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Immobilization of Heavy Metals in Tannery Sludge by Subcritical water Treatment

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Waste sludge discharged from tannery industry is a potential source of environmental pollution due to the hazardous heavy metals (HMs) such as chromium, copper and led. Surface water and soil pollutions by these HMs as a result of improper treatment and disposal of tannery sludge have become a great health-hazard concern to the society.There are various immobilization techniques for HMs that have been proposed and/or are being practiced. The hydro-thermal treatment utilizing subcritical water (SCW) is one of the new technologies, which is regarded as environmentally friendly and sustainable. The SCW technology can stabilize and reduce the volume of organic sludge as well as immobilize HMs to reduce direct toxicity and the risk. The study investigates immobilization of HMs, which are contained in tannery sludge in high concentrations, under the SCW conditions by forming a particular crystalline mineral that captures HMs. Based upon the preliminary SCW treatment experiments, which were conducted at moderate temperature of up 280 °C and under the saturated pressure with amended silica and calcium, and leaching tests, it was observed that heavy metal concentrations in the leachate from tannery sludge decreased after the SCW treatment. This implies that the SCW treatment has a potential as an immobilization technology for HMs contained in tannery sludge. Experiments are currently being undertaken in order to optimize the SCW conditions and silica/calcium amendment ratio, to identify the mechanism of immobilization and to evaluate stability of the immobilized HMs.

1. Introduction

Concern over environmental toxicology and demand for safe disposal of industrial tannery waste are the topics of research interest for long time (Gangopadhyay et al., 2000). The leather production is associated with the generation of huge amount of solid waste in the form of tannery sludge during processing. Disposal of the tannery sludge has become a serious problem because the waste contains various hazardous materials, especially HMs, which have direct toxic effects on aquatic ecosystem (Thierno et al., 2015) and posses indirect health risk to the human being through bioaccumulation in the food chain (Nzihou and Stanmore, 2013).
Accumulation and bio-availability of hazardous metals are the important factors in disposal and utilization of tannery sludge. In order to reduce the risk of toxicity of HMs in the tannery sludge, there are two approaches that can be applied; removal of HMs and immobilization of HMs in the sludge (Shi et al., 2013a) Various methods such as chemical extraction (Silva et al., 2005), bio-leaching and bio-remediation have been applied for the heavy metal removal from the tannery sludge (Pathak et al., 2008). But these methods are time consuming and it has been observed that it is very difficult to control the removal efficiency in the removal operation.
HMs immobilization is widely used in treating contaminated sludge and soil due to its simplicity and cost effectiveness (Devi and Saroha, 2014). One of the materials that are known to immobilize HMs is tobermorite, which is a naturally occurring crystalline mineral, but can be synthesized under moderately high temperature hydro-thermal conditions.

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Hydro-thermal treatment, especially subcritical water (SCW) technology, is regarded as environmentally friendly and has been used for treatment of organic matters such as sewage sludge. However, there is no study reported in the literature investigating the immobilization of HMs in tannery sludge under SCW conditions.
Therefore, the present study focuses on SCW treatment of tannery sludge for immobilization of the HMs by formation of tobermorite or similar crystalline minerals. HMs present in the tannery sludge can be partitioned by hydrochar and trapped strongly by the pore space of tobermorite, which can be formed depending upon temperature and Ca/silica ratio under the SCW conditions.
In the study, XRD and SEM are used to establish the optimal SCW conditions and Ca/silica ratio to from tobermorite. Mitigation of toxicity of HMs in tannery sludge and their bio-availability are also examined by sequential extraction procedure and by the Toxicity Characterizing Leaching Test (TCLP).

2. Methodology

2.1 Sample preparation

De-watered anaerobically digested tannery sludge was used in this study. After sampling the sludge was ground by ball mill to small particles and kept at 4 ºC in enclosed plastic bag until the experiments (Shi et al., 2013b). Collected rice husk was washed with 5 M sodium dodecyl sulphate solution and then air dried for overnight, followed by soaked in 0.5 M sulfuric acid and rinsed with tap water, distilled water and MQ water, separately. The prepared rice husk was air dried overnight and oven dried at 105 °C for 24 h. 2 gm of oven dried rice husk was put in to a crucible and ignited at 600 °C for 2 h for Ig-loss determination. The final product, amorphous silica from rice husk, is used in the experiment (Bakar et al., 2016).
10 g of tannery sludge powder mixed with amorphous silica and calcium carbonate with pre-determined Ca and silica ratios 0.81 (wt/wt), was mixed in a beaker. This starting material is first mixed with 6 mL of 2 M NaOH solution. MQ water is then added to the total volume of 100 mL.

