Simultaneous Removal of Heavy Metals from Surface Water by Physico-chemical Treatment Process

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Simultaneous removal of heavy metals, arsenic, lead, and chromium from contaminated surface water by coagulation and flocculation using ferric sulfate, alum and lime was studied. The method was effective provided arsenite (As III) was oxidized to arsenate (As-V); hexavalent chromium (Cr-VI) was reduced to trivalent chromium (Cr-III) and the contamination level of the heavy metals were below 200 \( \mu g \cdot L^{-1} \). When they were around 2000 \( \mu g \cdot L^{-1} \), further treatment with activated carbon was necessary to bring down the metal contamination level below 50 \( \mu g \cdot L^{-1} \), which is the World Health Organization (WHO) limit for recycle and reuse of water. pH significantly influenced the removal efficiency. Details of treatment processes are discussed.

Keywords: Surface water, heavy metal removal, physico-chemical treatment, activated carbon.

Introduction

Incidents of heavy metal contamination of river water due to industrial discharge have caused great concern in several developed and developing countries.\(^1\)\(^-\)\(^2\) Heavy metals present in water causes extensive damage to human and to the environment. In developing countries, with the rise in population, economic growth and improvement in living standard, the need for more and cleaner water is becoming increasingly urgent. Hence, there is a need to develop technologies for the removal of heavy metal contaminants from wastewater.

Treatment technologies for removal of various heavy metals from contaminated water have been investigated by different authors and are well documented in literature.\(^3\)\(^-\)\(^5\) Conventional treatment of surface water by coagulation and flocculation is a simple and effective process, which not only remove colloidal and suspended particulate matters but also remove heavy metals. Removal of heavy metals by conventional treatment steps is attractive as they are widely used in municipal water treatment plants. Its capital expense is low as existing facilities can be used. The significant advantages of using conventional process are (i) design and operation of conventional treatment plants are well established, (ii) required chemicals are cheap and easily available, and (iii) multiple treatment objectives can be easily achieved.

Traditionally, coagulation and flocculation process is applied to source water in municipal water treatment plants to remove non-settleable and slowly settleable solids. Colloidal particles present in water and wastewater carry electronegative charge but the colloidal dispersion has no electrical charge. This is because the primary charge of colloidal particles is counterbalanced by the charge of the aqueous phase. This results in electrical double layer at each interface between the solid and water. Repulsive electrical forces and attractive van der Waals forces interact between the particles in a solution, which produces a potential barrier for removal of colloidal particles and thus the dispersion becomes stable. By coagulation process, the repulsive barrier is removed. This helps to promote aggregation of smaller particles into larger particles and thus they are removed from the solution.\(^6\)\(^-\)\(^7\) At low dosages of coagulants, charge neutralization by hydrolyzed metal coagulant species takes place, which contributes to the formation of flocs through aggregation of destabilized colloidal particles. At high dosage of coagulants, the constituent metal of the coagulant precipitates as an amorphous metal hydroxide floc in which the colloidal particles become entrapped. Dissolved heavy metals like lead, arsenic and chromium can also be removed during coagulation through adsorption on the surface of the colloidal particles or entrapment inside the growing particles. The heavy metals can also be removed by incorporation into the bulk phase rather than on the surface of the precipitate only.\(^8\)\(^-\)\(^9\)
Although physico-chemical methods employed for the treatment of heavy metals is well established, details of the removal technology are scanty. This is especially true, when a number of heavy metals are present together in the surface water. There are very few reports on the simultaneous removal of heavy metals from natural water. Hence, the present investigation is aimed at finding out the effectiveness of the conventional physico-chemical processes for removal of lead, arsenic and chromium when all of them are present in the surface water at a relatively high concentration.

**Materials and methods**

All chemicals used were analytical grade. They were used without further purification with the exception of granular activated carbon. Activated carbon granules of 1-mm diameter used in adsorption column were obtained from a local supplier. They were washed thoroughly with de-ionized water and dried before use in an oven at 105 °C for 24 h.

