

# Removal of tungsten oxyanions from industrial wastewater by precipitation, coagulation and flocculation processes

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Received 22 August 2006; received in revised form 6 March 2007; accepted 6 March 2007

Available online 12 March 2007

## Abstract

Tungsten removal from industrial wastewater by precipitation, coagulation and flocculation processes using ferric chloride is reported. Suitable process conditions (pH, ferric chloride concentration) were established in jar tests performed with wastewater samples. Alkaline wastewater was treated with ferric chloride and pH was adjusted to various points using sulphuric acid. Tungsten removal was found to be most efficient (98–99%) in acidic conditions (pH < 6). The process conditions were also found to be suitable for operation of an industrial scale wastewater treatment facility. More than 97% of tungsten were removed and the residual concentration was smaller than 10 ppm.

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**Keywords:** Heavy metal removal; Oxyanion; Tungstate; Tungsten; Wastewater

## 1. Introduction

The removal of heavy metals has become an important process in industrial wastewater treatment since heavy metals are known to be toxic to humans and the environment. Various treatment methods for the removal of heavy metals, such as Cd, Cr, Cu, Ni, and Zn from contaminated wastewater streams are described in the literature [1]. Tungsten (W) is a heavy metal which is widely used in industry, e.g. in manufacturing of tungsten carbide hard materials. However, there is limited information about techniques for removal of tungsten. The negative effects of tungsten upon the environment have only been addressed recently by Strigul et al. [2]. Beside other negative effects, Strigul et al. pointed out that dissolved tungsten species can significantly decrease microbial yield and biomass production at concentrations as low as  $10^{-5}$  ppm. The negative effect

of tungsten on microbial systems could possibly deteriorate process performance of biological wastewater treatment systems and lead to accumulation of tungsten in the waste sludge and the receiving water bodies. In this context, Luxembourg has imposed an emission limit of 2 ppm for the discharge of tungsten containing wastewater to the sewer system [3].

Precipitation, coagulation and flocculation processes are widely used techniques for the removal of heavy metals [1]. In this study, the removal of tungstate from alkaline wastewater originating from the galvanization facility of an industry that produces hard materials based on tungsten carbide is reported. Tungstate was successfully removed in jar testing experiments and later in industrial scale treatment by precipitation, coagulation and flocculation processes with ferric chloride.

## 2. Materials and methods

Jar testing was performed using tungstate containing wastewater ( $c_{0,W} = 321$  ppm) originating from a galvanization facility. The wastewater ( $1 \text{ dm}^3$ ) was transferred to a beaker and ferric ion ( $\text{Fe}^{3+}$ ) was added in different amounts (390 and 780 ppm) using iron(III) chloride (40%, w/w, Brenntag). This corresponded to a molar ratio ( $\text{Fe}^{3+}/\text{W}$ ) of 4 and 8, respectively. The contents

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Table 1  
Removal of tungstate using various pH values and coagulant concentrations

Treatment type	pH	$c_{0,W}$		$c(Fe^{3+})$		Ratio $Fe^{3+}/W$		$c_{res.,W}$		Removal%
		ppm	$mol\ m^{-3}$	ppm	$mol\ m^{-3}$	Mass	Molar	ppm	$mol\ m^{-3}$	
Jar test	4	321	1.75	390	6.98	1.2	4.0	4	0.02	99
Jar test	6	321	1.75	390	6.98	1.2	4.0	7	0.04	98
Jar test	8	321	1.75	390	6.98	1.2	4.0	74	0.40	77
Jar test	10	321	1.75	390	6.98	1.2	4.0	260	1.41	19
Jar test	4	321	1.75	780	13.96	2.4	8.0	1	0.00	100
Jar test	6	321	1.75	780	13.96	2.4	8.0	5	0.03	98
Jar test	8	321	1.75	780	13.96	2.4	8.0	49	0.27	85
Jar test	10	321	1.75	780	13.96	2.4	8.0	164	0.89	49
Industrial	5	278	1.51	156	2.79	0.6	1.8	6	0.03	98
Industrial	5	285	1.55	156	2.79	0.5	1.8	3	0.02	99
Industrial	5	225	1.22	156	2.79	0.7	2.3	9	0.05	97

of the beaker was continuously stirred by mechanical agitation (Ika). The pH was measured (HANNA pHep) and adjusted to various operating points (pH 4, 6, 8 and 10) using sulphuric acid (Biesterfeld). The tungsten concentration of the raw wastewater and the supernatant obtained after treatment and settling was measured by ICP-OES (Horiba/Jobin-Yvon, JY 138 Ultrace).

Batch treatments were performed in an industrial scale treatment tank ( $5\ m^3$ ) equipped with mechanical stirrer and pH control. Ferric ion was dosed with a concentration of 156 ppm and pH was adjusted to 5 before settling and dewatering of the sludge in a filter press. The W concentration of the supernatant was measured as described above.

