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Removal of Heavy Metals from Textile Wastewater using Zeolite

Normala Halimoon and Rachel Goh Soo Yin

Department of Environmental Sciences, Faculty of Environmental Studies, Universiti Putra Malaysia, 43400 Serdang, Selangor, Malaysia.

Abstract

Heavy metals such as lead (Pb), chromium (Cr), cadmium (Cd) and copper (Cu) are widely used for production of colour pigments of textile dyes. Textile dyes pollutants are being released to the environment at various stages of operation therefore it is necessary that the pollutants are treated before discharge using zeolite with and without alum. A study was carried out to compare the effectiveness of treatment using zeolite with and without alum for the removal of heavy metals (Pb, Cu, Cd, Cr) in textile effluent. The concentrations of these heavy metals in the textile wastewater samples were reduced to more than 50 percent after treating with zeolite. The sequence in increasing order of removal efficiency of these heavy metals using zeolite was Cd < Pb < Cr < Cu. When the textile wastewater sample was treated using zeolite and 10 mg/L of alum, 80% of the heavy metals (Cd and Cu) were removed. The most effective treatment prior to removal of heavy metals from textile wastewater sample is by using zeolite with the addition of 10 mg/L of alum as flocculants.

Keywords: textile wastewater; zeolite; heavy metals; alum

1. Introduction

As the world population increases, demands of clothing and apparel increase with the improving sense of fashion and lifestyle thus textiles are manufactured to meet the growing demands. In some countries such as India and Sri Lanka; textile production becomes their source of income that contributes to their Gross Domestic Product (GDP). However, this has brought both consequences to such countries either in a positive way which is an improvement of economy or in a negative way attributed to environmental pollution.

The textile industries have been dubbed as worst offenders of pollution contributors as they used more than 2000 types of chemicals and over 7000 types of dyes. They also produce heat from effluents released, increased pH, as well as water saturation with dyes, de-foamers, bleaches, detergents, optical brighteners and equalizers during operations. Due to this, pollutants from the textile production sector are being released to the environment at various stages of operation. In addition, effluent or wastewater from textile production discharged to the water body without proper treatment also seep through the aquifer and pollute the underground water in many ways. Besides colour visibility which brings displeasing aesthetics, heavy metal constituents in the effluent also resulted in negative ecological impacts to the water-body, environment as well as deterioration of human health.

Heavy metals particularly, lead (Pb), chromium (Cr), cadmium (Cd) and copper (Cu) are widely used for the production of colour pigments of textile dyes. Such heavy metals can exist in naturally in the structures of textile or they can penetrate into fibres of textile during production, dyeing process or through protective agents used during storage. These heavy metals which has transferred to the environment are highly toxic and can bioaccumulate in the human body aquatic life, natural water-bodies and also possibly trapped in the soil. (Mathur *et al.*, 2005).

Wastewater treatment is essential to allow human and industrial effluents to be disposed without bringing danger to human health as well as to prevent unacceptable damage to the natural environment (Li *et al.*, 2004). Conventional wastewater treatment consists of combination of several processes namely, physical, chemical and biological, to remove solids, organic matter and, sometimes nutrients from the wastewater. Improvements of determining the effects of wastewater discharges have led to the adoption of stringent environmental laws, which define the degree of treatment necessary to protect water quality. In Malaysia, under the Environmental Quality Act (1979), there are regulations on discharge of wastes into Malaysian waters. The regulations focus on prohibition of discharging environmentally hazardous substances, pollutants or wastes into Malaysian waters in contravention to acceptable conditions as specified by the Act.

Zeolite are hydrated aluminosilicate minerals and have a micro porous structure. Zeolite are used in various applications such as adsorption, catalysis, ion-exchange, petrochemical cracking, and removal of gas and solvents and also used in many industrial activities due to their unique porous structure. Zeolite converts solid and liquid hazardous wastes into environmentally acceptable products (Shevade *et al*., 2004).

