The Effects and Processes for Removal of Chromium in Activated Sludge Treatment

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ABSTRACT
The presence of chromium in wastewater can impact the efficiency of activated sludge treatment plants that do not usually treat chromium contaminated wastewater. Pretreatment regulations have been passed by the United States Environmental Protection Agency (EPA) for industries who produce chromium contaminated wastewater. Two forms of chromium exist: trivalent chromium (Cr(III)) and hexavalent chromium (Cr(VI)), which is more toxic than Cr(III). Activated sludge that has acclimated to chromium can efficiently remove chromium from wastewater. An increased concentration of suspended solids and a decreased activated sludge age can aid in the removal efficiency; however, a higher concentration of chromium present in wastewater can lead to decreased filamentous bulking and nitrification. Chromium’s toxicity decreases the diversity of microorganisms, but low doses of chromium do not affect microorganisms such as γ-Proteobacteria and free swimming ciliates that are present in activated sludge. These microorganisms aid in the chromium removal process provided by activated sludge.

KEYWORDS
Activated Sludge, chromium, removal, biosolids, toxicity

INTRODUCTION
Activated sludge treatment is a biological solution to wastewater treatment. Municipal wastewater treatment plants not only receive wastewater from residential areas, but also from industrial and commercial establishments. Influent can contain compounds or metals that the treatment plant does not usually treat and can have potentially negative effects on the efficiency and quality of treatment achieved by the plant.

Chromium is a naturally occurring metal and is often found in rocks, plants, soil, volcanic dust and gases, animals and humans. Chromium can have negative impacts on activated sludge systems if high enough concentrations of the metal are present in wastewater. Leather tanning, electroplating, wood preservation, textile manufacturing, and pulp processing facilities are most frequently the source of chromium contaminated wastewater.

The United State Environmental Protection Agency (EPA) has established the National Pretreatment Program, which requires industries who discharge chromium containing wastewater to remove most of the toxic metal with pretreatment. The municipal wastewater treatment plants can then proceed in treating the water to ensure that chromium does not affect the aquatic life or drinking water sources (U.S. EPA, 1999). The main concern for municipal treatment plants is receiving chromium contaminated wastewater that can interfere with the activated sludge process.

In order to fully understand the effects and processes for removal of chromium in activated sludge, a brief background on the behavior of chromium and the regulations regarding chromium removal will be discussed. The method of chromium removal and the toxic effect of chromium on activated sludge will also be discussed. Finally, chromium's effect on the activated sludge microbiology will be addressed.

CHROMIUM STATES
Chromium is commonly found in the most stable states of hexavalent chromium (Cr(VI)) and trivalent chromium (Cr(III)). Cr(VI) is more toxic than Cr(III) and less common in the natural environment. One aspect of the removal process is to ensure that aquatic life, animals, and humans are not exposed to chromium. According the EPA Technology Transfer Network (2007), humans consume about 2.0 µg/L of chromium in water per day and about 60 µg/L of chromium in food a day. The human body has the ability to reduce Cr(VI) to Cr(III) via metabolic processes. Upon exposure to large concentrations of chromium, humans can develop health problems, which include acute respiratory effects, cancer, reproductive and developmental effects (US EPA Technology Transfer Network, 2007).
WASTEWATER TREATMENT REGULATIONS

Municipal wastewater treatment plants are generally not able to treat large concentrations of heavy metals, such as chromium, that come from industrial effluents (US EPA, 1999). Hence, pretreatment is required of industrial wastewater sources by Title 40 of the Code of Federal Regulations (CFR) in an effort to limit or eliminate chromium loading in municipal treatment plants (US EPA, 1999). Chromium can negatively affect the efficiency of activated sludge treatment processes and increase the chance of emitting chromium into the environment. A lack of pretreatment would also reduce the ability of the wastewater to be recycled or reused.

CHROMIUM REMOVAL WITH ACTIVATED SLUDGE

Traditional methods of chromium removal from wastewater usually require chemical processes; however, biological processes like activated sludge have also been proven to be efficient in chromium removal. In order to fully understand the importance and impact that chromium can have on an activated sludge treatment plant, the following topics are discussed:

- Removal mechanisms,
- Reduction of Cr(VI) to Cr(III),
- Absorption capacity of activated sludge,
- Suspended solids affect on absorption,
- Activated sludge age affect on removal, and
- Chromium effect on biomass acclimation.

