin S., Nur-A-Tomal MS., Green environment suffers by discharging of high chromium containing wastewater from the tanneries at Hazaribagh, Bangladesh, *Sustainable Water Resources Management*, 2015, vol. 1, pp. 343-347, 2015.

[6] Kilic E., Puig R., Baquero G., Font J., Colak S., Gürler D., (2011). Environmental optimization of chromium recovery from tannery sludge using a life cycle assessment approach, *Journal of Hazardous Materials*, vol. 192, pp. 393-401, 2011.

[7] Byrne P., Taylor KG., Hudson-Edwards KA., Barrett JES., Speciation and potential long-term behaviour of chromium in urban sediment particulates, Journal of Soils and Sediments, vol. 17, pp. 2666-2676, 2017.

[8] Wang G., Koopmans GF., Song J., Temminghoff EJ., Luo Y., Zhao Q., Japenga J., Mobilization of heavy metals from contaminated paddy soil by EDDS, EDTA, and elemental sulfur. *Environmental Geochemistry and Health*, vol. 29, pp. 221-235, 2007.