Zeolite is considered as effective adsorbent because it can adsorb heavy metals from the wastewater sample (Erdem *et al.,* 2004). The general chemical formula of zeolite is $(M^{+}_{2}, M^{2+})O.Al_2O_3.gSiO_2.zH_2O$. M^+ is usually sodium ion, Na or potassium ion, K and M^{2+} is magnesium ion, Mg, calsium ion, Ca or iron ion, Fe, also more rarely lithium, Li, strontium, Sr and barium, Ba ions may substitute for M^+ or M^{2+}. Fe^{3+} is assumed to substitute into the tetrahedral framework position. The M^+ cations are exchangeable as they are relatively innocuous; therefore, the heavy metals cations can substitute into the structure of zeolite in this case, lead, copper, cadmium and chromium.

On the other hand, alum is commonly known as aluminium sulfate, acts as a flocculating agent whereby wastewater in this case, is clarified by catching the very fine suspended particles in a gel like precipitate of aluminum hydroxide (Cical *et al.*, 2005). Alum is used in a wide range of industries such as purification of drinking water, wastewater treatment plant and paper manufacturing. The use of conventional wastewater treatment processes has faced increasing challenges due to stringent requirements for the release of treated wastewater to the environment as the industrial sectors grow rapidly in line with the improvised economy. At present, concerns are raised on the scope of environmental issues regarding the use of hazardous chemicals, as such, containing heavy metals in many processes and operations of textile manufacturing. The objectives of this study is to identify the contents of heavy metals namely lead, copper, cadmium and chromium in textile wastewater, and to remove the heavy metals from textile wastewater using zeolites with and without alum. Therefore, studies have been carried out for evaluation of using cheaper yet effective methods in treating the wastewater containing heavy metals in textile manufacturing.

2. Materials and Methods

The wastewater samples of this study were obtained from the manufacturing of sewing thread factory, which is located at 2°15’20.66”N of latitude and 102°8’40.10”E of longitude of Malacca is about one kilometre from the South Malacca sea. The fresh wastewater samples were collected from the influent collection of the wastewater treatment plant of the factory after off-peak hours of production using eight one-litre plastic bottles.

The pH and temperature of the wastewater samples were recorded using pH meter of HACH Model. Before collecting the wastewater sample, the plastic bottles were washed thoroughly using distilled water. The samples were then placed in an ice-storage box containing ice packs to preserve and maintain their composition from degradation by microbes.

For the preservation, collected wastewaters samples were added with 5 ml nitric acid of 2.0 M per 1 litre of samples. The samples were refrigerated at approximately 4°C. Through addition of nitric acid and refrigeration, the heavy metal precipitation will be prevented and to allow the samples to last longer (USEPA, 1983).

Standard solutions of Pb (0 to 20 ppm), Cu (0 to 2.0 ppm), Cd (0 to 0.4 ppm) and Cr (0 to 2 ppm) were prepared from their stock solutions (1000 ppm). These standard solutions were used in the Atomic Absorption Spectrometry (AAS) analysis. Before the initial concentration of heavy metals in wastewater samples was done, the samples were filtered using Whatman filter paper with diameter size of 47 mm mechanically. The filtered sample was poured into plastic test-tubes for analysis using AAS.

One gram of zeolite powder was added into 1 liter of wastewater sample in 1.5 L shake flask. Next, the samples were shaken using orbital shaker for an hour at 200 rpm and incubated in the refrigerator for one day after treatment with zeolite. After the incubation period, alum was added into the zeolite-treated flasks of samples. Another flask of sample remained as a control with the only treatment of zeolite. Jar Test was carried out for the four bottles of samples. There were four dosages of alum added into the samples, namely, 10 mg/L, 20 mg/L, 30 mg/L and 40 mg/L respectively. The Jar Test was carried out at the speed of 100 rpm for two minutes to allow rapid mixing of the samples. Next, the speed was slowed down to 20 rpm and mixed for 20 minutes. The flocs formed during the Jar Test were allowed to settle for 30 minutes. This Jar Test method was adapted from Golob *et al.* (2004). The experiments were replicated three times.