Removal mechanisms

For the reasons stated above, removal of chromium during pretreatment is important. Traditional processes such as chemical precipitation, electrochemical treatment, and ion exchange have been used for pretreatment of industrial wastewater. Another approach to chromium removal is the use of activated sludge. According to Koçberber and Dönmez (2006), the microorganisms in activated sludge can be an effective tool in the removal of heavy metals from wastewater. The efficiency of biological removal resides in the microorganisms’ tolerance and ability to absorb chromium. Three methods of biological Cr(VI) removal with activated sludge exist (Koçberber and Dönmez, 2006; Imai and Gloyna, 1988):

1. Positively charged Cr(VI) is attracted to the negatively charged cell wall of the microorganisms;
2. Adsorption of Cr(VI) into microorganisms; and
3. Reduction of Cr(VI) to Cr(III), which is then settled.

Reduction of Cr(VI) to Cr(III)

The most common removal mechanism of chromium is the reduction of Cr(VI) to Cr(III). The Cr(III) is then adsorbed by the activated sludge and precipitated as Cr(OH)₃ (Imai and Gloyna, 1988; Stasinakis, Thomaidis, Mamanis, and Karivali et al., 2003). Figure 1 represents the phases of Cr(III) in an activated sludge wastewater sample after 12 hours of agitation with (a.) a 1mg/L initial Cr(III) concentration and (b.) a 10 mg/L Cr(III) initial concentration. As shown by the chart, a majority of the Cr(III) is absorbed by the activated sludge, while only 1% of the Cr(III) remained in solution. Figure 2 shows the phases of Cr(VI) in an activated sludge wastewater sample with (a.) a 1 mg/L of Cr(VI) initial concentration and (b.) a 10 mg/L of Cr(VI) initial concentration. Contrary to the Cr(III), the Cr(VI) mostly remained in a dissolved state. This observation shows that the ability of activated sludge to remove Cr(III) is greater than Cr(VI).
The rate of Cr(VI) reduction by activated sludge is also important to ensure proper removal. Cr(VI) reduction has been shown to be a function of both the initial concentration of Cr(VI) present in the wastewater and the activated sludge concentration. The Cr(VI) reduction rate tends to increase with an increased initial Cr(VI) concentration and lower activated sludge concentration (Stasinakis, Thomaidis, Mamais, and Karivali et al., 2003).

The oxidation of Cr(III) to Cr(VI) has also been investigated. Studies show that the oxidation of Cr(III) generally does not take place in activated sludge (Imai and Gloyna, 1988; Stasinakis et al., 2003 chemosphere). However, the oxidation of Cr(III) at very slow rates has been observed in the presence of dissolved oxygen (DO). The reason for not observing Cr(III) oxidation under standard activated sludge conditions is that Cr(III) is absorbed before the oxidation reaction is facilitated (Imai and Gloyna, 1988).

**Absorption Capacity of Activated Sludge**

Activated sludge has the ability to achieve a Cr(III) removal efficiency of 95 percent (Stasinakis, Thomaidis, Mamais, and Karivali et al., 2003). A longer solids retention time (SRT) and higher pH increase the absorption capacity of activated sludge (Imai and Gloyna, 1988). Cr(III) is more efficiently removed due to being less toxic than Cr(VI). In the presence of an anoxic tank proceeded by an aerobic activated sludge tank, as shown in Figure 3 below, approximately 96 to 99 percent of the chromium present is in the form of Cr(III) (Stasinakis et al., 2004). This finding indicates that the anoxic reactor aids in reducing the Cr(VI) to Cr(III), which is important in increasing the chromium absorption by the activated sludge bacteria.
Studies show that despite the fact Cr(III) is more efficiently removed, Cr(VI) removal by activated sludge is possible. An activated sludge process can remove about 40 percent of Cr(VI) in solution but is dependent upon sludge acclimation and a longer hydraulic retention time (HRT) (Stasinakis et al., 2004). Despite the ability of activated sludge to remove Cr(VI), Cr(VI) reduction to Cr(III) presents ideal absorption capacity.