2.2 Experimental Procedure

SCW experiments were carried out by an SCW reactor system developed and fabricated by OM LABTECH CO., LTD. It consists of a 200 mL stainless steel cylindrical reactor with a thermocouple and pressure gauge to monitor the reaction temperature and internal pressure, respectively. The reactor is designed to operate at the temperature up to 400 °C. The reactor has an internal agitator paddle at a fixed speed of 300 rpm. The system is fitted with rapid cooling system by water running in the cooling coil around the heater and an electric fan.
SCW experiment was conducted with 10 g of tannery sludge powder or the mixture of tannery sludge power and amorphous silica loaded into the reactor and treated under SCW conditions (up to 280 ºC under the saturation steam pressure for 0.5 to 1 h. After solid-liquid separation by vacuum filtration, the collected solid residue, which is the hydrochar, was oven dried at 105 °C for 24 h, and crushed and stored in enclosed plastic bag at 4 ºC.

Table 1. Chemical characteristics of tannery sludge (Results express on dry basis).

Characteristic	Items	Value
Micro nutrients	Potassium %	0.04
	Calcium %	4.53
	Phosphorus %	0.09
	Magnesium mg/kg	0.36
	Sodium mg/kg	0.36
	Al %	4.52
Heavy Metals	Fe mg/kg	1265
	Cr mg/kg	12950
	Pb mg/kg	14
	Cu mg/kg	76
	Zn mg/kg	36
	Mn mg/kg	44

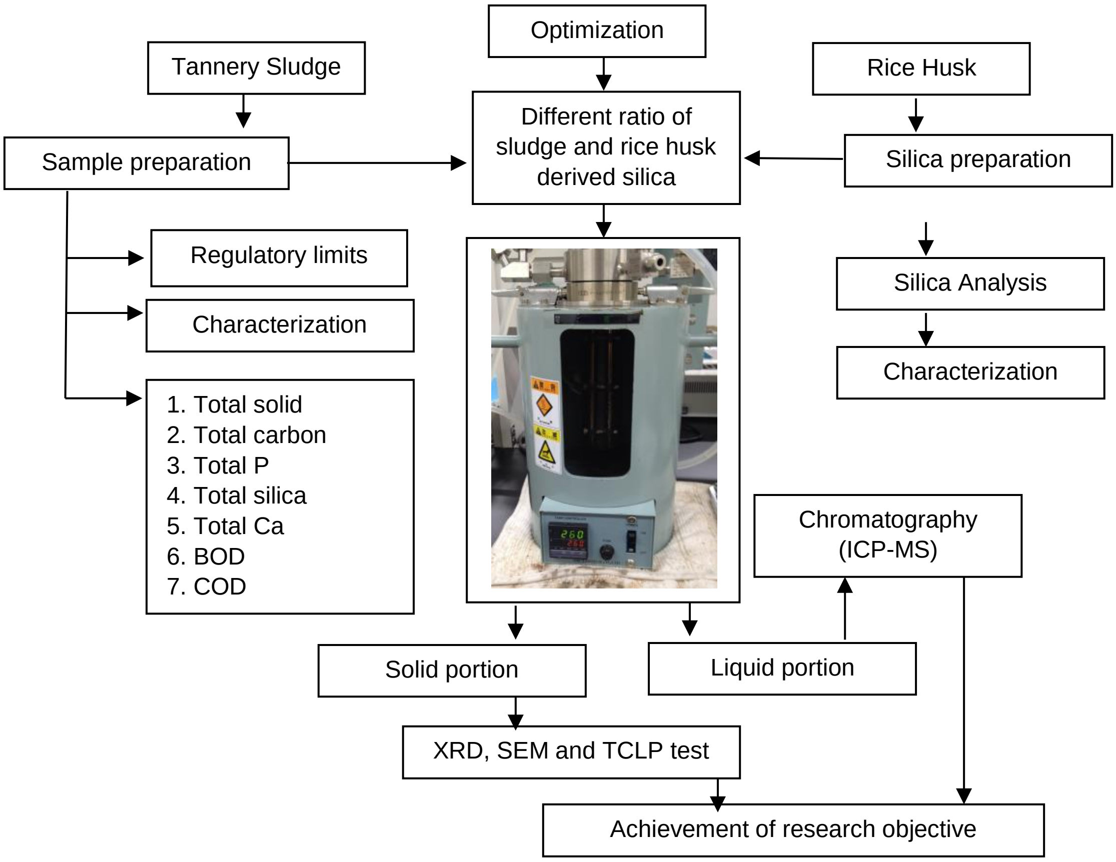

Figure 1: Flow chart of the study.

