

CHEMISTRY EXTENDED ESSAY

INVESTIGATION OF REMOVING Cr(VI) IONS FROM AQUEOUS
SOLUTIONS
BY USING WASTE MATERIALS AS ADSORBENT

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ABSTRACT

In the chemistry course of national program our teacher has talked about the pollution problems related to our environment. Subject attracted my interest since all of us should be sensitive for a clean environment and to leave a clean world to the next generations. A short research led me to interest with the industrial wastes which pollute our waters. After learning the severe effects of heavy metals on human health I make a research on how to remove heavy metals from waste waters. I found that adsorption is most effective and economical method in removing heavy metals. Therefore I planned to use some waste plastics as adsorbent. By this way I was expected to remove heavy metals and convert waste plastics into useful materials. Working with the removal of Cr(VI) ions and using of PET, PAN and Cotton occurred spontaneously due to literature information and availability of the laboratory asked for help.

A toxic metallic element with a density usually 4-5 times greater than the density of water is classified as a heavy metal. Chromium and chromium compounds are cancer causing agents. Therefore, studying the removal of chromium ions with waste materials from aqueous solutions was planned. Then I asked the research question; “***Under atmospheric conditions and at room temperature, how does removal of Cr(VI) ions from aqueous solutions is affected by the solution pH, adsorption time and Cr(VI) concentration when PET, PAN and cotton are used as adsorbents?***”

Waste water bottles (PET), synthetic wool (PAN), and cotton (natural polymer) were used as adsorbent in the removal of Cr(VI) ions from aqueous solutions. Maximum Cr(VI) adsorptions are obtained at pH=5.0-5.5. Time experiments showed a fast adsorption of Cr(VI) ions onto adsorbents. Highest maximum adsorption capacity is obtained with PAN, about 3.61 ± 0.15 mg Cr(VI)/g PAN in 400.0 ± 1.1 ppm Cr(VI) solution.

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1. INTRODUCTION

Metals are naturally occurring in nature. 35 of them concern us due to their occupational and residential exposure and 23 are heavy metals such as chromium, mercury, cadmium etc. Small amounts of these elements are necessary for a good health. However, large amount may cause chronic or acute toxicity which may damage the mental and central nervous function, the blood composition and vital organs such as lungs, kidneys, and liver.

The sources of water pollution are classified as point and non-point sources. Sources that clearly discharge pollutants into waters such as factories and septic systems are point sources. Sources of pollution due to fertilizing, construction sites and mines are non-point sources. Among the most frequently discharged metals from point-sources of pollution are; copper, zinc, chromium, and nickel [1].

1.1. Heavy Metal Emission

Anthropogenic sources, specifically mining operations are the main sources of heavy metal emission [2-5]. Most serious effect is due to dissolved heavy metal compounds in waters. These compounds may stay in river bed sediments or contaminate lakes and underground sources [4,5].

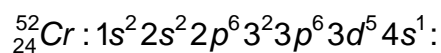
Heavy metals are metallic elements with densities 4-5 times higher than the density of water [2-7]. They are toxic in each concentration [6]. Substances with undesirable effects on the environment by decreasing the quality of life are defined as pollutant. Therefore, presence of pollutants in soil, air and water is defined as environmental pollution [6,8].

1.2. Effects of Heavy Metals on Human Health

Heavy metals stay in nature without decomposing. Small amount of these elements enter our bodies by nutrition. Small amount of some heavy metals such as Fe, Se, Zn etc. are essential for the metabolism of our body. However, at high concentrations they are toxic and poisonous, e.g., target organs of cadmium are the liver, placenta, kidneys, lungs, brain, and bones; copper causes liver and kidney damage, stomach and intestinal irritation, and anemia; long exposure to nickel may result in heart and liver damage, and skin irritation.

1.3. Effects of Chromium

Chromium is the element with symbol Cr and atomic number 24. It is a hard, bright metal which has many decorative applications. Electron configuration of Cr;



Differentiating electron enters to 3d instead of 4s due to half filled subshell stability. In reactions it may lose inner 3d electrons as well as the outer 4s electron by forming more than one type of cation. The most common oxidation states of chromium are II, III, and VI. Cr(VI) is one of the most toxic water pollutants [9-10]. Chromium pollution occurs due to weathering of mafic rocks and industrial waste [11-13].

Chromium and chromium compounds cause cancer of paranasal sinus, nasal cavity, lungs, and stomach. However, small amount of chromium

is required for the maintenance of glucose, lipid and protein metabolism [14].

The use of some chromium compounds are given in Table 1.1.

Table 1.1. Applications of some chromium compounds

Cr(VI) Compounds	Application
Chromium Trioxide, CrO_3	Chromium plating, aluminum anodizing, ceramic glazes, colored glass, inks, and paints, inorganic pigments.
Lead Chromate, PbCrO_4	Pigment in oil and industrial paints, rubber and plastics, watercolors, and printing fabrics.
Sodium Dichromate, $\text{Na}_2\text{Cr}_2\text{O}_7$	Inks, electric batteries, manufacture of chromic acid, other chromates and chrome pigments, corrosion inhibiting paints, and colorant for glass.
Zinc Chromate, ZnCrO_4	Paints for metals, varnishes and pigments in aerospace paints.

1.4. Removing of Heavy Metals

Environmental pollution increased with the increase in the world population and developed industrial applications. Therefore, removal of heavy metals from air, soil, and waters has received attention of many researchers. Different heavy metal removal techniques from wastewater have been developed [15]. Techniques that are applied in the removal of heavy metals can be given as; chemical precipitation, coagulation–flocculation, reverse osmosis, ultra-filtration and ion exchange. Among these techniques, adsorption has outstanding advantages over the others [16].

1.5. Adsorption

Removing of dissolved substances from gaseous and liquid solutions by using solid materials is defined as adsorption. Adsorption is a useful, most widely applied technique for the purification of water and air [17]. In adsorption process, dissolved substance which is defined as adsorbate accumulates on the surface of solid material which is defined as adsorbent. Adsorbate binds to the surface of the adsorbent as the result of binding forces. Schematic description of adsorption is given in Fig. 1.1.

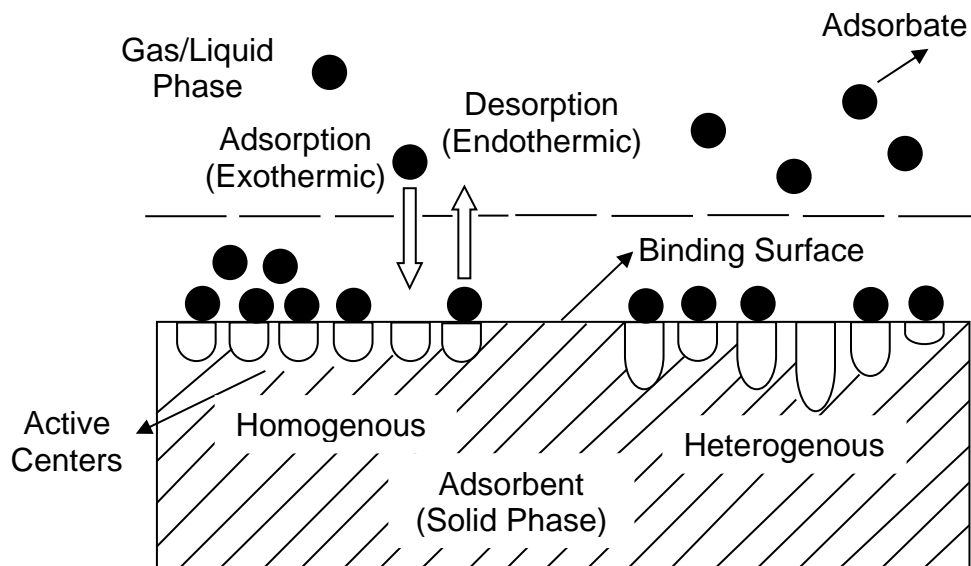


Figure 1.1. Schematic representation of adsorption process

1.6. Adsorbents

All solids, including metals and plastics, have an adsorption capacity. Examples to natural solids which are used as adsorbents can be given as;

coals, clays and some metal oxides. Examples to synthetic solids may be activated coal, silica gel, and ceramics [18].