**Suspended Solids Effect on Absorption**
Stasinakis, Thomaidis, Mamais, and Karivali et al. (2003) have shown that an increased suspended solids (SS) concentration leads to increased removal of Cr(III). The removal efficiency correlated with SS was based on the idea that higher SS concentrations allowed for more surface area for adsorption of Cr(III). Alternatively, no correlation between Cr(VI) and SS concentration was found (Stasinakis, Thomaidis, Mamais, and Karivali et al., 2003).

**Activated Sludge Age Effect on Removal**
The affect of activated sludge age on the removal efficiency of both Cr(III) and Cr(VI) was also considered. While Cr(III) is the ideal chromium state for activated sludge removal, the removal efficiency decreases as the age of the activated sludge increases (Stasinakis, Thomaidis, Mamais, and Karivali et al., 2003). Stasinakis, Thomaidis, Mamais, and Karivali et al. (2003) theorize that Cr(III) fills the absorption sites and reduces the adsorption capacity of the sludge. To further support this theory, the adsorption of Cr(III) in chromium acclimated sludge was found to be less than that of un-acclimated sludge (Stasinakis, Thomaidis, Mamais, and Karivali et al., 2003).

The removal efficiency of Cr(VI) was not affected by whether or not the activated sludge was acclimated (Stasinakis, Thomaidis, Mamais, and Karivali et al., 2003). Additionally, the activated sludge age also has no effect on the removal efficiency of Cr(VI) (Stasinakis, Thomaidis, Mamais, and Karivali et al., 2003).

**Chromium Effect on Biomass Acclimation**
Cr(VI) and Cr(III) affect the rate of biomass accumulation. While Cr(VI) has been established as more toxic than Cr(III), Cr(VI) has shown less inhibition on the activated sludge growth rate than Cr(III) at concentrations less than 70 mg/L (Gikas and Romanos, 2006). At concentrations greater than 70 mg/L Cr(VI) is more inhibitive than Cr(III) (Gikas and Romanos, 2006). One of the main indicators of chromium’s effect on biomass growth is the presence of an increased lag time. As the concentration of Cr(III) and Cr(VI) increase, the lag time also increases (Gikas and Romanos, 2006). This trend can be seen in Figure 4 and 5 for Cr(VI) and Cr(III), respectively. The optimum biomass growth rate contains 10 mg/L Cr(VI) or 10 mg/L Cr(III) when the HRT is greater than about 17 hours and 11 hours, respectively.
Cr(VI) and Cr(III) have been shown to stimulate biomass growth up to 25 mg/L and 15 mg/L, respectively (Gikas and Romanos, 2006). As shown in Figure 6, the exposure of biomass to heavy metals actually increases the growth rate up to an optimum concentration at which point the addition of more metal has a reverse reaction. The observation that chromium stimulates growth is supported by this theory. Figure 6 also demonstrates that an increasing concentration of metal can lead to biomass degeneration and eventually to zero growth. According to Gikas and Romanos (2006), biomass growth is no longer supported at Cr(VI) and Cr(III) concentrations of 320 mg/L and 160 mg/L, respectively.
CHROMIUM EFFECTS ON ACTIVATED SLUDGE PROCESSES

While the activated sludge process is adequate for chromium removal, the toxicity of chromium can have a negative impact on the efficiency of the processes that occur in activated sludge. Chromium can interfere with the nitrification, chemical oxygen demand (COD) removal, and filamentous bulking.