The concentrations of the four heavy metals (Pb, Cd, Cr and Cu) in samples treated with only zeolite and another with zeolite and alum were analysed using AAS. Analysis of Variance (ANOVA) was used to analyse data obtained in AAS analysis.

3. Results and Discussion

3.1. Initial heavy metals concentrations in textile wastewater

Fig. 1 shows the initial heavy metals concentrations of textile wastewater samples. The concentrations for lead, copper, cadmium and chromium are 0.64, 0.19, 0.41 and 0.06 mg/L, respectively.

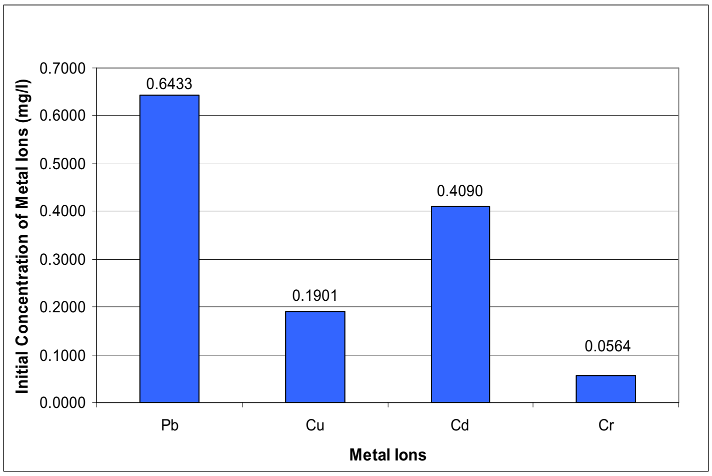

Figure 1. Initial concentration of metals ion (mg/L) in wastewater samples (*P≤0.05*).

The initial concentration of Pb in wastewater is highest because the influent from production process discharged contained high levels of Pb and low levels of Cr on the sampling day. Heavy metals present as impurities in a dye or chelated as part of the dye molecule. In metal complex dyes, the metal is coordinated or forms a chemical bond with the organic dye molecule. Thus, it is an indispensable constituent of the dye and governs the fastness absorb the colours. Schrott (1992) studied the general contents of heavy metals in the dyes that have been introduced by the condition of synthesis are as follows; 100 ppm of lead, 20 ppm of cadmium, 100 ppm chromium, 250 ppm of copper, 4 ppm of mercury as well as 200 ppm nickel. In this study, the levels of heavy metals concentration have contributed during production into the textile wastewater. Besides, the variations of the heavy metals concentration in the wastewater sample were due to the different types of dyestuff used in different production of threads when the samples were taken.

The waste liquor discharged during the thread processing operations are mainly; contains of wasted liquor from dispersed dyestuff, reduction clearing and soaping treatment during polyester dyeing wasted liquor from bleaching process of polyester, where optical brighteners is used, as well as liquor of the levelling or migrating treatment of multicoloured disperse or polyester dyeing wasted liquor from bleaching process of polyester, where optical brighteners is used, liquor of the levelling or migrating treatment of multicoloured disperse or polyester dye cheeses contributed to the wastewater discharge wasted liquor come from lubrication of dyed cheeses in the dyeing machine, scouring, bleaching, dyeing, rinsing and oxidation treatments of vat dyes or cotton dyeing wasted liquor from soaping treatment of reactive dyeing and acid dyes for nylon thread dyeing. All listed wasted liquors have contributed to the heavy metals constituents (Pb, Cu, Cd, Cr) in this study.

3.2. Lead

Fig. 2 shows the Pb concentrations with different types of treatment with an initial concentration of 0.64 mg/L. The reduction of final concentrations of lead was observed after treatment with zeolite alone and also treatment with zeolite added with different dosages of alum. The *P*-value is 0.002 which is less than $\alpha = 0.05$, therefore this result is statistically highest at this level (*P≤0.05*).