2.3 Analysis

Heavy metal concentration in tannery sludge and hydrochar were determined by acid digestion. 1 g of dry solid was mineralized in an oven for 4 h at 550 °C. Then, the sample was added with 25 mL of 3:1 mixture of nitric acid and perchloric acid and was heated gently on hot plate for 4 h. The resultant colourless solution was evaporated to near dryness. After completion of digestion and cooling of the residue, 0.01 N HNO_3 was added to the total volume of 25 mL (Ramteke and Moghe, 1988).

X-ray diffraction analysis was carried out to identify the crystalline solid phases using Multipurpose X-ray diffractometre D8 ADVANCED /TSM (BrukerAXS)

HMs were analysed by leaching test following the procedure of the Toxicity Characteristic Leaching Procedure (TCLP). The US EPA TCLP procedure involves 1 gm before and after SCW treated solid sample powder in 20 mL of 0.1 M acetic acid in a poly propylene centrifuge tube and shaking for 18 h on a rotary incubator shaker at 32 rpm at the pH 2.88. The mixture was filtered by a 0.45 um nylon filter and the concentration of the HMs in the leachate (filtrate) was determined using ICP-MS (Perkin Elmer Optical Emission Spectophotometer, Optima 7300DV) (Devi and Saroha, 2014).

3. Results and Discussions

Changes in characteristics of tannery sludge after SCW treatments are summarized in Table 2. In Table 2, SRC, SR200/30, SR280/30 and SR280/60 represent no treatment, treatment at 200 °C for 30 min, treatment at 280 °C for 30 min and treatment at 280°C for 1 h, respectively.

Table 2: Physical and chemical characteristics of sludge before and after SCW process.

Items	SRC	SR200/30	SR280/30	SR280/60
Decomposition %	0	12.34	18.54	36.21
Moisture %	86.78	72.23	62.40	51.90
Total P (mg/L in LS)	ND	17.51	19.17	24.40

It can be seen in Table 2 that the decomposition % of tannery sludge increased with temperature (Shi et al., 2013a). Increase in total phosphorus in leachate was observed as treatment temperature increased. The pH of the aqueous phase ranged from acidic to alkaline. The colour of the aqueous phase and solid residue was changed grey to black with the increase in temperature (Shi et al., 2013a, Hu et al., 2010). It was shown that stabilization of tannery sludge as well as large reduction in volume were achieved by SCW treatment.

3.1 Heavy metals distribution analysis

Partitioning of HMs in hydrochar and liquid are shown in Figures 2, 3 and 4. Figure 2 shows that residual Cr and Fe have increased by 8.5 % and 29 %, respectively, compared to the untreated sample at the temperature of 200 ºC and 30 min of reaction time. Even though it was observed that both residual Cr and Fe decreased at the temperature of 280 ºC and 30 min of reaction time, the residual ratios slightly increased as the reaction retention time was extended to 60 min. The behaviours of Cu were much different. As shown in Figure 3, the residual % of Cu increased constantly as the temperature increased. It was also observed that, like Cr and Fe, the reaction time has significant effects on residual Cu in the solid residue, whereas Pb showed the maximum residual % at 200 ºC and 30 min.

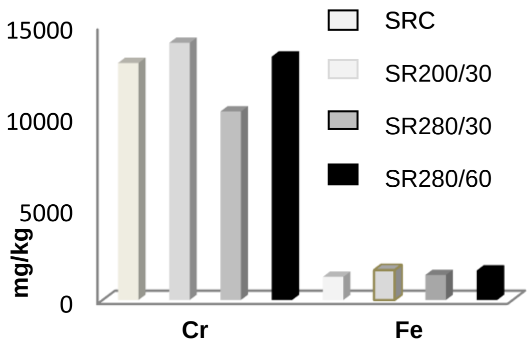

Figure 2: Total contents of Cr and Fe in solid phase before and after SCW treatment