Nitrification

Ammonium removal by wastewater treatment plants is essential in preventing eutrophication, preventing toxicity in receiving waters, and to limiting the chorine demand. Nitrification can be disturbed by Cr(VI) (Stasinakis, Thomaidis, Mamais, and Papanikolaou et al., 2003). Cr(VI) increases the ammonium concentration while decreasing the nitrate concentration. An anoxic-aerobic activated sludge system improves the ability of microorganisms to perform nitrification (Stasinakis, Thomaidis, Mamais, and Papanikolaou et al., 2003). Stasinakis, Thomaidis, Mamais, and Papanikolaou et al. (2003) found that a treatment system exposed to continuous loading of 5 mg/L of Cr(VI) was able to slowly recover from the toxic effects of Cr(VI). Over 12 days the testing system’s ammonium removal rate increased from 30% to 57%. Shock loading also inhibited the nitrification process by decreasing the ammonium removal, which achieved no more than 45% removal (Stasinakis, Thomaidis, Mamais, and Papanikolaou et al., 2003). Adversely, ammonium can affect Cr(VI) removal, but nitrate present in wastewater does not affect the process of Cr(VI) reduction (Stasinakis et al., 2004).

The nitrification process can also be disturbed by the presence of Cr(III). Considering that Cr(III) is not as toxic as Cr(VI), a concentration of up to 20 mg/L of Cr(III) continuous loading does not inhibit the nitrification process (Stasinakis, Thomaidis, Mamais, and Papanikolaou et al., 2003). Concentrations of Cr(III) greater than 25 mg/L has the potential to inhibit ammonium removal (Stasinakis, Thomaidis, Mamais, and Papanikolaou et al., 2003). Compared to Cr(VI), nitrification in the presence of Cr(III) is able to achieve pre-loading conditions in about 7 days (Stasinakis, Thomaidis, Mamais, and Papanikolaou et al., 2003). Shock loading of Cr(III) has been shown to not impact nitrification (Stasinakis, Thomaidis, Mamais, and Papanikolaou et al., 2003).

COD Removal

The toxicity of Cr(VI) can also impact the efficiency of COD removal. An increased concentration of Cr(VI) decreases the COD removal efficiency (Stasinakis, Thomaidis, Mamais, and Papanikolaou et al., 2003). While 1 to 3 mg/L of Cr(VI) does not have an significant impact on COD removal, decreased
efficiency occurs with Cr(VI) concentrations greater than 5 mg/L; however, 5 mg/L of Cr(VI) decreased COD removal by less than 10 percent (Stasinakis, Thomaidis, Mamais, and Papanikolaou et al., 2003).

Under shock loading conditions with a concentration of 5 mg/L of Cr(VI), no reduction in COD removal efficiency is observed (Stasinakis, Thomaidis, Mamais, and Papanikolaou et al., 2003). Ertugrul et al. (2006) also observed little to no impact on microorganisms during the first day of shock loading of 5 mg/L and 10 mg/L Cr(VI). Shock loading of 5 mg/L and 10 mg/L Cr(VI) decreases COD removal efficiency during the second day, and requires 3 and 5 days, respectively, to recover to a steady state condition (Ertugrul et al., 2006). As the concentration of Cr(VI) increases, a more pronounced effect of Cr(VI) on microorganisms is observed. A high concentration of MLSS and SRT aids the microorganisms’ Cr(VI) tolerance and decreases the effect of Cr(VI) on COD removal capacity (Ertugrul et al., 2006).

Filamentous Bulking

Sludge bulking properties are negatively correlated with an increased concentration of chromium (Stasinakis, Thomaidis, Mamais, and Papanikolaou et al., 2003). Cr(VI) decreases the size of the activated sludge flocs and deteriorates bulking. Deteriorated bulking takes several days to observe and is more prevalent with Cr(VI) concentrations greater than 3 mg/L (Stasinakis, Thomaidis, Mamais, and Papanikolaou et al., 2003). Cr(VI) attacks the floc forming bacteria’s extensions beyond the floc and reduces floc sizes. At the same time, shock loading of Cr(VI) does not affect settling characteristics (Stasinakis, Thomaidis, Mamais, and Papanikolaou et al., 2003).

CHROMIUM EFFECTS ON ACTIVATED SLUDGE MICROBIOLOGY

The microorganisms in the activated sludge can also be affected by chromium. Some microorganisms are not able to survive when exposed to chromium but others help in reduction and removal of chromium. Additionally, the rate of loading and concentration of chromium exposure can have different impacts on the biological life in activated sludge.