Alum [K₂SO₄Al₂(SO₄)₃ · 24 H₂O], ferric sulfate [Fe₂(SO₄)₃ · 9 H₂O], lime (CaO) were used as the treatment agents. Calcium hypochlorite [Ca(OCl)₂ · 2 H₂O] and ferrous sulfate (FeSO₄ · 7 H₂O) were used for oxidation of (As-III) to (As-V) and for reduction of (Cr-VI) to (Cr-III) respectively. Primary standard stock solutions of arsenite (As-III), trivalent chromium (Cr-III), chromate (Cr-VI) and divalent lead (Pb-II) were made from AS₂O₃, Na₂HAsO₄ · 7 H₂O, CrCl₃ · 6 H₂O, K₂Cr₂O₇ and Pb(NO₃)₂ respectively. Secondary standard solutions were freshly made from primary standard stock solutions of 1 g l⁻¹. Hydrochloric acid and sodium hydroxide were used for pH adjustment. All solutions were made with ultra high quality water. Adsorption experiments were conducted in a 90 cm glass column with granular activated carbon bed. The flow rate of the effluent through the column was 50 l m⁻² min⁻¹.

Samples were analyzed with Baird Inductively Coupled Plasma Atomic Emission Spectrometer (ICPAES). The detection limit by this instrument for arsenic, lead and chromium were 3.0 µg l⁻¹, 2.0 µg l⁻¹, and 0.3 µg l⁻¹, respectively. Before analysis, all samples were filtered through 0.45 µm Millipore Filter prior to feeding the column. The concentration of contaminating heavy metals, left in solution after treatment with activated carbon column, sufficient amount of supernatant solution was collected and filtered through 0.45 µm Millipore Filter prior to feeding the column. The concentration of contaminating heavy metals, left in solution after treatment with activated carbon column, was determined by analyzing the effluent solution from the adsorption column using ICPAES.

**Results and discussion**

**Ferric Sulfate Treatment**

Raw water collected in batches from the Klang River, Kuala Lumpur, was kept in refrigerated condition at 4 ± 1 °C. For each experimental run, pH, concentration of lead, arsenic and chromium were noted for raw river water. The raw water contained Arsenic 7.0 µg l⁻¹, lead 3.0 µg l⁻¹, and chromium 3.0 µg l⁻¹. The pH of the river water was 7.4. The river water was spiked with contaminating metals arsenic (As-III), lead (Pb-II) and chromium (Cr-VI) to get the desired concentration as per requirement of the experimental runs. In the Jar Test procedure, to avoid any metal contamination, Teflon coated magnetic flyers and magnetic mixing devices were used. The treatment steps consisted of adding 10 µg l⁻¹ calcium hypochlorite for oxidation of arsenite (As-III) to arsenate (As-V) with thorough mixing for 15 min. This was followed by the addition of sufficient quantity of ferrous sulfate, approximately 12 times that of the concentration of Cr-VI and these were mixed thoroughly for half an hour to convert all chromate (Cr-VI) to trivalent chromium (Cr-III). Then coagulating agent was added by employing rapid mixing at 100 rpm for 1 min followed by—slow mixing at 50 rpm for 20 min. Following slow mixing, magnetic stirring device was put off and the solution was allowed to settle for a period of 45 min. pH of the treated solution was measured and samples were withdrawn at 4 cm below the top surface of the supernatant for analysis. Care was taken to avoid any disturbance to the settled solids while withdrawing samples. For conducting adsorption experiment in granular activated carbon column, sufficient amount of supernatant solution was collected and filtered through 0.45 µm Millipore Filter prior to feeding the column. The concentration of contaminating heavy metals, left in solution after treatment with activated carbon granules, was determined by analyzing the effluent solution from the adsorption column using ICPAES.
efficiency was observed for, both, arsenic and lead whereas for chromium it was around 8% (Experiments 3 and 4).

Experiments were also carried out in the absence of calcium hypochlorite and ferrous sulfate to find out the efficacy of ferric sulfate for the removal of arsenic, lead and chromium (Experiments 5 and 6). From the results, it is evident that it is difficult to remove trivalent arsenic and hexavalent chromium from contaminated river water with ferric sulfate as a coagulant. Only after converting arsenite (As-III) to arsenate (As-V) and reducing hexavalent chromium (Cr-VI) to trivalent chromium (Cr-III) could they be removed from the wastewater. However, ferric sulfate was effective in removing both divalent and tetravalent lead.