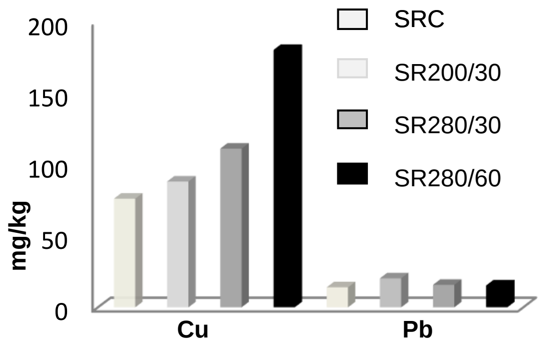

Figure 3: Total contents of Cu and Pb in solid phase before and after SCW

As shown in Figure 4, HMs dissolved from sludge into liquid phase during the SCW treatment were the highest in the SR200/30 solid residue. At higher temperature, 280 ºC, the HMs concentrations in liquid phase decreased substantially, Figure 4. Considering the high concentrations of residual HMs in solid fraction, Figure 3 and the low concentrations of HMs in liquid phase Figure 4, it is implied that HMs were immobilized in the solid phase as a result of SCW treatment.

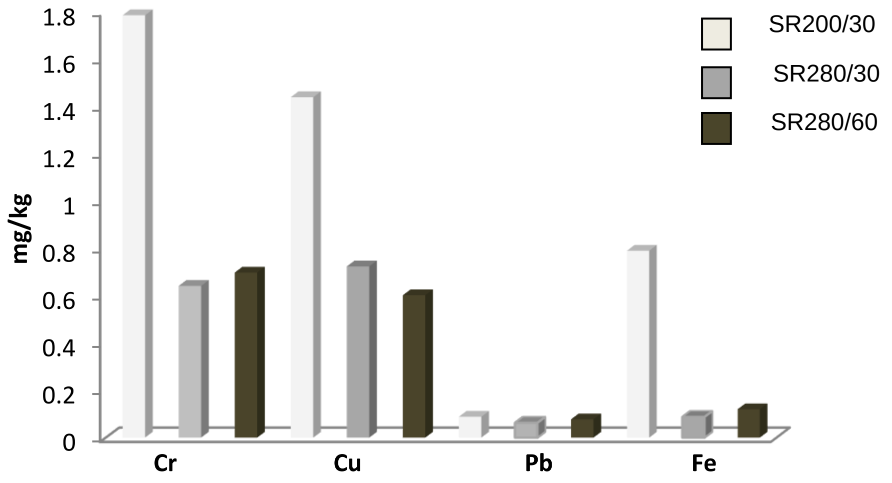

Figure 4: The total content of Cr, Cu, Fe and Pb in liquid phase after SCW treatment

The XRD analysis of subcritical residue sample of 280 ºC/ 30 min (Figure 5.) has shown that there is formation of CaO.6 SiO_2 5 H_2O, which is very much closer to formation of tobermorite, after the SCW treatment. It also implies that a product of SCW treatment effectively immobilized HMs in the solid residue.

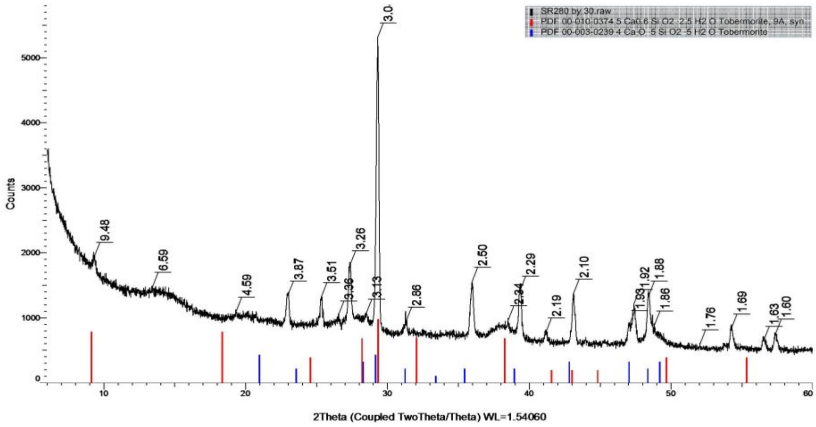

Figure 5: XRD pattern of SR280/30 solid residue

3.2 Leaching studies

Leaching is the process by which a liquid dissolves and remove the soluble component of a material (Estokova et al., 2015). Leach abilities of HMs in solid residues after SCW were determined and shown in Figure 6. It was observed that both of the increasing temperature and reaction time have the positive effects on reducing leaching potential (Devi and Saroha, 2014; Shi et al., 2013a).