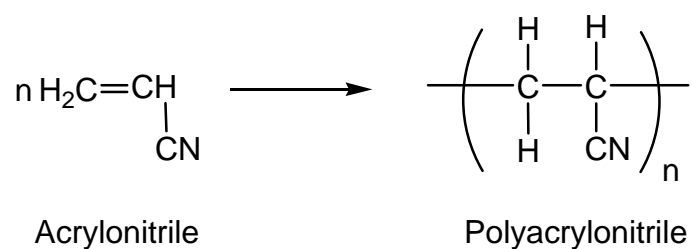
Adsorbents can be classified as inorganic adsorbents such as activated carbon, and Al_2O_3 [19-20], biological adsorbents such as several fungi and bacterias [21-22], and organic adsorbents such as ion-exchange resins and chelating polymers [23-24].

1.7. Polymers

A polymer is a large molecule built up by the repetition of small, simple chemical units. Polymers can be classified as natural and synthetic polymers. Natural polymers are rubber, cellulose, wool, etc. Synthetic polymers are chemically synthesized plastics and fibers [25].

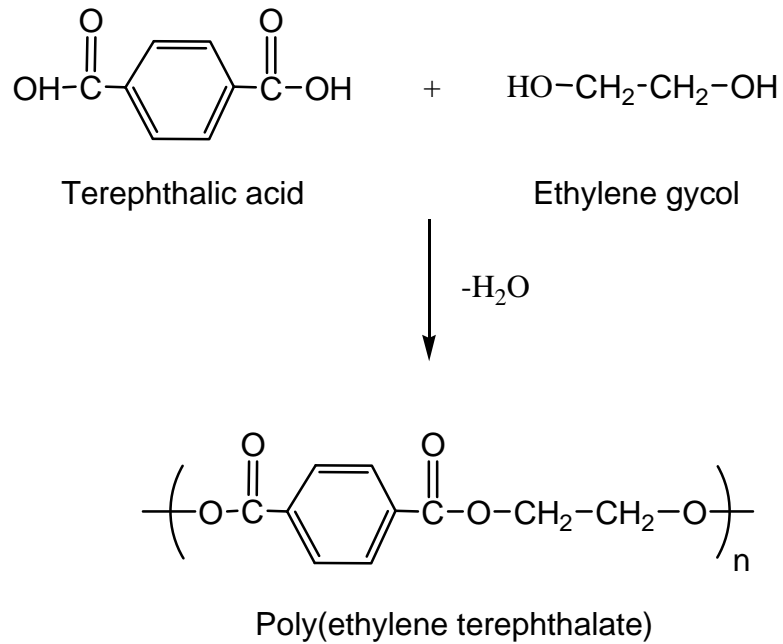
1.7.1. Polyacrylonitrile

Polyacrylonitrile (PAN) is a hard, rigid thermoplastic polymer. PAN is used instead of wool in clothing and home furnishings. Acrylonitrile polymerizes to PAN by addition polymerization. Acrylic fibers are flexible and soft. They produce lightweight lofty yarns [27].



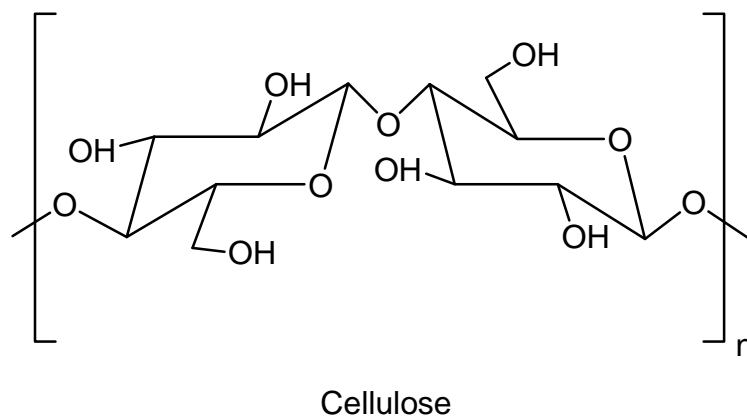
1.7.2. Poly(ethylene terephthalate)

Poly(ethylene terephthalate) (PET) forms strong, stiff synthetic fiber and resin. Condensation polymerization of terephthalic acid and ethylene glycol produces PET. It is used in artificial silk, carpets, and automobile tire yarns [27].



1.7.3. Cellulose

Cellulose is a polysaccharide. About 1/3 of all vegetables is cellulose. It is processed to produce papers, plastics and photographic films [28].



Research question:

The problems with environmental pollution and toxic effects of heavy metals led me to think on developing a method in which environmental pollutants are used in removing toxic heavy metals from wastewaters. The use of PET, PAN and Cotton as adsorbent and working with the removal of Cr(VI) occurred spontaneously due to found literature knowledge, material sources and availability of the laboratory asked for help. Therefore, the research question becomes; ***How does removal of Cr(VI) ions from aqueous solutions is affected with the solution pH, adsorption time and Cr(VI) concentration when PET, PAN and cotton are used as adsorbent at room temperature?***

1.8. Aim of The project

Environmental pollution problem became important because of the increase in world population and development in industrial applications. Presence of toxic and polluting materials in air, soil, and water is a serious environmental problem that affects our health. Therefore, these materials should be removed from the environment. Cr(VI) is a highly toxic water pollutant. Therefore, it was planned to use the waste plastics as adsorbent in removing Cr(VI) ions from aqueous solutions. By this way, it was also hoped to convert waste plastics into useful materials.

2. EXPERIMENTAL

2.1. Chemicals

$K_2Cr_2O_7$, Acros Organics, was used for the preparation of Cr(VI) solutions. Potassium hydrogen phthalate, potassium dihydrogen phthalate supplied by Carlo Erba, NaOH by Riedel-de Haën, KCl and HCl by Merck A.G. and used for the preparation of buffer solutions.

2.2. Instruments

- Precissa XB 220A model analytical balance
- Heidolph Unimax 1010 model mechanical shaker
- GBC, 933AA model flame-atomic absorption spectrometer

Research question:

How does removal of Cr(VI) ions from aqueous solution is affected with the solution pH when PET, PAN and cotton are used as adsorbent at room temperature?

Independent variables: Solution pH

Dependent variables: Amount of adsorbed Cr(VI) ions

Controlled variables: Initial Cr(VI) concentration, Amount of adsorbent, Temperature, Rate of mixing, time

2.3. Effect of Solution pH

Effect of solution pH on the maximum adsorption capacity of the adsorbents was determined by the adsorptions carried out with 30.0 ± 0.1 mL 100.0 ± 0.3 ppm solutions buffered to different pHs.

2.3.1. Adsorbents

Empty water bottles (PET), commercial synthetic wool (PAN) and commercial Cotton were used as adsorbent in the removal of Cr(VI) ions from aqueous solutions (Fig. 2.1). In order to increase Cr(VI) adsorption of PET, it was treated with 5 M NaOH for 5 hours at 70°C on a magnetic stirrer (Fig. 2.2).

