4. CHROMIC WASTWATER – CHEMICAL TREATMENT METHOD

INTRODUCTION

Chromium is an element that exists primarily in two different oxidation states, hexavalent Cr(VI) and trivalent Cr(III). The oxidation state of the Cr has a significant effect on the transport and fate of Cr and on the type and cost of treatment required to reduce Cr concentrations less than regulatory health-based standards. Cr(VI) is far more mobile than Cr(III) and more difficult to remove from water and wastewater. It is also the toxic form of Cr, approximately 10 to 100 times more toxic than Cr(III). The EPA classifies Cr(VI) as a known human carcinogen via inhalation and classify Cr(III) as not known to cause cancer. The compounds of Cr(VI) are used in many industrial applications primarily for their anti-corrosive properties. Cr(VI) can be generated during welding on stainless steel or metal structures coated with chromate paint. It is also a component of pigments in paints, inks and plastics and textile dyes. Chromic sewages are produced during chromium plating baths, chromium passivation and other processes in which chromium compounds are used. Also, the tanning industry and textile manufacturing is the source of chromic sewages. Industrial wastewaters containing chromium (H_2CrO_4, CrO_4^{2-}) have specific yellow colour. The concentration of Cr(VI) in such wastewaters ranges between 5 and 200 mg/L. The sewage containing Cr(VI) is very toxic, and without treatment can't be disposed to the sewage system.

There are several methods for chromium removal from wastewater, including chemical precipitation, sorption, ion exchange, reverse osmosis and electrodialysis.

Chemical precipitation is based on the formation of a separable solid substance from a solution, either by converting the substance into an insoluble form or by changing the composition of the solvent to diminish the solubility of the substance in it. The removal of chromium can be accomplished by the addition of reducer like for example ferrous sulphate. Ferrous ion first reduces hexavalent chromium to trivalent form by simultaneous oxidation of ferrous ion to ferric. The resulting forms can be precipitated as $Cr(OH)_3$ by NaOH or lime.

The chemical reactions of H_2CrO_4 with reducers are as follows:

(a) ferric sulfate ($FeSO_4$):

$$6\,FeSO_4 + 6\,H_2SO_4 + 2\,H_2CrO_4 \rightarrow Cr_2(SO_4)_3 + 3\,Fe_2(SO_4)_3 + 8\,H_2O$$

(b) sodium bisulfite ($NaHSO_3$):

$$6\,NaHSO_3 + 3\,H_2SO_4 + 4\,H_2CrO_4 \rightarrow 2\,Cr_2(SO_4)_3 + 3\,Na_2SO_4 + 10\,H_2O$$

(c) sodium sulfite (Na_2SO_3):

$$3\,Na_2SO_3 + 3\,H_2SO_4 + 2\,H_2CrO_4 \rightarrow Cr_2(SO_4)_3 + 3\,Na_2SO_4 + 5\,H_2O$$

(d) gaseous SO_2:

$$3\,SO_2 + 2\,H_2CrO_4 \rightarrow Cr_2(SO_4)_3 + 2\,H_2O$$

The laboratory work aims to investigate the efficiency of the chemical treatment method of chromic industrial wastewater with the use of sodium sulphite as a reducer and application of sodium hydroxide for precipitation of trivalent chromium as hydroxides.

MATERIALS & EQUIPMENT

- Glass beakers
- Graduated cylinders
- Conical flasks with corks
- Filter papers
- Pipette
- Timer/stopwatch
- Magnetic stirrer with a stirring bar

PROCEDURE

Before you start:

- Determine the amount of Cr(VI) in raw chromic wastewater in two prepared samples and calculate the average in mg/L.
- Determine the titre of sodium sulfite solution Na_2SO_3 (our reducer) in two prepared samples and calculate the average in mg/L.
- Calculate the theoretical dose (D_t) of reducer required for reduction of Cr(VI) to Cr(III) using the results obtained from step (1) and (2).

Dose calculations guide:

- Reaction: $3\ Na_2SO_3 + 3\ H_2SO_4 + 2\ H_2CrO_4 \rightarrow Cr_2(SO_4)_3 + 3\ Na_2SO_4 + 5\ H_2O$
  3 mole $Na_2SO_3 \rightarrow 2$ mole H_2CrO_4 (as Cr(VI))
- Calculate molar mass (M) of Na_2SO_3 and Cr(VI).
- Based on results obtained from step (1), calculate the amount of Na_2SO_3 required for chromium reduction in mg/L.
- Then using the data obtained in step (2) and knowing the amount of Na_2SO_3 required for chromium reduction, calculate the theoretical dose (D_t) of Na_2SO_3 in mg/L and mL/ 0.5 L.