The percentages of lead removal from textile wastewater samples upon additional zeolite with different concentrations of alum were as follows; 10 mg/L, 61.03% (0.39 mg/L) > 30 mg/L, 60.68% (0.39 mg/L) > 40 mg/L, 60.63% (0.39 mg/L) > 20 mg/L, 56.09% (0.36 mg/L), respectively. Treatment of the wastewater sample using zeolite alone removed 55.34% (0.36 mg/L) of lead from the sample.

Based on the experiment done, lowest percentage of wastewater treatment was using zeolite whereas the highest percentage was by adding zeolite and 10 mg/L of alum. Therefore, the most efficient removal of lead from textile wastewater is the treatment using zeolite with 10 mg/L of alum. According to Ogunfowokan *et al.* (2007), the best removal of heavy metals especially Pb was by using 10 mg/L of alum. With zeolite alone, the lead ions or particles are probably adsorbed into the pores of the zeolite not as effective as compare to the former, as lead ions normally exist in the state of +2 which is more stable than at the state of +4 (Lim, 2004), thus, zeolite has less capability to adsorb the stable ions.

The removal of heavy metals is very efficient at the dosage of 10 mg/L of alum, and of pH of slightly

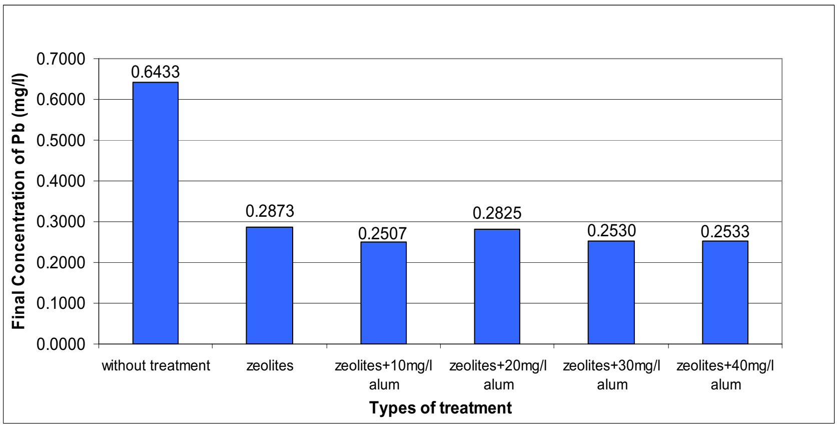

Figure 2. Final Concentration of Pb with Different Types of Treatment (*P≤0.05*)

alkaline, near pH 8. In a research by Fatoki and Ogunfowokan (2002), it was stated that when the dosage of alum increases, the percentage of removal of heavy metals increases. The dosages of alum applied by these two researchers are 0 mg/L, 3 mg/L, 5 mg/L, 8 mg/L and 10 mg/L. The optimum dosage for an effective removal of heavy metals is 10 mg/L with the pH of 7.8. However, in this study, when the alum dosages are increased from 10 mg/L to 20 mg/L, 30 mg/L, and 40 mg/L, the percentage of removal of heavy metals decreases. Therefore, it can be observed that the optimum dosage for the removal of heavy metals is at dosage of 10 mg/L of alum with the pH of near 8.

3.3. Copper

Fig. 3 shows the Cu concentration with different types of treatment with an initial concentration of 0.19 mg/L. The result was showed the final concentrations of Cu after treatments with zeolite and the additional of different dosages of alum. The percentages of removal of Cu from textile wastewater sample after additional of zeolite with different concentrations of alum as follows; 10 mg/L, 88.52% (0.1683 mg/L) > 30 mg/L, 88.43% (0.1681 mg/L) > 20 mg/L, 86.94% (0.1653 mg/L) > 40 mg/L, 82.29% (0.1534 mg/L) > with zeolite alone, 64.74% (0.1231 mg/L), respectively.