Further experiments were carried out with river water containing different concentrations of contaminants in the range 200 μg l⁻¹ to 2000 μg l⁻¹ with ferric sulfate dose maintained at 40 mg l⁻¹. The results are shown in Figure 1. From the figure it can be observed that the metal ion concentration in the treated water increased with increasing concentration in the raw water. It can also be seen that a dose of 40 mg/l of ferric sulfate along with calcium hypochlorite and ferrous sulphate can treat water containing 560 μg l⁻¹ of arsenic, 320 μg l⁻¹ of lead and 400 μg l⁻¹ of chromium. This dose level brings down the individual heavy metal concentration below the admissible level. World Health Organization (WHO) has set an admissible level of 50 μg l⁻¹ for each of the three heavy metals. River water beyond this contamination level will need further treatment.

The effect of various concentrations of heavy metals on percentage removal with ferric sulfate dose at 40 mg l⁻¹ was also determined. The results showed that the removal efficiency remained unaffected despite the wide changes in the concentration of heavy metals from 200 μg l⁻¹ to 2000 μg l⁻¹. The average level of removal of arsenic, lead and chromium were 92%, 85% and 88% respectively (Table 4).

![Figure 1](image)

**Figure 1** - Effect of initial mass concentration of the heavy metals in the river water on their removal by ferric sulfate coagulation (○ - As, □ - Cr, △ - Pb)

### Table 1 – Effect of ferric sulfate on the removal of arsenic, lead and chromium from river water

<table>
<thead>
<tr>
<th>Expt. No.</th>
<th>Metal</th>
<th>Metal mass conc. γ/μg l⁻¹</th>
<th>Calcium hypochlorite γ/mg l⁻¹</th>
<th>Ferrous sulfate γ/mg l⁻¹</th>
<th>Ferric sulfate γ/mg l⁻¹</th>
<th>pH of treated water</th>
<th>Metal mass fraction removal w/%</th>
</tr>
</thead>
</table>
Alum Treatment

Tests similar to ferric sulfate treatment were done using alum as the coagulating agent (Table 2). A 20 mg l⁻¹ dose of alum could remove 80–82 % arsenic, 85 % lead and 83–84 % chromium. When alum dose was increased to 60 mg l⁻¹, removal efficiency increased by about 10 % for arsenic and lead, and by about 5 % for chromium. Test conducted in the absence of calcium hypochlorite and ferrous sulfate again showed that alum is also ineffective in removing arsenic and chromium without converting them to As-V and Cr-III respectively. However, it was effective for removal of lead.

The effect of 40 mg l⁻¹ alum dose on the removal efficiency at various concentrations of the heavy metals is shown in Figure 2. From the figure it is evident that 40 mg l⁻¹ dose of alum along with calcium hypochlorite and ferrous sulfate can be used to treat raw river water having contamination level of arsenic, lead and chromium up to 420 µg l⁻¹, 520 µg l⁻¹ and 340 µg l⁻¹ respectively. River water beyond this contamination level will need further treatment, as the treated water will contain contaminants above the admissible level. The effect of various concentrations of metal ions on the removal efficiency for 40 mg l⁻¹ dose of alum was also studied. Again, the removal efficiency remained unaltered when contamination level of heavy metals was increased from 200 µg l⁻¹ to 2000 µg l⁻¹. The average removal efficiency for arsenic, lead and chromium were 88 %, 90 % and 85 % respectively (Table 4). From these experiments it can be concluded that a dose level of 40 mg l⁻¹ of alum along with calcium hypochlorite and ferrous sulfate is effective in removing major portion of these three heavy metals from river water.