Procedure

- Preparation of the adsorbents:

- Prepare 5.0 M NaOH by dissolving 50.0 g NaOH in 250 mL distilled water in a 500 mL beaker
- Add PET pieces into NaOH solution and mix
- Heat mixture at 70°C for 5 hours
- After 5 hours filter solution and wash the polymer for 4-5 times
- Dry the samples in an oven at 60-70°C
- Cut PAN and Cotton into small pieces and use as received



Figure 2.1. Materials used as adsorbent, a) PAN, b) PET, c) Cotton

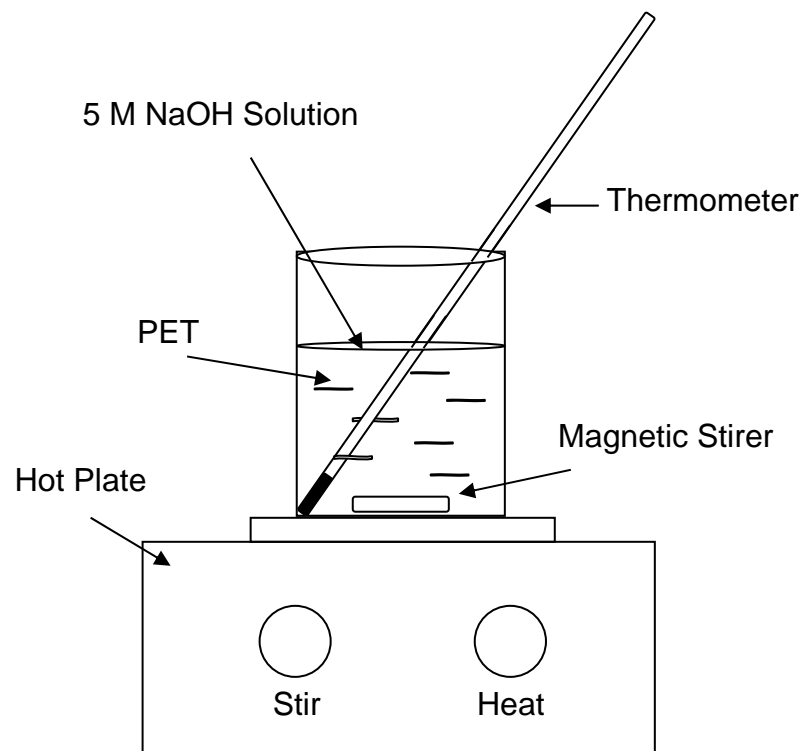


Figure 2.2. Treatment of PET with 5 M NaOH

2.3.2. Buffer Solutions

Buffer solutions were prepared according to CRC handbook [29].

- Preparation of 250 mL 0.20±0.01 M KCl solution:

$$\text{Molar mass of KCl} = 74.60 \text{ g / mol}$$

$$0.2 \text{ mol / L} \times 74.60 \text{ g / mol} = 14.92 \text{ g KCl / L}$$

$$(14.92 \text{ g KCl / 1000 mL}) \times 250 \text{ mL} = 3.73 \pm 0.01 \text{ g KCl}$$

Procedure

- Weigh 3.73±0.01 g KCl
- Dissolve with distilled water in a 250 mL volumetric flask

- Preparation of 250 mL 0.10±0.01 M Potassium hydrogenphthalate, C₈H₅KO₄, solution:

$$\text{Molar mass of C}_8\text{H}_5\text{KO}_4 = 204.10 \text{ g / mol}$$

$$0.1 \text{ mol / L} \times 204.10 \text{ g / mol} = 20.41 \text{ g C}_8\text{H}_5\text{KO}_4 / \text{L}$$

$$(15.10 \text{ g C}_8\text{H}_5\text{KO}_4 / 1000 \text{ mL}) \times 250 \text{ mL} = 5.10 \pm 0.01 \text{ g C}_8\text{H}_5\text{KO}_4$$

Procedure

- Weigh 5.10±0.01 g C₈H₅KO₄
- Dissolve with distilled water in a 250 mL volumetric flask

- **Preparation of 250 mL 0.10±0.01 M Potassium dihydrogenphosphate, KH_2PO_4 , solution:**

$$\text{Molar mass of } \text{KH}_2\text{PO}_4 = 136.10 \text{ g / mol}$$

$$0.1 \text{ mol / L} \times 136.10 \text{ g / mol} = 13.61 \text{ g } \text{KH}_2\text{PO}_4 / \text{L}$$

$$(13.61 \text{ g } \text{KH}_2\text{PO}_4 / 1000 \text{ mL}) \times 250 \text{ mL} = 3.40 \pm 0.01 \text{ g } \text{KH}_2\text{PO}_4$$

Procedure

- Weigh 3.40±0.01 g KH_2PO_4
- Dissolve with distilled water in a 250 mL volumetric flask

- **Preparation of 250 mL 0.10±0.01 M NaOH solution:**

$$\text{Molar mass of } \text{NaOH} = 40.00 \text{ g / mol}$$

$$0.1 \text{ mol / L} \times 40.00 \text{ g / mol} = 4.00 \text{ g } \text{NaOH} / \text{L}$$

$$(4.00 \text{ g } \text{NaOH} / \text{L} / 1000 \text{ mL}) \times 250 \text{ mL} = 1.00 \pm 0.01 \text{ g } \text{NaOH}$$

Procedure

- Weigh 1.00±0.01 g NaOH
- Dissolve with water in a 250 mL volumetric flask

- **Preparation of 250 mL 0.10±0.01 M and 0.20±0.01 M HCl solutions from concentrated HCl solution (37%, 1.19 g/mL):**

$$\text{Molar mass of } \text{HCl} = 36.50 \text{ g / mol}$$

$$0.1 \text{ mol / L} \times 36.50 \text{ g / mol} = 3.65 \text{ g } \text{HCl} / \text{L}$$

$$0.2 \text{ mol / L} \times 36.50 \text{ g / mol} = 7.30 \text{ g } \text{HCl} / \text{L}$$

$$(3.65 \text{ g HCl} / 1000 \text{ mL}) \times 250 \text{ mL} = 0.91 \text{ g HCl}$$

$$(7.30 \text{ g HCl} / 1000 \text{ mL}) \times 250 \text{ mL} = 1.83 \text{ g HCl}$$

Since the concentrated HCl solution is 37%,

$$\frac{100 \text{ g concentrated HCl}}{37 \text{ g HCl}} \times 0.91 \text{ g HCl} = 2.47 \text{ g concentrated HCl}$$

$$\frac{100 \text{ g concentrated HCl}}{37 \text{ g HCl}} \times 1.83 \text{ g HCl} = 4.93 \text{ g concentrated HCl}$$

Hence, the volumes that should be taken;

$$1.19 \text{ mL} / \text{g HCl} \times 2.47 \text{ g HCl} = 2.07 \pm 0.01 \text{ mL concentrated HCl}$$

$$1.19 \text{ mL} / \text{g HCl} \times 4.93 \text{ g HCl} = 4.14 \pm 0.01 \text{ mL concentrated HCl}$$

Procedure

- Take 2.07 ± 0.01 mL and 4.14 ± 0.01 mL concentrated HCl by a pipette into separate 250 mL volumetric flasks and fill with water up to mark

- Example: Preparation of $\text{pH}=1.00 \pm 0.01$ buffer solution

Procedure

- Take 25.0 ± 0.3 mL 0.20 M KCl and 67.0 ± 0.6 mL 0.20 M HCl with a graduated cylinder into a 100 mL volumetric flask
- Complete the volume to 100 mL with distilled water

Details of the preparation of buffer solutions are given in Table 2.1.