In comparison, the highest removal of copper from wastewater sample with usage of using zeolite and 10 mg/L of alum (*P≤0.05*) compared to the removal of copper from wastewater sample by using zeolite alone, which is the lowest among the others. Cu^{2+} exist in the solutions as complex ions and water is the weaker ligand in this complex, thus, it is displaced by aluminium ions, Al^{3+} of alum easily and the heavy metal ions were aggregated into flocs (Lim, 2004).

3.4. Cadmium

Fig. 4 shows an the initial concentration of cadmium, Cd in the textile wastewater sample is 0.41 mg/L. After the treatments with zeolite and zeolite by different dosages of alum, the final concentrations of Cd were significantly (*P≤0.05*) decrease as compare to the initial concentration. Cd was the most highest heavy metals being removed by zeolite with 10 mg/L of alum

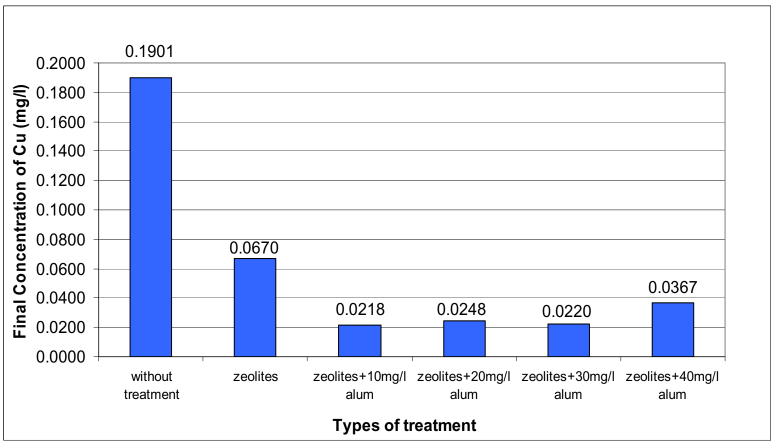

Figure 3. Final Concentration of Cu with Different Types of Treatment (*P≤0.05*).

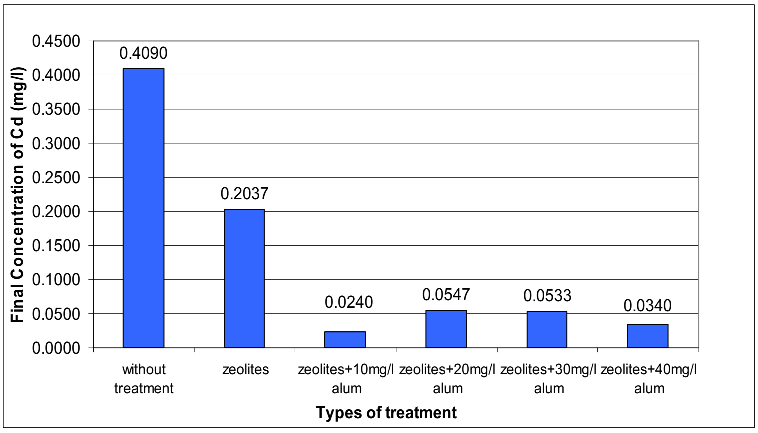

Figure 4. Concentration of Cd with Different Types of Treatment (*P≤0.05*)

(94.13% (0.39 mg/L)), followed by 40 mg/L of alum (91.69% (0.38 mg/L)), 20 mg/L of alum (86.63% (0.36 mg/L)) and 30 mg/L of alum (86.96% (0.35 mg/L)) respectively. The lowest percentage of removal of cadmium from the wastewater sample is 50.20% (0.21 mg/L) which is by using zeolite only.