Toxicity

Besides having an effect on the processes which occur within activated sludge, chromium also affects activated sludge microorganisms by causing decreased biomass, activity, and microbial density (Francisco et al., 2002). Cr(VI) is about 100 times more toxic than Cr(III), since Cr(III) is less soluble. (Francisco et al., 2002). The toxicity of chromium interferes with the oxidation reactions that occur in microorganisms (Imai and Gloyna, 1988). According to Dilek and Yetis (1992) as sited by Madoni et al. (1995), 50 mg/L of Cr(VI) is toxic to bacterial communities.

A study evaluated the activated sludge removal efficiency of Cr(VI) from wastewater that contained 8 percent salt ion and determined that microbial growth was able to occur at concentrations less than 400 mg/L of Cr(VI) (Koçberber and Dönmez, 2006). The presence of salt also decreased the toxicity of Cr(VI) at higher Cr(VI) concentrations (Koçberber and Dönmez, 2006).

Chromium Reducing Bacteria

Studies have determined the common bacteria found in chromium contaminated wastewater. Francisco et al. (2002) identified several bacteria presented in Figure 7, which were mostly γ-Proteobacteria, in a tanning facility chromium contaminated wastewater sample. Mainly strains of Acinetobacter were identified by culture samples. The culture may not have identified all the strains of bacteria in the sample, which implies that additional bacteria strains could be present and resistant to chromium. The fact that the bacteria presented below were found suggests that they are resistant to Cr(VI). Some Acinetobacter also partially reduce Cr(VI) to Cr(III) and assist in chromium removal (Francisco et al., 2002). Partial reduction of Cr(VI) implies that bacteria work together to reduce Cr(VI).
The impact of chromium on protozoan communities is also important considering the role protozoa have in improving the effluent quality and indicating the effectiveness of the wastewater treatment process. Vorticella, Opercularia, stalked ciliates, free swimming ciliates, and rotifers have all been identified as common microorganisms in wastewater. Additional common protozoa identified in a wastewater sample by Madoni et al. (1995) are presented in Table 1. Chromium exposure tends to decrease the diversity of protozoa within activated sludge. Stasinakis, Thomaidis, Mamais, and Papanikolaou et al. (2003) found that with exposure to 1 mg/L of Cr(VI), free swimming ciliates increase while rotifers decrease. A concentration of 3 mg/L of Cr(VI) impacts filamentous bulking, and free swimming ciliates dominate due to an increased bacteria food source available. Ultimately at a concentration of 5 mg/L of Cr(VI), chromium is completely toxic to the protozoa in activated sludge to the point were no protozoa are present (Stasinakis, Thomaidis, Mamais, and Papanikolaou et al., 2003).
Table 1. Common protozoa identified in a mixed liquor activated sludge sample (Madoni et al., 1995)

<table>
<thead>
<tr>
<th>Taxa</th>
<th>Cell number 25 µ/L</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Min</td>
<td>Max</td>
</tr>
<tr>
<td><strong>Free-Swimming Ciliates</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><em>Drepanomonas revoluta</em></td>
<td>9</td>
<td>19</td>
</tr>
<tr>
<td><strong>Crawling Ciliates</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><em>Aspidisca cicada</em></td>
<td>158</td>
<td>186</td>
</tr>
<tr>
<td><em>Aspidisca lyncus</em></td>
<td>1422</td>
<td>1672</td>
</tr>
<tr>
<td><em>Chilodonella uncinata</em></td>
<td>39</td>
<td>76</td>
</tr>
<tr>
<td><em>Euplotes sp.</em></td>
<td>28</td>
<td>53</td>
</tr>
<tr>
<td><em>Trochilia minuta</em></td>
<td>39</td>
<td>142</td>
</tr>
<tr>
<td><strong>Attached ciliates</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><em>Carchesium sp.</em></td>
<td>4</td>
<td>9</td>
</tr>
<tr>
<td><em>Episylis sp.</em></td>
<td>1</td>
<td>8</td>
</tr>
<tr>
<td><em>Opercularia coarctata</em></td>
<td>45</td>
<td>53</td>
</tr>
<tr>
<td><em>Opercularia minima</em></td>
<td>131</td>
<td>233</td>
</tr>
<tr>
<td><em>Vorticella convallaria</em></td>
<td>43</td>
<td>72</td>
</tr>
<tr>
<td><em>Vorticella octava</em></td>
<td>27</td>
<td>57</td>
</tr>
<tr>
<td><strong>Suctoria</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><em>Podophrya sp.</em></td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td><em>Tokophrya quadripartita</em></td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td><strong>Testate amoeba</strong></td>
<td>2</td>
<td>8</td>
</tr>
<tr>
<td><strong>Total microfauna</strong></td>
<td>1950</td>
<td>2590</td>
</tr>
</tbody>
</table>