Table 2.1. Preparation of buffer solutions*

pH ±0.01	Buffer	Preparation ($V_{\text{total}}=100 \text{ mL}$)**
1.00	KCl/HCl	25.0±0.1 mL 0.20 M KCl + 67.0±0.1 mL 0.20 M HCl
2.00	KCl/HCl	25.0±0.1 mL 0.20 M KCl + 6.5±0.1 mL 0.20 M HCl
3.00	C ₈ H ₅ KO ₄ /HCl	50.0±0.1 mL 0.10 M C ₈ H ₅ KO ₄ + 22.3±0.1 mL 0.10 M HCl
4.00	C ₈ H ₅ KO ₄ /HCl	50.0±0.1 mL 0.10 M C ₈ H ₅ KO ₄ + 0.10±0.01 mL 0.10 M HCl
5.00	C ₈ H ₅ KO ₄ /NaOH	50.0±0.1 mL 0.10 M C ₈ H ₅ KO ₄ + 22.6±0.1 mL 0.10 M NaOH
5.50	C ₈ H ₅ KO ₄ /NaOH	50.0±0.1 mL 0.10 M C ₈ H ₅ KO ₄ + 36.6±0.1 mL 0.10 M NaOH
6.00	KH ₂ PO ₄ /NaOH	50.0±0.1 mL 0.10 M KH ₂ PO ₄ + 5.6±0.1 mL 0.10 M NaOH

C₈H₅KO₄: Potassium hydrogenphthalate, KH₂PO₄: Potassium dihydrogenphosphate

*Acid/Base amounts are taken from the handbook and formation of given buffers are accepted without performing any measurement

** Solutions are diluted to 100 mL

2.3.3. Preparation of 1000 mL 500.0±0.3 ppm Cr(VI) Stock Solution

$$\frac{500 \text{ mg Cr(VI)}}{1000 \text{ mL}} \times 500 \text{ mL} = 500 \text{ mg Cr(VI)} \text{ is needed.}$$

Molar mass of K₂Cr₂O₇ = 294.2 g / mol

Atomic mass of Cr = 52 amu

Thus, 2x52 = 104.0 g Cr presents in 294.2 g K₂Cr₂O₇.

Hence, 500 mg (0.5 g) Cr(VI) presents in,

$$\frac{294.2 \text{ g K}_2\text{Cr}_2\text{O}_7}{104.0 \text{ g Cr}} \times 0.5 \text{ g Cr} = 1.4144 \text{ g} \pm 0.0002 \text{ K}_2\text{Cr}_2\text{O}_7$$

Procedure

- Weigh 1.4144±0.0002 g K₂Cr₂O₇ on analytical balance
- Dissolve with distilled water in a 1 L volumetric flask

Uncertainties in the concentrations and obtained results are calculated according to K. A. Tsokos [30] all over the text by using the informations given in Table 2.2.

Table 2.2. Uncertainty of the used glassware and instrument

Instrument	Uncertainty (\pm)*
Balance, analytical	0.0002 g
1 mL pipet	0.006 mL
5 mL pipet	0.01 mL
10 mL pipet	0.02 mL
25 mL pipet	0.03 mL
25 mL graduated cylinder	0.3 mL
50 mL graduated cylinder	0.4 mL
100 mL graduated cylinder	0.6 mL
100 mL volumetric flask	0.08 mL
500 mL volumetric flask	0.2 mL

*Given uncertainties with the instrument/glassware (used to find out the uncertainties in calculations)

Uncertainty in 500.0 ± 0.3 ppm stock solution calculated as;

$$C = \frac{m}{V}, \text{ then,}$$

$$\frac{\Delta C}{C_o} = \frac{\Delta m}{m_o} + \frac{\Delta V}{V_o} = \frac{0.0002}{1.1144} + \frac{0.2}{500.0} = 0.0005$$

$$\Delta C = C_o \times \frac{\Delta C}{C_o} = 500.0 \times 0.0005 = 0.3.$$

Concentration of the stock solution is, $C = 500.0 \pm 0.3$ ppm

2.3.4. Preparation of 30 mL 100.0 ± 0.3 ppm Cr(VI) Solution

100.0 ± 0.3 ppm Cr(VI) solution was prepared according to equation

2.1.

$$C_1 \times V_1 = C_2 \times V_2 \quad (2.1)$$

C_1 : Concentration of the stock solution, V_1 : Volume of the stock solution that should be taken. C_2 and V_2 are the concentration and volume of the adsorption solution. Thus, the necessary volume of the stock solution;

$$V_1 = \frac{C_2 \times V_2}{C_1} \quad (2.2)$$

$$V_1 = \frac{100.0 \text{ ppm} \times 30.0 \text{ mL}}{500.0 \text{ ppm}} = 6.0 \text{ mL}$$

Procedure

- Take 6.0 mL 500.0±0.3 ppm stock solution into a flask with a pipette
- Add 21.0 mL distilled water and 3.0 mL buffer solution

Uncertainty in the concentration of the solutions;

$$\text{Amount of Cr(VI) in 6.0 mL of stock solution} = \frac{500.0 \text{ mg}}{1000.0 \text{ mL}} \times 6.0 \text{ mL} = 3.0 \text{ mg}$$

$$\frac{\Delta m}{m_o} = \frac{\Delta m}{m_o} + \frac{\Delta V}{V_o} = \frac{3.0}{500.0} + \frac{0.02}{6.00} = 0.009$$

$$\text{Therefore, } \Delta m = m_o \times \frac{\Delta m}{m_o} = 3.0 \times 0.009 = 0.03. \text{ Hence, } m = 3.00 \pm 0.03 \text{ mg}$$

$$\text{Total dilution volume, } V_{Tot} = 6.0 + 21.0 + 3.0 = 30.0 \text{ mL}.$$

$$\text{Uncertainty in the volume; } 0.02 + 0.03 + 0.01 = 0.06 \text{ mL}.$$

$$\text{Hence, } V_{Tot} = 30.0 \pm 0.1 \text{ mL}.$$

Since, $C = \frac{m}{V}$, then,

$$\frac{\Delta C}{C_o} = \frac{\Delta m}{m_o} + \frac{\Delta V}{V_o} = \frac{0.03}{3.00} + \frac{0.1}{30.0} = 0.01$$

Therefore, $\Delta C = C_o \times \frac{\Delta C}{C_o} = 30.0 \times 0.01 = 0.3$. Hence, $C = 100.0 \pm 0.3 \text{ ppm}$.

Procedure

- Take six 100 mL Erlen Meyer flasks for each adsorbent. Label six as PET, six as PAN and six as Cotton
- Weigh ~0.3 g from each adsorbent and put into Erlen Meyer flasks of each set
- Take eighteen 50 mL volumetric flasks
- Take 6.0 mL 100.0 ± 0.3 ppm Cr(VI) solution, add 21.0 mL distilled water and 3.0 mL pH=1.0, 2.0, 3.0, 4.0, 5.0 and 6.0 buffer solutions
- Write pH of the used buffer on each flask, e.g., PET-pH=2.0, PAN-pH=4.0 or Cotton-pH=5.0, etc.
- Start adsorption by pouring the solutions onto adsorbents
- Put flasks onto mechanical shaker (Fig. 2.3)
- Shake mixtures at 100 rpm for two hours at room temperatures
- At the end of adsorption filter the solutions
- Take 1.0 mL solution into a flask and add 9.0 mL distilled water
- Analyze Cr(VI) concentration with AAS as described in section 2.3.5
- Calculate adsorbed amount of Cr(VI) ions and find the pH that maximum adsorption takes place

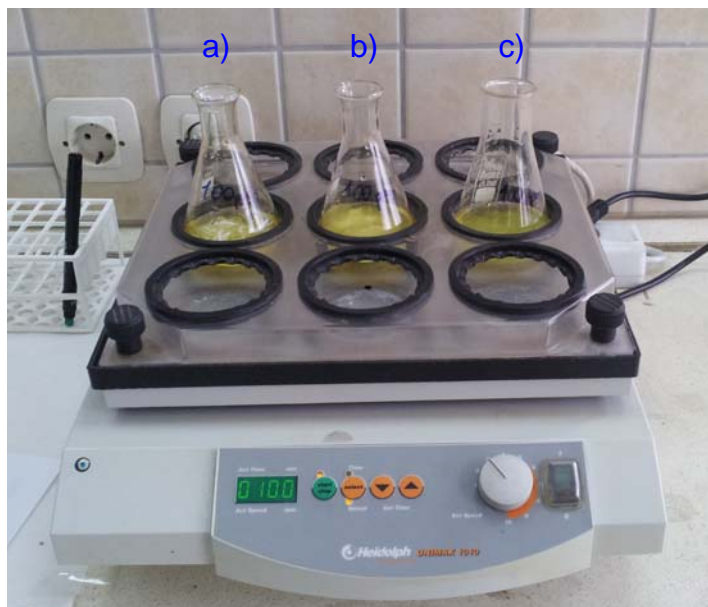


Figure 2.3. Shaking the solutions at 100 rpm. a) PAN, b) Cotton, c) PET

2.3.5. Atomic Absorption Spectrophotometer

The Cr(VI) concentration of the solutions was measured on a GBC 933AA model flame-Atomic Absorption Spectrophotometer (AAS). A photograph of the instrument is given in Figure 2.3. Analyses were carried out at Kırıkkale University, Chemistry department. Analyses were carried out by running the solutions and controlling the instrument from the computer. Atomization medium was air/acetylene.