Hence, the highest efficiency of cadmium removal from textile wastewater sample is by the treatment of zeolite with 10 mg/L of alum because cadmium has very high affinity to bind to the surface with small amount of alum and form flocs (Singh *et al.,* 2000). Also, since alum can work in the pH range of 5 to 8, it works best to form cadmium salt precipitate and aggregates them into flocs easily then compare to zeolite alone. The coagulation process, dealing with destabilisation of colloidal particles depends of pH and aluminium (III) ions concentration (Pernitsky and Edzwald, 2006). The pH in this case has not much influence as the wastewater sample, after addition of zeolites and alum, is within the range of effective alum performance.

3.5. Chromium

Fig. 5 shows the concentration of Cr in the treated textile wastewater after treated with different type of treatments. The initial concentration of Cr in the wastewater is 0.06 mg/L was significantly (*P≤0.05*) decreases after treatment with zeolite alone and with additional of different dosages of alum.

The percentages of removal of Cr from textile wastewater sample after treatment as following order; with zeolite alone 56.25% (0.032 mg/L) > additional with different concentrations of alum, 10 mg/L (54.49% (0.031 mg/L)) > 20 mg/L (49.17% (0.028 mg/L)) > 30 mg/L (32.03% (0.018 mg/L) > 40 mg/L (27.31% (0.015 mg/L)), respectively.

Among the treatments, the removal of Cr with zeolite alone showed the highest percentage of removal, which is a difference from the removal of Pb, Cu and Cd. Cr ions mostly exist in +3 states and +6, of high densities; therefore it is much harder to remove by alum, which the aluminium ion is of +3 states (Lim, 2004).

The removal efficiency of heavy metals using zeolite in increasing order is as Cd < Pb < Cr < Cu (Fig. 6). The rate of adsorption of metals by zeolite decreases when the concentration of the metals concentration increases in aqueous solution. From the result obtained, the initial concentrations of the heavy

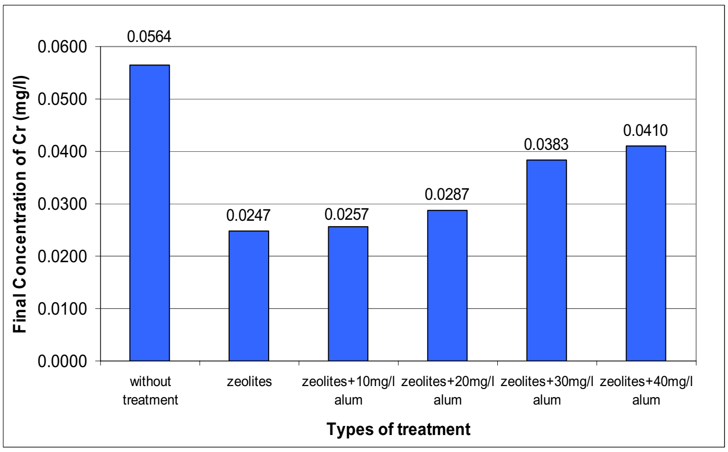

Figure 5. Concentration of Cr with Different Types of Treatment (*P≤0.05*)

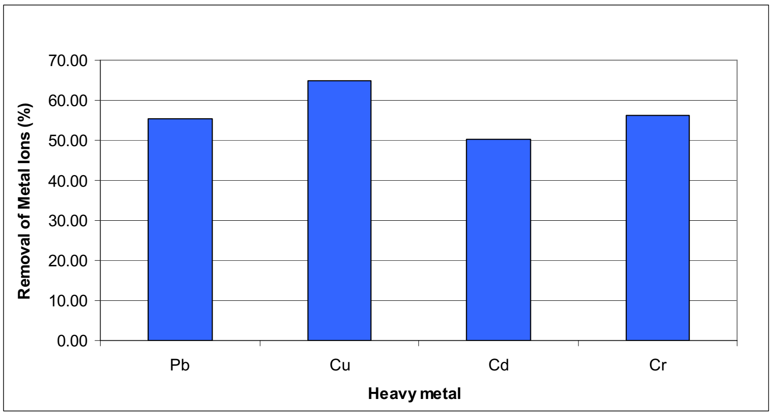

Figure 6. Percentages of Heavy Metals Removal by Zeolite

metals are high, particularly for Pb, whereby the ability to adsorb Pb cations, thus, it involved less energetically less favourable sites of zeolite in the uptake of heavy metals. The diffusion rate is high through the zeolite pores but was hindered when the ions passed through smaller channels of the zeolite. The maximal exchange of ions attained for copper (II) ions was 66.10% according to Erdem *et al.* (2004) in comparison to this study, the percentage of copper cations removed is 64.74%.