Lime Treatment

Studies were conducted to find out the effectiveness of lime for the removal of the three heavy metals from contaminated river water. The results of the experiment are shown in Table 3. At a lime
dose of 100 mg l$^{-1}$, removal efficiency of arsenic, lead, and chromium were 80%, 75% and 73%, respectively. No substantial change in removal efficiency was observed when concentration of arsenic, lead and chromium were increased to around 2000 μg l$^{-1}$ (Experiment 2). With an increase of lime dose to 400 mg l$^{-1}$, a significant change in the removal pattern of heavy metals was observed. Thus at, both, high and low levels of contamination (Experiments 3 and 4), the removal efficiency of the heavy metals from raw water increased on the average by 20%. It is also seen that lime was not effective in removing As-III without oxidizing it to As-V and also Cr-VI without reducing it to Cr-III. Lime was however effective against both forms of lead (Experiments 5 and 6). Studies were also conducted to find out the efficacy of lime treatment at various levels of contaminant (Figure 3). From the figure it can be noted that a dose of 200 mg l$^{-1}$ of lime along with calcium hypochlorite and ferrous sulfate can treat contaminated river water containing arsenic, lead and chromium in the range of 350 μg l$^{-1}$, 660 μg l$^{-1}$, and 500 μg l$^{-1}$, respectively.

The removal efficiency was also measured at various metal concentrations in raw water and it was found to be unaffected with a change in mass concentration of these metals. An average removal efficiency for arsenic, lead and chromium were 97%, 92% and 90% respectively (Table 4). Again the removal efficiency was unaffected when mass concentration of heavy metals was increased from

<table>
<thead>
<tr>
<th>Expt. No.</th>
<th>Metal</th>
<th>Metal mass conc. γ/μg l$^{-1}$</th>
<th>Calcium hypochlorite γ/mg l$^{-1}$</th>
<th>Ferrous sulfate γ/mg l$^{-1}$</th>
<th>Lime dose γ/mg l$^{-1}$</th>
<th>pH of treated water</th>
<th>Metal mass fraction removal w/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>As (III) Pb (II) Cr (VI)</td>
<td>202 205 208</td>
<td>10 10 10</td>
<td>2.4 2.4 2.4</td>
<td>100 100 100</td>
<td>9.8 9.8 9.8</td>
<td>80 75 73</td>
</tr>
<tr>
<td>2</td>
<td>As (III) Pb (II) Cr (VI)</td>
<td>2025 2035 2040</td>
<td>10 10 10</td>
<td>24 24 24</td>
<td>100 100 100</td>
<td>9.6 9.6 9.6</td>
<td>81 76 73</td>
</tr>
<tr>
<td>3</td>
<td>As (III) Pb (II) Cr (VI)</td>
<td>202 205 208</td>
<td>10 10 10</td>
<td>2.4 2.4 2.4</td>
<td>400 400 400</td>
<td>12.1 12.1 12.1</td>
<td>98 95 93</td>
</tr>
<tr>
<td>4</td>
<td>As (III) Pb (II) Cr (VI)</td>
<td>2025 2035 2040</td>
<td>10 10 10</td>
<td>24 24 24</td>
<td>400 400 400</td>
<td>11.9 11.9 11.9</td>
<td>97 93 92</td>
</tr>
<tr>
<td>5</td>
<td>As (III) Pb (II) Cr (VI)</td>
<td>202 205 208</td>
<td>– – –</td>
<td>– – –</td>
<td>100 100 100</td>
<td>9.8 9.8 9.8</td>
<td>12 73 10</td>
</tr>
<tr>
<td>6</td>
<td>As (III) Pb (II) Cr (VI)</td>
<td>202 205 208</td>
<td>– – –</td>
<td>– – –</td>
<td>400 400 400</td>
<td>12.1 12.1 12.1</td>
<td>13 93 9</td>
</tr>
</tbody>
</table>

Table 4 – Effect of treatment methods on the average removal efficiency of heavy metals.

<table>
<thead>
<tr>
<th>Treatment method</th>
<th>Dosage level γ/mg l$^{-1}$</th>
<th>Average removal mass fraction w/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ferric sulphate</td>
<td>40</td>
<td>92 85 88</td>
</tr>
<tr>
<td>Alum</td>
<td>40</td>
<td>88 90 85</td>
</tr>
<tr>
<td>Lime</td>
<td>200</td>
<td>97 92 90</td>
</tr>
</tbody>
</table>
level 200 μg l\(^{-1}\) to 2000 μg l\(^{-1}\). From the experimental results it can be interpreted that a lime dose of 200 mg l\(^{-1}\) in the pH range of 11.3 to 11.5 is suitable for the treatment of contaminated river water. A high dose of 400 mg l\(^{-1}\) increased the removal efficiency only marginally.