**Chromium Loading Effect on Microorganisms**

During continuous loading of chromium, nitrifying bacteria have been determined to be more sensitive to chromium exposure than bacteria involved with COD removal due to the longer recovery time required by the nitrifying bacteria (Stasinakis, Thomaidis, Mamais, and Papanikolaou et al., 2003). The impact of chromium on nitrifying bacteria compared to COD reducing bacteria can be attributed to the smaller quantity of nitrifying bacteria present in the system. COD reducing bacteria consist of many different types of bacteria that work together; therefore, Cr(VI) has to be toxic to several species to impact COD removal.

Shock loading of chromium can be lethal to biological communities. Madoni et al. (1995) determined lethal doses of Cr(VI) for different strains of ciliates, which are presented in Table 2. The difference in toxicity levels indicates that certain strains of ciliates are more resistant to chromium than others.
Table 2. Toxic LC$_{50}$ 24-hour concentrations (mg/L) of Cr(VI) to ciliate strands (Madoni et al., 1995)

<table>
<thead>
<tr>
<th>Metal Ciliate Species</th>
<th>Cr(VI) (mg/L)</th>
<th>Cr(VI) (mg/L) 95% Confidence Limits</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aspidisca cicada</td>
<td>138</td>
<td>124-151</td>
</tr>
<tr>
<td>Aspidisca lynceus</td>
<td>145</td>
<td>121-170</td>
</tr>
<tr>
<td>Chilodonella uncinata</td>
<td>10.6</td>
<td>8.37-13.1</td>
</tr>
<tr>
<td>Euplotes sp.</td>
<td>38.6</td>
<td>27.7-57.5</td>
</tr>
<tr>
<td>Opercularia coarctata</td>
<td>211</td>
<td>166-269</td>
</tr>
<tr>
<td>Opercularia minima</td>
<td>164</td>
<td>130-200</td>
</tr>
<tr>
<td>Trochilia minuta</td>
<td>9.25</td>
<td>4.52-13.7</td>
</tr>
<tr>
<td>Vorticella convallaria</td>
<td>101</td>
<td>78-122</td>
</tr>
<tr>
<td>Vorticella octava</td>
<td>80</td>
<td>68.4-92.5</td>
</tr>
</tbody>
</table>

CONCLUSION

Traditional treatment methods for chromium removal have been proven to be effective, but the use of activated sludge has also been proven to be an efficient method of chromium removal. The reduction of Cr(VI) to Cr(III) in combination with activated sludge can achieve 95 percent removal efficiency by adsorption. Additionally, a lower activated sludge age will also ensure a higher removal rate. Microorganisms such as γ-Proteobacteria and free swimming ciliates tend to be resistant to chromium, and aid in the removal process. Chromium inhibits activated sludge processes by limiting nitrification and filamentous bulking.

A substantial amount of research has been recently completed concerning the effect chromium on activated sludge and the ability of activated sludge to remove chromium from wastewater. The research provides a basis from which the use activated sludge for chromium removal can grow. Biological chromium removal could possibly be more economical than traditional methods of chromium removal considering that the activated sludge communities are mostly self sufficient after establishment. In municipal wastewater treatment facilities, an activated sludge system may need to be coupled with a process to ensure nitrification. The activated sludge would also need to be monitored to ensure the reduction of Cr(VI) to Cr(III), proper bulking, and settlement. Activated sludge treatment has the ability to be a promising method of chromium removal.
REFERENCES