The adsorption occurrence depends on the charge densities of the cations. The cations of heavy metals involved in this study are Pb^{2+}, Cu^{2+}, Cd^{3+} and Cr^{3+}. All the heavy metals cations are hydrated as hexa-aqua complex ions in the solution, passed through zeolite in this hydrated form (Erdem *et al.*, 2004). The result obtained showed that Cd has the least percentage of removal by zeolite is proved by the size of Cd cations. Although the charge densities for cadmium is higher than Cu and Cr cations, it appears that the diameter of Cd hydrated ions is bigger, therefore, had minimum adsorption.

There are three stages of floc formation during coagulation process namely lag, growth and steady state. Due to action of coagulant, the collision radii of particles increase to form small sizes of primary flocs in lag region. Meanwhile in growth region, the primary flocs formed increase in size and become larger as the flocs joined together. The structures of the larger flocs changed continually as the internal bonds break under shear and reform at more favourable points where the attractive force or repulsive force is lower. In steady state, when the balance between the aggregation rate and breakage rate is reached for a given shear, the floc formation is completed and the size reaches a steady state (Wang *et al.,* 2009). Therefore, based on floc aggregation process, the rate and amount of heavy metals in this case, maybe influenced through this coagulation mechanism. In which, larger positive charge of the metal complexes tend form unstable flocs and aggregate with other flocs and thus increase in size due to charge neutralisation and the heavy metals are being removed at a higher rate.

On the other hand, Al ions concentration is very important as it focuses more to the charge densities when it reacts to destabilise the colloidal particles. Pb^{2+} are relatively stable, whereby the high charge density Al ions has not much influence in the displacement of the lead (II) ions. Therefore, removal of Pb^{2+} exhibits the lowest percentage under dosage of 10 mg/L of alum. The removal of Cu^{2+} and Cd^{2+} are high as these transition metal complexes are able to form ligands with the Al^{3+} species. Thus, these heavy metal complexes are able to adsorb into the aluminium hydroxide formed during precipitation in coagulation and flocculation process in the form of flocs (Pernitsky and Edzwald, 2006).

4. **Conclusions**

In treatment with zeolite, the removal of heavy metals from textile wastewater sample is high whereby the percentage of removal is more than 50 percent of the initial concentration. The removal of heavy metals from textile wastewater is effective using zeolite. The percentage of heavy metals removal in textile wastewater by zeolite and with an additional with different concentration of alum is different. Cu was the most heavy metal being removed by zeolite (64.74%), followed by Cr (56.26%), Pb (55.34%) whereas Cd being the lowest at 50.20%. On the other hand, when zeolite was added with 10 mg/L of alum, the removal of heavy metals from textile wastewater sample was higher than treatment with zeolite alone. The heavy metals can be removed from the textile wastewater samples up to 80 percent for heavy metals such as Cd and Cu. The sequence of removal efficiency of heavy metals from textile wastewater sample by using zeolite with an addition of 10 mg/L of alum in increasing order is Cd < Cu < Pb < Cr. Therefore, it can be observed that removing heavy metals from textile wastewater is effective using zeolite, however, the most effective way of heavy metals removal from textile wastewater is by using zeolite with an addition of 10 mg/L alum.

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Correspondence to
Dr. Normala Halimoon,
Department of Environmental Sciences,
Faculty of Environmental Studies,
43400 UPMSerdang, Selangor,
Malaysia.
Tel: (603)8946 6743,
Fax: (603)8943 8109,
E-mail: hmala@env.upm.edu.my