AAS was calibrated before analysis with Cr(VI) solutions with known concentrations. Calibration solutions were prepared from 100.0 ± 0.3 ppm Cr(VI) solution. Preparation of the solutions is described in Table 2.3.

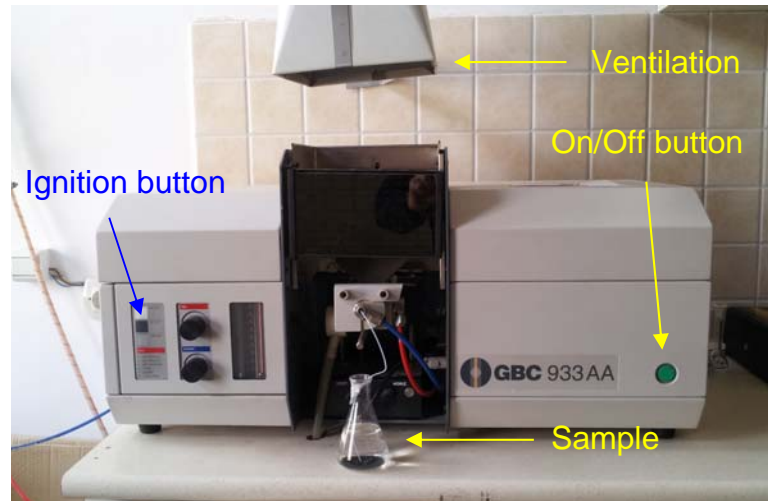


Figure 2.4. GBC 933AA model flame Atomic Absorption Spectrophotometer

Procedure

- Example: Preparation of 100.0 mL 4.0±0.1 ppm Cr(VI) solution

$$V_1 = \frac{C_2 \times V_2}{C_1} = \frac{4.0 \text{ ppm} \times 25.0 \text{ mL}}{100.0 \text{ ppm}} = 1.0 \text{ mL}$$

- Take 1.0 mL 100.0±0.3 ppm Cr(VI) solution by a pipette into a 25.0 mL volumetric flask
- Add 21.0 mL distilled water and 3.0 mL pH=5.0 buffer

Uncertainties in the concentration of calibration solutions are calculated as described in section 2.3.4. The details are given in Table 2.3.

Table 2.3. Preparation of calibration solutions

Concentration Ppm (± 0.1)	$V_{\text{(Stock Solution)}}$ mL (± 0.1)	$V_{\text{(Water)}}$ mL (± 0.1)	$V_{\text{(Buffer)}}$ mL (± 0.1)
4.0	1.0	21.0	3.0
8.0	2.0	20.0	3.0
12.0	3.0	19.0	3.0
16.0	4.0	18.0	3.0
20.0	5.0	17.0	3.0

$$V_{\text{solution}} = 25.0 \pm 0.1 \text{ mL}$$

Procedure

- Operation of AAS

- Operate the instrument and run chromium analysis program
- Push ignition button
- Calibrate instrument with standard solutions
- Run solutions with unknown concentrations

Research question:

How does removal of Cr(VI) ions from aqueous solution is affected by the adsorption time when PET, PAN and cotton are used as adsorbent at room temperature?

Independent variables: Adsorption time

Dependent variables: Amount of adsorbed Cr(VI) ions

Controlled variables: Initial Cr(VI) concentration, Amount of adsorbent, Solution pH, Temperature, Rate of mixing

2.4. Effect of Adsorption Time

Variation in the amount of adsorbed Cr(VI) with time was studied with 30.0 mL 100.0±0.3 ppm Cr(VI) solution for 15, 30, 60, 90 and 120 min.

Procedure

- Take six 100 mL Erlen Meyer flasks for each adsorbent. Label six as PET, six as PAN and six as Cotton
- Weigh ~0.3 g from each adsorbent and put into the flask of each set
- Take eighteen 50 mL volumetric flasks
- Take 6.0 mL 100.0±0.3 ppm Cr(VI) solution by a pipette to each volumetric flask
- Add 21.0 mL distilled water and 3.0 mL pH=5.0 buffer solution
- Write adsorption periods on the flasks, e.g., PET-15 min, PAN-60 min or Cotton-120 min, etc.
- Start adsorption by pouring the Cr(VI) solutions onto adsorbents
- Note initial adsorption time and immediately put flasks onto mechanical shaker (Fig. 2.3)
- Shake mixtures for desired time at 100 rpm
- At the end of 15 min, take out the flasks labeled as PET-15 min, PAN-15 min and Cotton-15 min and immediately filter the solutions
- Take 1.0 mL from each solution to separate flasks and add 9.0 mL distilled water to each
- Filter the remained solutions at the end 30, 60, 90 and 120 min as described above and dilute 1.0 mL of each with 9.0 mL of water. Note: Do not forget to label the flasks before use

- Analyze Cr(VI) concentration of the solutions
- Calculate adsorbed amount of Cr(VI) ions for each period

Research question:

How does removal of Cr(VI) ions from aqueous solution is affected by the initial Cr(VI) concentration when PET, PAN and cotton are used as adsorbent at room temperature?

Independent variables: Initial Cr(VI) concentration

Dependent variables: Amount of adsorbed Cr(VI) ions

Controlled variables: Amount of adsorbent, Solution pH, Temperature, Rate of mixing, time, pH

2.5. Effect of Solution Concentration

Effect of initial concentration on the adsorption capacities of adsorbents were studied with 30.0, 60.0, 100.0, 150.0, 250.0, and 400.0 ppm Cr(VI) solutions.

Solutions were prepared as described in Section 2.3.4. Details are given in Table 2.4.

Table 2.4. Preparation of solutions with different Cr(VI) concentration

Concentration ppm	V _(Stock Solution) mL (± 0.1)	V _(Water) mL (± 0.1)	V _(Buffer) mL (± 0.1)
30.0 \pm 0.2	1.8	25.2	3.0
60.0 \pm 0.3	3.6	23.4	3.0
100.0 \pm 0.3	6.0	21.0	3.0
150.0 \pm 0.5	9.0	18.0	3.0
250.0 \pm 0.7	15.0	12.0	3.0
400.0 \pm 1.1	24.0	3.0	3.0

$$V_{\text{solution}}=30.0\pm 0.1 \text{ mL}$$

Procedure

- Take six 100 mL Erlen Meyer flasks for each adsorbent. Label six as PET, six as PAN and six as Cotton
- Weigh ~ 0.3 g from each adsorbent, put into the flasks of each set
- Take eighteen 50 mL volumetric flasks
- Take calculated amount of 500.0 \pm 0.3 ppm Cr(VI) solution into volumetric flasks. Follow the instructions given in Table 2.4. e.g., for the preparation of 30.0 \pm 0.2 ppm Cr(VI) solution take 1.8 mL of stock solution into a flask, add 25.2 mL water and 3.0 mL pH=5.0 buffer
- Write the concentration on each flask, e.g., PET-30 ppm, PAN-100 ppm or Cotton-400 ppm
- Start adsorption by pouring Cr(VI) solution onto adsorbent
- Put flasks onto mechanical shaker and shake mixtures at 100 rpm for two hours (Fig. 2.3)
- At the end of adsorption filter the solutions
- Take 1.0 mL solution to a flask and add 9.0 mL distilled water. Note: Be careful to take the solution to the flask labeled with same concentration.