**Effect of pH**

Tests were conducted to find out the effect of pH variation on the removal efficiency of heavy metals from surface water. Raw river water containing arsenic, lead, and chromium at mass concentration level of 2021 μg l\(^{-1}\), 2025 μg l\(^{-1}\) and 2015 μg l\(^{-1}\), respectively, was treated with ferric sulfate and alum in the pH range 4 to 9. pH was adjusted by the addition of dilute hydrochloric acid or sodium hydroxide solution. The dose level for both coagulants were 40 mg l\(^{-1}\). Figure 4 shows pH significantly influences the removal efficiency by ferric sulfate. There was a significant increase in removal efficiency when pH was increased from 4 to 6. However, only a marginal increase in removal efficiency was observed when pH was increased from 6 to 7. Beyond pH 7, removal efficiency of the three heavy metals remained unaffected. Thus from Figure 4 it can be interpreted that contaminated surface water can be effectively treated with ferric sulfate dose of 40 mg l\(^{-1}\) in the operating pH range of 6.5 to 8.0.

When alum at a dose level of 40 mg l\(^{-1}\) was used as coagulant, it was observed that the removal efficiency increased when pH of the treated solution was increased from pH 4 to 5 (Figure 5). It is observed that at pH 4, mass fraction removal of arsenic, lead, and chromium were \(w = 72\%\), \(75\%\), \(70\%\), respectively; whereas, at pH 5 it increased to \(w = 83\%\), \(85\%\) and \(80\%\), respectively. A marginal change in percentage removal was noted when the solution pH was raised from 5 to 6 and thereafter it remained unchanged. Thus, from Figure 5 it is evident that by using alum as a coagulating agent at a dose level of 40 mg l\(^{-1}\), contaminated river water can be effectively treated in the operating pH range 5.5 to 8.0. This is a wider range compared to the pH range of 6 to 8 for ferric sulfate as a coagulant. From the above experiments, it has been observed that both ferric sulfate and alum are effective in removing arsenic, lead and chromium in the pH range of 6 to 8. The average removal efficiency in this pH range was about 85–90% even when the contamination levels of the metals were as high as 2 mg l\(^{-1}\).

Both, ferric sulfate and alum form hydroxide flocs, i.e. Fe(OH)\(_3\) and Al(OH)\(_3\), in the pH range of pH 4 to 9. These flocs during their formation may have entrapped or enmeshed heavy metals and removed them from the water body during the sedimentation process. The flocs may have also adsorbed heavy metals from the solution on their surface and thus removing them. Hence, the removal mechanism of lead, oxidized form of arsenic, and reduced form of chromium from treated water may either be by enmeshment of heavy metals inside the growing flocs of Fe(OH)\(_3\) or Al(OH)\(_3\) or by the adsorption on the surface of flocs or simultaneously by, both, enmeshment and adsorption.

In the case of alum treatment, it was expected that it would give better results than that of ferric sulfate treatment, as ferrous sulfate was used for reduction of hexavalent chromium, which itself was oxidized to ferric state and ultimately may have contributed Fe(OH)\(_3\) floc. Thus, in the case of alum treatment, both, ferric hydroxide and aluminum hydroxide flocs were available for the removal of heavy metals. In practice, we have found a dose of 40 mg l\(^{-1}\) of alum in the pH range 4 to 6 was more effective than the same dose level of ferric sulfate.
It must be pointed out that river water may have several other inorganic solutes e.g. phosphates, calcium, magnesium, manganese, etc. These inorganic solutes may have also competed with arsenic, lead and chromium for the available surface of ferric or aluminum hydroxide flocs for adsorption. Hence the removal efficiency of heavy metals in actual river water may increase or decrease depending on the types of inorganic solutes present in the raw river water.

Experimental runs with a dose level of 200 mg l\(^{-1}\) of lime were conducted to find out the effect of pH variation on the metal removal from surface water. Thus, from Figure 6 it is observed that the removal efficiency of arsenic, lead and chromium was increased from 90 %, 88 %, 85 % at pH 8.0 to 95 %, 91 % and 88 %, respectively at pH 10.0. With further increase of pH up to 12.0, the removal efficiency of corresponding metals only slightly increased. Hence, it can be interpreted that a lime dose of 200 mg l\(^{-1}\) in the operating pH range of 10.0 to 12.0 is effective for the removal of heavy metals arsenic, lead and chromium from contaminated raw river water.

