CHAPTER 4

EXPERIMENTAL PART

Chapter 4
Experimental Part

4.1. **Batch Study**:

The batch experimental set-up used in the present work is shown schematically in figure (4.1) and photographically in figure (4.2). It consists mainly of 2 liters Plexi-glass vessel, a dc digital motor and 45^o pitched turbine impeller. The impeller was fixed in an epoxy insulated steel shaft which was connected to the digital motor. The Plexiglass vessel was 25 cm height and 15 cm diameter. Precaution was taken during run to avoid any vibrational motion in the rotating impeller. Four baffles were fixed on the wall of the vessel. Each baffle was set a part by 90^o angle from the other.

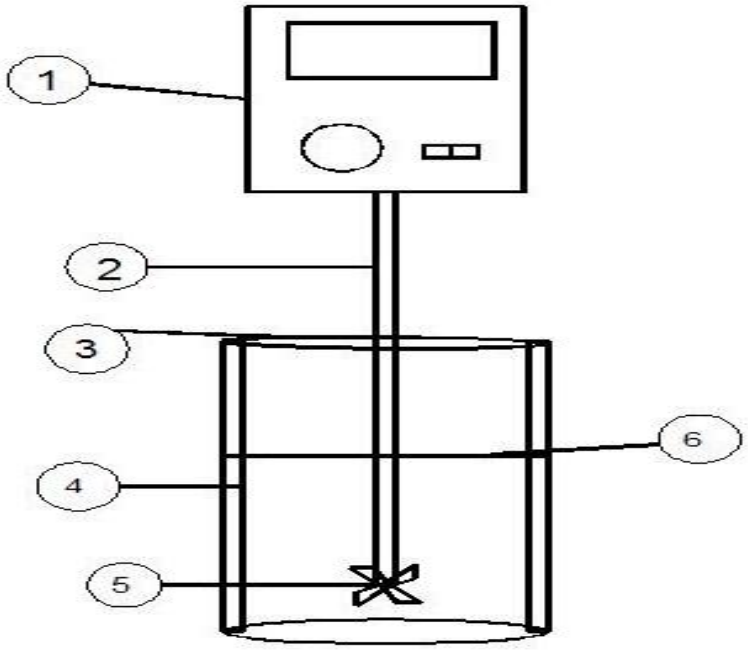

Figure 4-1 Schematic diagram of the batch experimental setup.

1- DC Digital motor
2- Insulated steel shaft
3- Plexiglas vessel
4- Baffle
5- 45^o pitched turbine impeller
6- solution level

Figure 4-2 A photo of the batch experimental setup

4.1.1 **Materials and Chemicals:**

The gel type strong base Diaion SA20A resin with (Cl^-) group which made by Mitsubishi Chemical was supplied by (Alexandria Petroleum Company). Table (4.1) shows the physical properties and specifications of the Diaion SA20A. Figure (4.3) shows the chemical structure of Diaion SA20A.

Table 4-1 The physical and chemical specification of DIAION SA20A.

Matrix	Gel Styrene divinylbenzene copolymer
Functional group	Dimethylethanolamine
Particle size range	0.3 – 1.18 mm
Uniformity coefficient	1.6 max
Ionic form as shipped	Cl^-
Volume change	15 max % $Cl^- \rightarrow OH$ form
Total exchange capacity	>1.3 meq/ml (Cl^- form)
Moisture holding capacity	45 to 52% (Cl^- form)
pH stability range	0 – 14
Operating pH range	0 – 12
Operating temperature	40^oC max. (OH^-) : 60^oC max. (Cl^-)

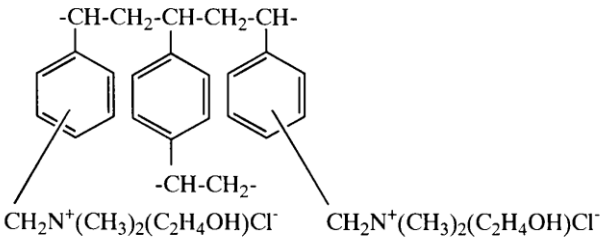

Figure 4-3 Chemical structure of DIAION SA20A resin.