- Analyze Cr(VI) concentration of solutions as described in section 2.3.5
- Calculate adsorbed amount of Cr(VI) ions for each solution

2.6. Data Collection and Processing

After adsorption, Cr(VI) concentration of the solutions was found to be out of calibration (higher than 20 ppm). Therefore, measurements were carried out with diluted solutions and measured concentration named as C_{Measured} . Actual Cr(VI) concentration of the solutions, C , is calculated according to eq. 2.3.

$$C = (C_{\text{Measured}} \times V_{\text{Dilution}}) \text{ ppm Cr(VI)} \quad 2.3$$

2.6.1. Effect of Solution pH on Adsorptions

- Effect of Solution pH on Cr(VI) adsorption of PET

Data of pH experiments of PET are given in Table 2.5.

Table 2.5. Data for Cr(VI) adsorption on PET with solution pH

pH	m_{PET}	Dilution	C_{Measured}	C
± 0.01	$\pm 0.0002 \text{ g}$	$\pm 0.03 \text{ mL}$	$\pm 0.03 \text{ ppm}$	$\pm 0.3 \text{ ppm}$
1.00	0.3003	1/10	9.73	97.3
2.00	0.3006	1/10	9.72	97.2
3.00	0.3020	1/10	9.65	96.5
4.00	0.3023	1/10	9.31	93.4
5.00	0.3035	1/10	8.81	88.1
5.50	0.3005	1/10	8.75	87.5
6.00	0.3012	1/10	8.75	87.5

$$C_0 = 100.0 \pm 0.3 \text{ ppm}, V_{\text{solution}} = 30.0 \pm 0.1 \text{ mL}, t = 7200.0 \pm 0.2 \text{ sec}, T = 25.0 \pm 0.1^\circ\text{C}$$

Adsorbed amount of Cr(VI) ions was calculated from the initial and final concentrations.

C_o : Initial Cr(VI) concentration, ppm

C : Cr(VI) concentration after adsorption

Then,

Amount of adsorbed Cr(VI) ions = $C_o - C$, ppm

Adsorbed amount in a certain volume,

Amount of adsorbed Cr(VI) ions in $V_{Soln} = \frac{C_o - C \text{ mg Cr(VI)}}{1000 \text{ mL}} \times V_{Soln}$

Dividing the calculated value by used weight of the adsorbent gives adsorbed amount of Cr(VI) ions in mg by 1 gram of adsorbent and this ratio is symbolized as q . q can be formulated as,

$$q = \frac{C_o - C \text{ mg Cr(VI)}}{1000 \text{ mL}} \times \frac{V_{Soln} \text{ mL}}{m} \quad (2.3)$$

m : Weight of the adsorbent in grams.

Adsorbed amount of Cr(VI) onto PET pieces is calculated according to

eq. 2.3. e.g., for pH=1.0,

$$q = \frac{(100.0 - 97.3) \text{ mg Cr(VI)}}{1000 \text{ mL}} \times \frac{30.0 \text{ mL}}{0.3003 \text{ g PET}} = 0.27 \pm 0.06 \text{ mg Cr(VI) / g PET}$$

Uncertainty in adsorbed amount of Cr(VI) ions was calculated as done previously (Section 2.3.4)

Solution concentration, $C_o = 100.0 \pm 0.3 \text{ ppm}$

9 (± 0.02) mL water was added to 1 (± 0.006) mL adsorption solution.

Therefore, $V_{Dilution} = 10.00 \pm 0.03 \text{ mL}$

Error in spectroscopic measurement = $\pm 0.001 \text{ ppm}$

For pH=1.0,

$$\frac{\Delta C}{C_o} = \frac{0.001}{9.734} + \frac{0.03}{10.00} = 0.003.$$

$$\Delta C \times C_o = 9.734 \times 0.003 = 0.03$$

Hence, $C = 97.3 \pm 0.3 \text{ ppm}$

$$C_o - C = 100.0 \pm 0.3 - 97.3 \pm 0.3 = 2.7 \pm 0.6 \text{ ppm}$$

Uncertainty in q,

$$\frac{\Delta q}{q_o} = \frac{0.6}{2.7} + \frac{0.05}{30.00} + \frac{0.0002}{0.3003} = 0.22$$

$$\Delta q = 0.27 \times 0.22 = 0.06$$

Hence, adsorption at pH=1.0 is,

$$q = 0.27 \pm 0.06 \text{ mg Cr(VI)/g PET}$$

Details of the calculations are given in Table 2.6.

Table 2.6. Effect of solution pH on Cr(VI) adsorption of PET

pH ±0.01	m _{PET} ±0.0002 g	C ±0.3 ppm	q ±0.06 mg Cr(VI)/g PET
1.00	0.3003	97.3	0.27
2.00	0.3006	97.2	0.28
3.00	0.3020	96.5	0.35
4.00	0.3023	93.1	0.68
5.00	0.3035	88.1	1.18
5.50	0.3005	87.5	1.25
6.00	0.3012	87.5	1.25

$$C_o = 100.0 \pm 0.3 \text{ ppm}, V_{\text{solution}} = 30.0 \pm 0.1 \text{ mL}, t = 7200.0 \pm 0.2 \text{ sec}, T = 25.0 \pm 0.1^\circ\text{C}$$

Results show the increase in Cr(VI) adsorption with the increase in pH.

- Effect of Solution pH on Cr(VI) adsorption of PAN

Variation in Cr(VI) adsorption of PAN with PH was studied as described in section 2.3. Obtained data are given in Table 2.7.

Table 2.7. Data for Cr(VI) adsorption on PAN with solution pH

pH ± 0.01	m_{PAN} ± 0.0002 g	Dilution ± 0.03 mL	C_{Measured} ± 0.03 ppm	C ± 0.3 ppm
1.00	0.3006	1/10	9.33	93.3
2.00	0.3009	1/10	9.31	93.1
3.00	0.3013	1/10	9.18	91.8
4.00	0.3003	1/10	8.94	89.4
5.00	0.3013	1/10	8.72	87.2
5.50	0.3009	1/10	8.69	86.9
6.00	0.3002	1/10	8.68	86.8

$C_o=100.0\pm 0.3$ ppm, $V_{\text{solution}}=30.0\pm 0.1$ mL, $t=7200.0\pm 0.2$ sec, $T=25.0\pm 0.1^\circ\text{C}$

Adsorbed amount of Cr(VI) ions onto PAN and uncertainties were calculated as described before. Results are given in Table 2.8.

Table 2.8. Effect of solution pH on Cr(VI) adsorption of PAN

pH ± 0.01	m_{PAN} ± 0.0002 g	C ± 0.3 ppm	q ± 0.06 mg Cr(VI)/g PAN
1.00	0.3006	93.3	0.67
2.00	0.3009	93.1	0.69
3.00	0.3013	91.8	0.82
4.00	0.3003	89.4	1.06
5.00	0.3013	87.2	1.28
5.50	0.3009	86.9	1.31
6.00	0.3002	86.8	1.32

$C_o=100.0\pm 0.3$ ppm, $V_{\text{solution}}=30.0\pm 0.1$ mL, $t=7200.0\pm 0.2$ sec, $T=25.0\pm 0.1^\circ\text{C}$

Results show that adsorbed amount of Cr(VI) increases with the increases in pH.

- Effect of Solution pH on Cr(VI) Adsorption of Cotton

Effect of pH on Cr(VI) adsorption of cotton was also studied. Obtained data are given in Table 2.9. Adsorbed amount of Cr(VI) ions and uncertainties were calculated as described previously. Results are given in Table 2.10.