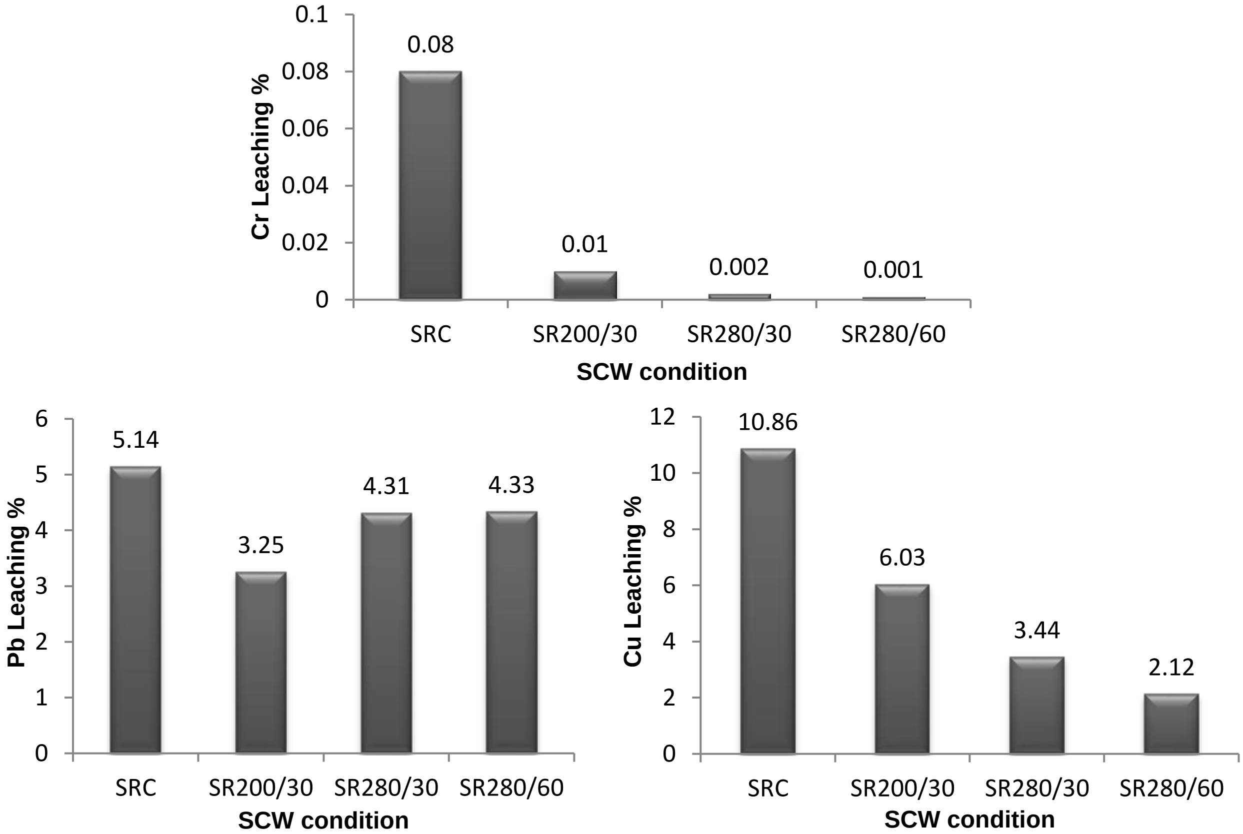

Figure 6: Reduction in HMs concentrations by SCW treatment

The HMs present in tannery sludge are a major obstacle for utilization of the sludge and hydrochar. The leaching characteristics of HMs in the sludge and hydrochar were evaluated by performing TCLP test. The results are summarized in Table 3. As can be seen in Table 3, the leachability of chromium was substantially reduced by SCW treatment with addition of rice husk silica. The concentrations of chromium in the leachate of SCW treated sludge were much below the limit set by US EPA. The effects on lead are not remarkable, but the initial concentration was already very low.

Table 3. Concentration of different heavy metals (mg/L) in leacheate (TCLP)

Sl	HM	SRC	SR 200/30	SR 280/30	SR 280/60	Limit*
1	Cr	11.24	0.198	0.116	0.1	5.0
2	Cu	4.42	2.6	2.54	2.0	Not listed
3	Pb	0.72	0.66	0.66	0.68	5.0
4	Fe	0.04	0	0	0	Not listed

* US EPA limit

4. Conclusions

The experimental results suggested that SCW treatment is a promising tannery sludge treatment method for immobilization of HMs, especially chromium, which is contained in tannery sludge at very high concentration. The data obtained by the study imply that tested HMs can be transformed in to more stable forms as captured by tobermorite or similar mineral in hydrochar. Further research work should be focused on enhancing the immobilization of HMs by more efficient formation of tobermorite with the optimized silica to calcium ratio, and lowering the required temperature for practical applications.

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