All the chemicals and reagents used in the present study are analytical reagent grade.

Table (2) shows the specifications and suppliers of all chemicals and reagents used in the present study.

Table 4-2 Different chemicals and reagents used in the present work and their suppliers and purities

Chemicals	**Supplier**	**Purity**	**Chemical formula**
Potassium dichromate.	chemical limited company(R.B)	98%	$K_2Cr_2O_7$
Sulphuric acid.	(SDFCL) sd- fine chem. Limited.	98%	H_2SO_4
Phosphoric acid.	El Nasr chemical co.	pure	H_3PO_4
Sodium hydroxide	El salam company	98%	NaoH
Hydrochloric acid	El salam company	98%	HCl
Diphenyl carbazide	Alpha chemika	95%	$C1_3H_{14}N_4O$
Acetone	El Nasr chemical co.	99%	C_3H_6O

4.1.2. **Analytical Method:** [85]

Determination of Cr^{+6} Using Spectrophotometric Method

Dissolved hexavalent chromium, in the absence of interfering amounts of substances such as molybdenum, vanadium, and mercury, may be determined colorimetrically by reaction with diphenylcarbazide in acid solution. A red violet color of unknown composition is produced. The reaction is very sensitive, the absorbancy index per gram atom of chromium being about 40,000 at 540 nm.

Using1, 5-diphenyl carbazide as a complexing agent. Diphenylcarbazide gives reaction with Cr (VI) in acid medium according to the following equation:

$$2CrO_4^{2-} + 3H_4L + 8H^+ \rightarrow Cr(HL)^{2+} + Cr^{+3} + H_2L + 8H_2O \quad (4.1)$$

H_4L: 1, 5-Diphenylcarbazide H_2L: Diphenylcarbazone

Preparation of Reagents:

- Reagent water: distilled water.
- Potassium dichromate stock solution: Dissolve 2.829gm of dried potassium dichromate, $K_2Cr_2O_7$ (analytical reagent grade), in reagent water and dilute to 1 liter.
- Potassium dichromate standard solution, two liters of freshly prepared solution of heavy metal
- Diphenylcarbazide solution: Dissolve 250 mg (1,5diphenylcarbohydrazide) in 50 mL acetone. Store in a brown bottle. Prepare weekly. Discard if the solution becomes discolored.
- 0.2N $H_2SO_4$to adjust solution pH to pH = 2.0
- Conc. H_3PO_4 as a catalyst
- Acetone (analytical reagent grade)

Procedure:

- Calibration curve of Cr(VI) was constructed for potassium dichromate with concentrations range from (0.1 to 1ppm).
- A sample of Cr(VI) was prepared and 0.25 mL of conc. H_3PO_4 were added to the sample.
- About two drops of 0.2N H_2SO_4 to adjust solution to pH 2.0 { pH meter(HI 2211 Hanna instruments)}.
- The sample was placed in a 100-mL volumetric flask, dilute to 100 mL with distilled water and mix.
- A 2.0 mL diphenylcarbazide solution was added to the flask and left to stand 5 to 10 minutes for full color development.
- An appropriate portion was transfered to a 1-cm absorption cell. The absorbance was measured at 540 nm using spectrophotometer (MODEL 4401/20, Bargain).

Figure 4-4) A photo for the analysis flasks

4.1.3. **Batch Experimental Methods**:

- The resin was conditioned by treating with certain amount of conc. HCl for 15 minutes and then was washed with distilled water several times.
- The resin was then soaked in 2M NaOH for 24 hours to change the ion-exchanger from RCl to ROH form.
- The resin was washed with distilled water until the pH reached 8 to 9. [28]
- The resin was air dried and stored for batch and fixed bed studies.