Table 2.9. Data for Cr(VI) adsorption on Cotton with solution pH

pH ± 0.01	m_{Cotton} ± 0.0002 g	Dilution ± 0.03 mL	C_{Measured} ± 0.03 ppm	C ± 0.3 ppm
1.00	0.3003	1/10	9.88	98.8
2.00	0.3006	1/10	9.88	98.8
3.00	0.3020	1/10	9.81	98.1
4.00	0.3023	1/10	9.40	94.0
5.00	0.3035	1/10	8.87	88.7
5.50	0.3011	1/10	8.82	88.2
6.00	0.3008	1/10	8.82	88.2

$$C_0 = 100.0 \pm 0.3 \text{ ppm}, V_{\text{solution}} = 30.0 \pm 0.1 \text{ mL}, t = 7200.0 \pm 0.2 \text{ sec}, T = 25.0 \pm 0.1^\circ\text{C}$$

Table 2.10. Effect of solution pH on Cr(VI) adsorption of Cotton

pH ± 0.01	m_{Cotton} ± 0.0002 g	C ± 0.3 ppm	q ± 0.06 mg Cr(VI)/g Cotton
1.00	0.3003	98.8	0.12
2.00	0.3006	98.8	0.12
3.00	0.3020	98.1	0.19
4.00	0.3023	94.0	0.59
5.00	0.3035	88.7	1.12
5.50	0.3011	88.2	1.18
6.00	0.3008	88.2	1.18

$$C_0 = 100.0 \pm 0.3 \text{ ppm}, V_{\text{solution}} = 30.0 \pm 0.1 \text{ mL}, t = 7200.0 \pm 0.2 \text{ sec}, T = 25.0 \pm 0.1^\circ\text{C}$$

An increase in adsorption with pH was also observed for Cotton. Obtained adsorption values are plotted against to pH. Figure 2.5 shows that low adsorptions values increase with the increase in pH. The maximum adsorptions are obtained at pH's 5.0-6.0. In order to prevent precipitation of Cr(VI) working pH was selected as 5.0.

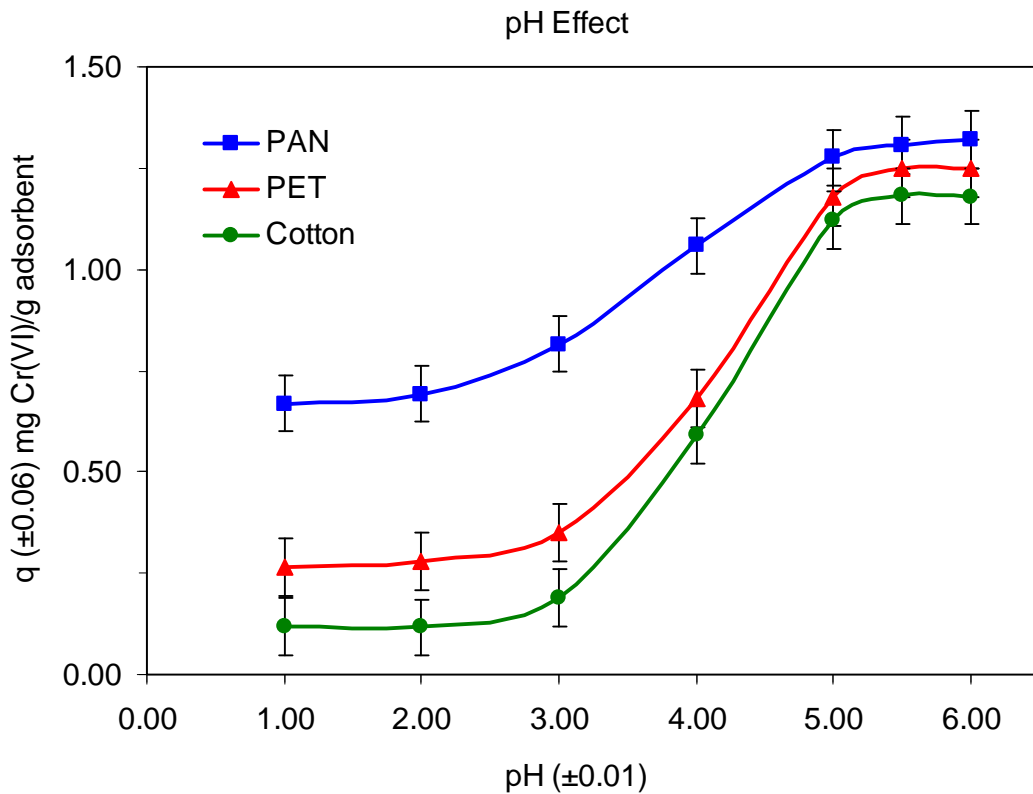


Figure 2.5. Variation in Cr(VI) adsorption with solution pH

$$C_0=100.0\pm 0.3 \text{ ppm}, V_{\text{solution}}=30.0\pm 0.1 \text{ mL}, t=7200.0\pm 0.2 \text{ sec},$$

$$T=25.0\pm 0.1^\circ\text{C}$$

2.6.2. Effect of Time on Adsorptions

- Effect of Time on Cr(VI) Adsorption of PET

Variation in adsorption with time was also studied. Experiments were carried out as described in section 2.3.4. Obtained results are given in Table

2.11. Adsorbed amount of ions was calculated from the initial and found concentrations as described in section 2.6.1 and are given in Table 2.12.

Table 2.11. Data for Cr(VI) adsorption on PET with time

Time ± 0.2 sec	m_{PET} ± 0.0002 g	Dilution ± 0.03 mL	C_{Measured} ± 0.03 ppm	C ± 0.3 ppm
900.0	0.3047	1/10	9.10	90.3
1800.0	0.3045	1/10	8.81	87.7
3600.0	0.3061	1/10	8.74	87.4
5400.0	0.3046	1/10	8.73	87.3
7200.0	0.3016	1/10	8.74	87.4

$C_0=100.0\pm 0.3$ ppm, $V_{\text{solution}}=30.0\pm 0.1$ mL, pH=5.00 \pm 0.01, T=25.0 \pm 0.1°C

Table 2.12. Effect of adsorption time on Cr(VI) adsorption of PET

Time ± 0.2 sec	m_{PET} ± 0.0002 g	C ± 0.3 ppm	q ± 0.06 mg Cr(VI)/g PET
900.0	0.3047	90.3	0.88
1800.0	0.3045	87.7	1.17
3600.0	0.3061	87.4	1.24
5400.0	0.3046	87.3	1.25
7200.0	0.3016	87.4	1.25

$C_0=100.0\pm 0.3$ ppm, $V_{\text{solution}}=30.0\pm 0.1$ mL, pH=5.00 \pm 0.01, T=25.0 \pm 0.1°C

Results show the increase in adsorption with time. The fast adsorption in the beginning slows down in about 60 min and almost reaches to equilibrium in 90 min.

- Effect of Time on Cr(VI) Adsorption of PAN

Variation in adsorption of Cr(VI) onto PAN with time was studied, also.

Obtained data are given in table 2.13.

Table 2.13. Data for Cr(VI) adsorption on PAN with time

Time ± 0.2 sec	m_{PAN} ± 0.0002 g	Dilution ± 0.03 mL	C_{Measured} ± 0.03 ppm	C ± 0.3 ppm
900.0	0.3003	1/10	9.04	90.4
1800.0	0.3006	1/10	8.75	87.5
3600.0	0.3020	1/10	8.65	86.5
5400.0	0.3023	1/10	8.64	86.4
7200.0	0.3035	1/10	8.63	86.3

$C_0=100.0\pm 0.3$ ppm, $V_{\text{solution}}=30.0\pm 0.1$ mL, pH=5.00 \pm 0.01, T=25.0 \pm 0.1°C

Adsorbed amount of Cr(VI) was calculated from the initial and remained concentrations. Results are given in Table 2.14.

Table 2.14. Effect of adsorption time on Cr(VI) adsorption of PAN

Time ± 0.2 sec	m_{PAN} ± 0.0002 g	C ± 0.3 ppm	q ± 0.06 mg Cr(VI)/g PAN
900.0	0.3003	90.4	0.96
1800.0	0.3006	87.5	1.25
3600.0	0.3020	86.5	1.34
5400.0	0.3023	86.4	1.35
7200.0	0.3035	86.3	1.35

$C_0=100.0\pm 0.3$ ppm, $V_{\text{solution}}=30.0\pm 0.1$ mL, pH=5.00 \pm 0.01, T=25.0 \pm 0.1

Results show that adsorption increases with time and slows down in about 60 min.