### 3. Results and discussion

The jar testing revealed that tungsten could be successfully removed from the wastewater by precipitation, coagulation and flocculation processes with ferric chloride (Table 1). The resulting residual tungsten concentrations  $c_{res.,W}$  and the removal efficiencies show that the treatment was strongly dependent upon pH. Removal was most efficient at low pH. In the pH region below 6, tungsten removal was almost found to be complete, i.e. 99 and 100% at pH 4, and the smallest residual tungsten concentration was 1 ppm. The result of the treatment also depended on the amount of precipitant/flocculant added to the wastewater. However, doubling the molar ratio  $Fe^{3+}/W$  from 4 to 8 resulted in a slight improvement of the overall removal efficiency only, which did hardly manifest in the optimum pH range from 4 to 6 (Fig. 1).

Tungsten was also successfully removed in the industrial scale treatment facility. A ferric ion concentration of 156 ppm and a pH of 5 were set as operating point. Tungsten was removed with more than 97% efficiency in all three batches and residual tungsten concentration in the supernatant was smaller than 10 ppm (Table 1). The process conditions can possibly be further optimised by seeking to strike the appropriate balance between the costs and impacts incurred through an increased coagulant use and the environmental benefits of attaining lower tungsten concentration in the wastewater. However, evaluation of impacts of tungsten upon biological wastewater treatment and

the environment is limited since the required ecotoxicological information is sparse.

The raw galvanization wastewater was strongly alkaline (pH > 8) and tungsten was most likely dissolved in the form of the tungstate oxyanion ( $WO_4^{2-}$ ) at that pH [4]. Further anionic

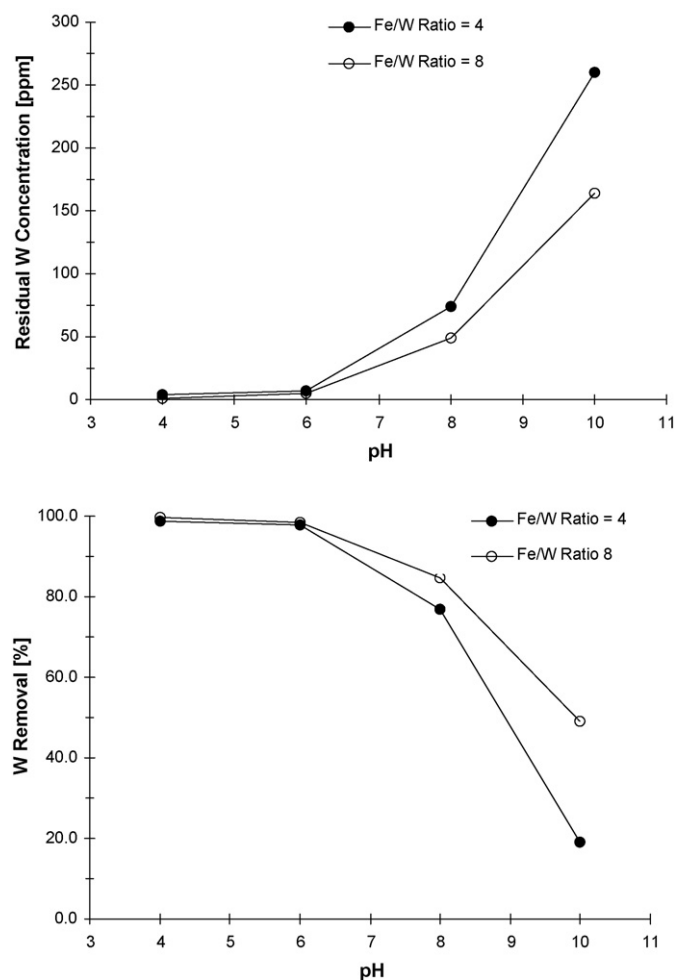


Fig. 1. Effect of pH on tungsten removal by PCF with ferric chloride expressed by residual tungsten concentration (top graph) and removal efficiency (bottom graph).

tungsten species like  $\text{HWO}_4^-$ ,  $\text{W}_2\text{O}_7^{2-}$ , and  $\text{HW}_2\text{O}_7^-$  occur sequentially when alkaline tungstate solutions are titrated down to acidic conditions [4]. Since pH was adjusted down to acidic regime (pH 4) during precipitation, coagulation and flocculation of the wastewater, various tungsten species were probably involved in the removal process.

We suggest that the main mechanism for tungsten removal was adsorption of tungstate and other tungsten oxyanions to iron hydroxide. Hydrolysis of the ferric ion produces ferric hydroxide flocks which are positively charged [5,6]. The positive charge of the ferric hydroxide surfaces is more important at low pH, which facilitates adsorption of the negatively charged tungsten oxyanions.

#### 4. Conclusions

We conclude that precipitation, coagulation, flocculation with ferric chloride can be used to remove tungstate oxyanions from industrial wastewater. Suitable process conditions (pH and ferric chloride concentration) were established by jar testing with wastewater samples. The method was found to be robust when applied in an industrial scale treatment facility.

#### Acknowledgements

The authors wish to thank the European Union (FEDER, Objective 2) and the Luxembourg's Ministry for Culture Higher Education and Research for project funding.

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