Short Communication (NS-2)

THE KINETICS OF Cr(III) OXIDATION IN DOMINANT SOILS OF COIMBATORE DISTRICT, TAMILNADU, INDIA

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ABSTRACT

Chromium has attained wide public and regulatory attention because of its toxicity to environmental ecosystem under certain oxidation state. An investigation was carried out with the main focus to find out whether irrigation of low concentration of Cr (III) containing treated tannery effluent to dominant soils of Coimbatore district favor oxidation of non-toxic Cr (III) to toxic Cr (VI). Significant transformation of Cr (III) to Cr (VI) in both soil types clearly indicate, that there was within shorter period of time. When the equilibration time, in batch study, was increased beyond 24 hours the oxidation of Cr (III) to Cr (VI) decreased which may be due to reduction of Cr (VI) to Cr (III) and adsorption of Cr (III) to nil minerals under the favorable soil pH conditions. Although the maximum concentration of water soluble Cr (VI) was only 5.3% of the spiked Cr (III) concentration at 5 mg L\(^{-1}\) the concentration of soluble Cr (VI) of 0.27 mg L\(^{-1}\) was beyond the critical limit of 0.05 mg L\(^{-1}\) for drinking water. Therefore it is essential imperative to exercise caution in the continuous application of Cr (III) containing tannery waste water to soils.

Key Words: Tannery effluent, Chromium transformation, Oxidizing agents, Red and black soil, Chromium toxicity.

INTRODUCTION

The use of industrial waste water in agriculture has emerged as an innovative alternative option to augment the traditional fresh water supply. However, the use of low quality industrial waste water imposes concerns regarding its suitability and impact on the natural ecosystem for a sustained development. Tanning industry is one such industry, which disposes enormous amount of water after the process of raw skin and hide. In terms of liquid waste the industries generate 680 x 10\(^6\) L waste water per day for the country. The waste generated from this industry contains various dissolved inorganic salts and organic wastes besides toxic trace metal chromium (Cr). Chromium exists in highly variable oxidation states from +2 to +6 and also known to form complex anionic and cationic ions, examples are Cr(OH)\(^{2+}\), CrO\(_4^{2-}\), CrO\(_3^{3-}\). Naturally occurring Cr compounds have principal valences of +3 (chromic) and +6 (chromate) and highly oxidized forms of Cr (Cr(VI)) are much less

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stable than Cr(III). Tanning industries use Cr(III) salt to process the skin and hides and the waste water discharged from the industries contains Cr(III) as the dominant species. The effluent treatment plants are supposed to remove the Cr salt by precipitation with MgO. However it has been reported that the treated wastewater contains traces to parts per million levels of Cr. This treated wastewater is irrigated to raise different crops in industries adjoining land area. The oxidation of Cr(III) in soil as an effect of the oxidizing ability of Mn compounds is the important chemical reaction in terms of transforming relatively non toxic Cr(III) to toxic Cr(VI) described the Cr(III)/Cr(VI) balance as a seesaw with Mn and organic matter, where the soil pH acts as a controllable master variable that helps to set the oxidizing reactivity of Mn oxides and the reducing properties of organic matter or other compounds.

Objectives

The studies on oxidation of Cr (III) to Cr (VI) in Indian soils are limited. Therefore the present study was conducted to investigate the kinetics of Cr (III) oxidation in dominant soils of Coimbatore district, Tamil Nadu, and study the effect of various concentrations of Cr(III) on water soluble and exchangeable Cr in those soils.

MATERIAL AND METHODS

Laboratory batch and incubation studies were conducted to investigate the transformation of Cr in two dominant soil types of Coimbatore district, Tamil Nadu namely, red soil (Typic haplustalfs – Sommayanur series) and black soil (Vertic ustropept – Periyaanaickenpalayam series). On the analytical side measurement of aqueous Cr (VI) formed in the Cr (III) spiked effluent in UV-VIS spectrophotometer posed lot of problems and interferences due to the colour already present in the effluent. Therefore for all the batch and incubation experiments, Cr (III) was spiked in double distilled water. The required quantity of chromium chloride (CrCl_3 \cdot 6H_2O) salt was spiked in the distilled water and prepared various concentrations (0, 5, 10, 40, 60 and 100 mg l^-1) of Cr (III) solution to conduct batch and incubation studies. The Cr (VI) was determined by Diphenyl carbazide method (DPC), and total Cr was analyzed from the filtrate in Flame Atomic Absorption Spectrophotometer (FAAS).

RESULTS AND DISCUSSION

The results on kinetics of Cr (III) oxidation to Cr (VI) under batch system in both soil types clearly indicate that, there was significant transformation of Cr (III) to Cr (VI) within shorter period of time (one hour). The oxidation of Cr (III) to Cr (VI) was higher in black soil (Fig. 2 a) (>5.3 times) than red soil (Fig. 1 a) within one hour duration in 5 mg L^-1 Cr (III) spiked treatment, due to the presence of high amounts of MnO_2 (585 mg kg^-1) compared to the concentration of MnO_2 present in red soil (489 mg kg^-1). The decrease in pH, from 6.8 to 5.8 in red soil (Fig. 1 a-b) and from 7.8 to 7.0 in black soil (Fig. 2 a-b) also favored the solubility and oxidation of Cr (III) to Cr (VI). Oxidation reaction increased with increasing concentration of spiked Cr (III) upto 60 mg L^-1 Cr (III) level and attained a stable marginal increase at 100 mg L^-1 Cr (III) treatment and this may be due to saturation of MnO_2 surface with Cr (III) ions. When the equilibration time was increased (24 hours) the oxidation of Cr (III) to Cr (VI)
increased (Fig. 1 b and Fig. 2 b), but beyond 24 hours the oxidation of Cr (III) to Cr (VI) decreased from 0.730 to 0.595 and from 0.810 to 0.745 mg L\(^{-1}\) in red and black soil respectively in 60 mg L\(^{-1}\) Cr (III) spiked treatment. This may be due to reduction of Cr (VI) to Cr (III) in the presence of reducing agents, namely, organic matter, Fe and S and adsorption of Cr (III) to soil minerals under the favorable soil pH conditions.

![Graphs showing effect of various concentrations of Cr(III) and equilibration time on soil pH, water soluble and exchangeable Cr(VI)](image)

The results of incubation experiments for both the soils also showed very similar trend for oxidation of Cr (III) to Cr (VI). However the concentrations of water soluble and exchangeable Cr (VI) was lower than the concentrations observed for batch studies.

**CONCLUSION**

Although the maximum concentration of water soluble Cr (VI) was only 5.3% of the spiked Cr (III) concentration at 5 mg L\(^{-1}\), the concentration of soluble Cr (VI) of 0.27 mg L\(^{-1}\) was beyond the critical limit of 0.05 mg L\(^{-1}\) for drinking water. Therefore it is essential and imperative to exercise caution in the continuous application of Cr (III) containing tannery waste water to soils to prevent contamination of groundwater with toxic hexavalent chromium.
REFERENCES


Declaration by the Author(s)

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