Next:

- Determine the pH of analysed chromic wastewater.
- Prepare 3 beakers and using the 1L graduated cylinder pour 0.5 L of the raw wastewater into each beaker.
- Place the beaker on the magnetic stirrer and then immerse the pH electrode in the solution (one by one).
- In each beaker adjust the pH to about 2.0-2.5 using H_2SO_4 solution, to reduce Cr(VI) to Cr(III).
- When the pH of wastewater will be about 2.0, add the proper amount of the reducer according to the table 3 in datasheet.
- After that start adjusting the pH to about 8.5-9.0 using NaOH solution, to precipitate chromium as $Cr(OH)_3$.
- Remove the beaker from the magnetic stirrer and allow to settle the deposit for 20 min.
- Filter 200 mL of treated chromic wastewater from each beaker and determine the concentration of Cr(VI) and Na_2SO_3 (table 4, data sheet).

DATA SHEET
CHROMIC WASTWATER – CHEMICAL TREATMENT METHOD

Table 1

	Cr(VI) concentration in raw wastewater			
	Amount of $Na_2S_2O_3$ used for titration	Cr(VI) concentration (calculated from eq. *Analytical methods*)	Average concentration of Cr(VI)	pH of raw wastewater
	mL	mg/L	mg/L	-
Sample 1				
Sample 2				

Table 2

	Reducer concentration		
	Amount of $Na_2S_2O_3$ used for titration	Na_2SO_3 concentration (calculated from eq. *Analytical methods*)	Average concentration of Na_2SO_3
	mL	mg/L	mg/L
Sample 1			
Sample 2			

Table 3

	Na_2SO_3 dose calculations		
	Tested reducer dose	Calculated dose of Na_2SO_3	Amount of Na_2SO_3 added
	-	mg/L	mL per 0.5 L
Beaker 1	0.6 D_t		
Beaker 2	D_t		
Beaker 3	1.4 D_t		

Table 4

	Na_2SO_3 remaining after treatment		Cr(VI) concentration after treatment	
	Amount of $Na_2S_2O_3$ used for titration	Na_2SO_3 concentration (calculated from eq. *Analytical methods*)	Amount of $Na_2S_2O_3$ used for titration	Cr(VI) concentration (calculated from eq. *Analytical methods*)
	mL	mg/L	mL	mg/L
Beaker 1				
Beaker 2				
Beaker 3				

LABORATORY REPORT
CHROMIC WASTWATER – CHEMICAL TREATMENT METHOD

Date: ……………… Student: ……………

Table 1

	Cr(VI) concentration in raw wastewater			pH of raw wastewater
	Amount of $Na_2S_2O_3$ used for titration	Cr(VI) concentration (calculated from eq. *Analytical methods*)	Average concentration of Cr(VI)	
	mL	mg/L	mg/L	-
Sample 1				
Sample 2				

Table 2

	Reducer concentration		
	Amount of $Na_2S_2O_3$ used for titration	Na_2SO_3 concentration (calculated from eq. *Analytical methods*)	Average concentration of Na_2SO_3
	mL	mg/L	mg/L
Sample 1			
Sample 2			

Table 3

	Na_2SO_3 dose calculations	
	Tested reducer dose	Calculated dose of Na_2SO_3
	-	mg/L
Beaker 1	0.6 D_t	
Beaker 2	D_t	
Beaker 3	1.4 D_t	

Table 4

	Na_2SO_3 remaining after treatment		Cr(VI) concentration after treatment	
	Na_2SO_3 concentration (calculated from eq. *Analytical methods*)	Percent of reducer remaining in solution after treatment	Cr(VI) concentration (calculated from eq. *Analytical methods*)	Removal efficiency of Cr(VI)
	mg/L	%	mg/L	%
Beaker 1				
Beaker 2				
Beaker 3				

- Prepare the graphs using the data from table 3 and 4: (1) Na_2SO_3 dose in mg/L vs. Na_2SO_3 remaining in treated wastewater in mg/L; (2) Na_2SO_3 dose in mg/L vs. removal of Cr(VI) in %.
- Discuss and summarize obtained results.