- A stock solution (1000 ppm)of Cr(VI) was prepared by dissolving 2.829gm of $K_2Cr_2O_7$ in distilled water and completed to 1 litre.
- Solutions of 2M NaOH and 2M HCl were used for pH adjustment.
- Solutions of different Cr(VI) concentrations were prepared by dilution technique.
- 5 grams of the resin were contacted with 2 litres of $K_2Cr_2O_7$ of certain concentrations at a certain rpm.
- Kinetics and equilibrium studies of Cr(VI) removal by ion exchange were studied under different operation parameters. Table [4-3] shows a summary of all the investigated parameters in batch studies and their typical ranges
- A preliminary test using varying agitation speeds showed that 350rpm was high enough to well suspend the ion exchange resin. Therefore, 350rpm was used for all the experimental test runs except in studying the effect of rpm.
- The kinetics of Cr(VI) removal was followed by withdrawing sample each 5 minutes during the course of the run.
- The concentration of Cr(VI) in samples were determined using spectrophotometers(MODEL 4401/20, Bargain) .
- The % Cr(VI) removal was calculated using the equation:

$$\% \text{ removal} = \left(\frac{C_o - C_t}{C_o}\right) * 100 \qquad (4.2)$$

Where C_0 is the initial Cr^{+6} concentration, C_t is the Cr^{+6} concentration at time t.

Table 4-3 Summary of all the investigated parameters in batch studies and their typical ranges

Parameter	**Range**
Initial concentration of potassium dichromate solution, ppm.	100-500
pH	2-6
Speed of agitation, rpm.	350-600
Temperature C^o	25-40
Amount of resin, gm.	2.5- 12.5
Contact time, minutes.	0 - 120

4.2. **Fixed Bed Column Studies:**

4.2.1. **Experimental Setup:**

Figure (4.5) show the experimental setup used in conducting column studies, whereas figure (4.6) shows a photograph of the experimental setup.

The fixed-bed column studies were performed using a down flow Plexi-glass column with an internal diameter of 1.1 cm and a length of 35cm. A porous supports (piece of cloth) were fixed at column inlet and outlet to ensure good liquid distribution and to prevent resin from leakage. A 2 cm layer of glass wool was placed at the inlet section to ensure good distribution of the fluid. Another 2 cm layer of glass wool was placed above the ion exchange bed to ensure compactness of the bed and uniform liquid distribution.

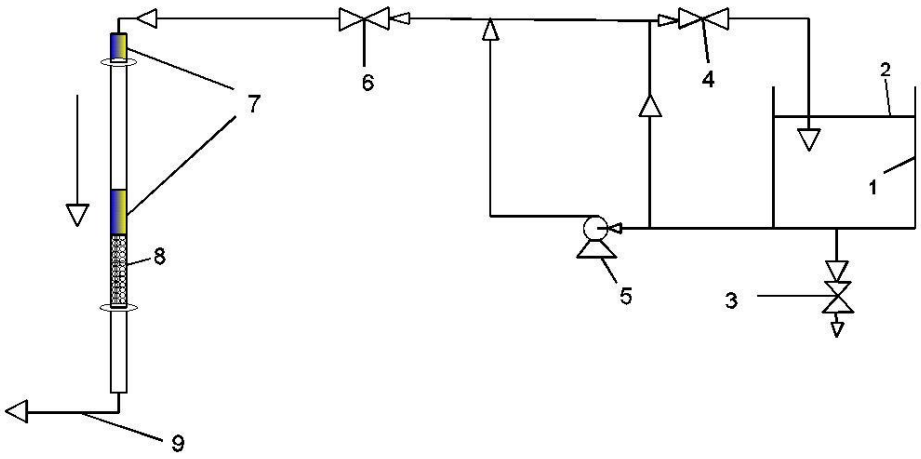

Figure 4-5 Schematic diagram of the experimental setup

1-Storage tank (influent)
2- solution level
3- Discharge valve
4- Bypass valve
5- Plastic pump
6- Main valve
7- Glass wool
8- Fixed bed of resin
9 - Effluent

Figure 4-6 a photograph of the experimental apparatus

Method:

Column was packed with 2.5, 5 and 7.5 g of Diaion SA20A to obtain a corresponding bed height of 4, 7and 12 cm respectively at 25± 2 ºC keeping flow rate, influent Cr(VI) concentration and pH constant at 60 ml/min , 500 mg/l and at pH = 4.28, respectively.

In another set of experiments the bed height was kept constant at 7 cm, while the flow rate was varied from 35 – 95 ml/min and the samples were collected at regular time intervals to determine the metal ion concentration in the effluent.