Again, the removal mechanism of heavy metals by lime may be either by precipitation or adsorption or both. The reason for the higher removal efficiency of heavy metals by lime treatment compared to that of ferric sulfate or alum treatment may be due to the formation of precipitates of Fe\(_2\)[AsO\(_4\)]\(_2\), Ca\(_3\)[AsO\(_4\)]\(_2\), Cr(OH)\(_3\), Pb CO\(_3\), Pb\(_2\)(OH)\(_2\)CO\(_3\), PbO\(_2\), CaCO\(_3\), etc. in the operating pH range 10.0 to 12.0.

### Activated Carbon Treatment

When the various metal concentrations in the raw water were about 2 mg l\(^{-1}\), the three coagulants used could not bring down their concentration below the acceptable limit of 50 \(\mu\)g l\(^{-1}\). Hence, for heavily contaminated water, it was felt that an additional step, such as the adsorption of heavy metals on Granulated Activated Carbon (GAC) should be employed. In order to find out the effectiveness of GAC in the removal of heavy metals, chemically treated river water was passed through an activated carbon adsorption column of 90 cm packed height at a flow rate of 50 l m\(^{-2}\) min\(^{-1}\). The average diameter of GAC particles was 1 mm. The effluent samples were analyzed in ICPAES for heavy metal mass concentration. Figure 7 shows the effect of GAC on the adsorption of the three heavy metals from ferric sulfate treated water. GAC was effective in removing the heavy metals even if the mass concentration were as high as 1000 \(\mu\)g l\(^{-1}\).

The effect of GAC in the removal of the remaining heavy metals from the alum treated water at operating pH 6.8 to 7.2 is shown in Figure 8. From the figure it is observed that when feed water...
contained arsenic, lead and chromium in the concentration levels of 363 \( \mu \text{g l}^{-1} \), 303 \( \mu \text{g l}^{-1} \) and 324 \( \mu \text{g l}^{-1} \), respectively, effluent water was found to contain only 6 \( \mu \text{g l}^{-1} \), 4.5 \( \mu \text{g l}^{-1} \) and 4.0 \( \mu \text{g l}^{-1} \), respectively. When feed water contained lower levels of contaminants i.e. 41 \( \mu \text{g l}^{-1} \), 32 \( \mu \text{g l}^{-1} \) and 36 \( \mu \text{g l}^{-1} \) of arsenic, lead and chromium, effluent water was found to contain only 1.5 \( \mu \text{g l}^{-1} \), 1.0 \( \mu \text{g l}^{-1} \) and 0.5 \( \mu \text{g l}^{-1} \), respectively.

GAC adsorption studies were also conducted on 100 mg l\(^{-1}\) lime treated water at the operating pH between 9.6 to 9.8. The results are shown in Figure 9. From the figure it is observed that GAC is again effective in removing the three heavy metals from lime treated water.

Thus, from the granular activated carbon adsorption studies, it has been observed that this method is very effective in the removal of heavy metals – arsenic, lead, and chromium from chemically treated river water and the average removal efficiency of each of the three heavy metals were more than 98 %.

**Conclusion**

The investigation revealed that river water which is artificially polluted with arsenic, chromium and lead, can be successfully treated by physico-chemical process using coagulants such as ferrous sulfate, alum or lime followed by adsorption on granulated activated carbon. The heavy metal mass concentrations can be simultaneously brought down to an acceptable level. This method is effective even if the concentration of each of the three heavy metals were as high as 2000 \( \mu \text{g l}^{-1} \). pH of the contaminated water significantly affected the removal efficiency. Hence, adequate control of the pH is necessary for the maximum removal of the contaminants. The three coagulants were ineffective in removing arsenite (As-III) and chromium (Cr-VI). They need to be converted to arsenate (As-V) and chromium (Cr-III) for the coagulants to be effective. However, they were effective for both Pb (II) and Pb (IV).

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**References**