- Effect of Time on Cr(VI) Adsorption of Cotton

Data of variation in adsorption of Cr(VI) onto cotton with time are given in Table 2.15.

Table 2.15. Data for Cr(VI) adsorption on Cotton with time

Time ± 0.2 sec	mPAN ± 0.0002 g	Dilution ± 0.03 mL	C _{Measured} ± 0.03 ppm	C ± 0.3 ppm
900.0	0.3329	1/10	9.10	91.0
1800.0	0.3433	1/10	8.72	87.2
3600.0	0.2920	1/10	8.85	88.5
5400.0	0.2962	1/10	8.82	88.2
7200.0	0.3144	1/10	8.74	87.4

$C_0 = 100.0 \pm 0.3$ ppm, $V_{\text{solution}} = 30.0 \pm 0.1$ mL, pH = 5.00 ± 0.01 , T = 25.0 ± 0.1 °C

Adsorbed amount of ions are calculated from the remained Cr(VI) concentration (Table 2.16).

Table 2.16. Effect of adsorption time on Cr(VI) adsorption of Cotton

Time ± 0.2 sec	mPAN ± 0.0002 g	C ± 0.3 ppm	q ± 0.06 mg Cr(VI)/g PAN
900.0	0.3329	91.0	0.81
1800.0	0.3433	87.2	1.12
3600.0	0.2920	88.5	1.18
5400.0	0.2962	88.2	1.20
7200.0	0.3144	87.4	1.20

$C_0 = 100.0 \pm 0.3$ ppm, $V_{\text{solution}} = 30.0 \pm 0.1$ mL, pH = 5.00 ± 0.01 , T = 25.0 ± 0.1

Similar to PET and PAN, a fast adsorption in the beginning which slows down in about 60 min and almost reaches to equilibrium in 90 min was observed for Cotton, also.

Time-adsorption curves show that Cr(VI) adsorptions are fast and maximum equilibrium adsorptions achieved in about 60 min (Fig. 2.6).

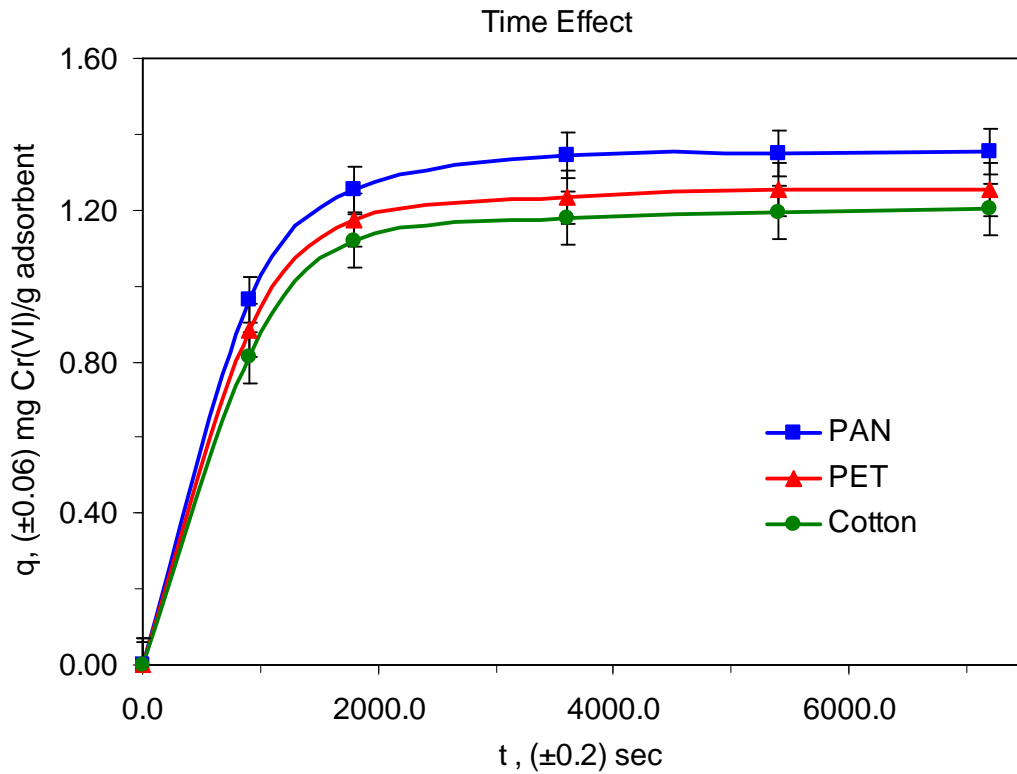


Figure 2.6. Variation in Cr(VI) adsorption with time

$C_0=100.0\pm 0.3$ ppm, $V_{\text{solution}}=30.0\pm 0.1$ mL, $\text{pH}=5.00\pm 0.01$,
 $T=25.0\pm 0.1$

2.6.3. Effect of Solution Concentration on Adsorptions

- Effect of solution concentration on Cr(VI) Adsorption of PET

Maximum adsorption capacity of PET was studied with solutions having different Cr(VI) concentrations. Obtained data are given in Table 2.17.

Table 2.17. Data for Cr(VI) adsorption on PET with concentration

C_0 ppm	m_{PET} ± 0.0002 g	Dilution ± 0.03 mL	$C_{Measured}$ ± 0.03 ppm	C ppm
30.0 \pm 0.2	0.2978	1/10	2.55	25.5 \pm 0.2
60.0 \pm 0.3	0.3061	1/10	5.14	51.4 \pm 0.3
100.0 \pm 0.3	0.3021	1/10	8.74	87.4 \pm 0.3
150.0 \pm 0.5	0.3066	1/10	13.31	133.1 \pm 0.5
250.0 \pm 0.7	0.3033	1/25	9.19	229.6 \pm 0.7
400.0 \pm 1.1	0.3042	1/50	7.57	378.6 \pm 1.1

$V_{solution}=30.0\pm 0.1$ mL, pH=5.00 \pm 0.01, t=7200.0 \pm 0.2 sec, T=25.0 \pm 0.1°C

Adsorbed amount of ions were calculated from the initial and final Cr(VI) concentrations as described in section 2.6.1 and results are given in Table 2.18.

Table 2.18. Effect of solution concentration on Cr(VI) adsorption of PET

C_0 ppm	m_{PET} ± 0.0002 g	C ppm	q mg Cr(VI)/g PET
30.0 \pm 0.2	0.2978	25.5 \pm 0.2	0.46 \pm 0.03
60.0 \pm 0.3	0.3061	51.4 \pm 0.3	0.84 \pm 0.05
100.0 \pm 0.3	0.3021	87.4 \pm 0.3	1.25 \pm 0.07
150.0 \pm 0.5	0.3066	133.1 \pm 0.5	1.65 \pm 0.09
250.0 \pm 0.7	0.3033	229.6 \pm 0.7	2.02 \pm 0.11
400.0 \pm 1.1	0.3042	378.6 \pm 1.1	2.11 \pm 0.15

$V_{solution}=30.0\pm 0.1$ mL, pH=5.00 \pm 0.01, t=7200.0 \pm 0.2 sec, T=25.0 \pm 0.1°C

Results clearly indicate that Cr(VI) adsorption increases with solution concentration. Maximum adsorption capacity of PET is found as 2.11 \pm 0.15 mg Cr(VI)/g PET in 400 ppm.

- Effect of solution concentration on Cr(VI) Adsorption of PAN

Maximum adsorption capacity of PAN was also studied. Obtained data are given in Table 2.19.

Table 2.19. Data for Cr(VI) adsorption on PAN with concentration

C_0 ppm	m_{PAN} ± 0.0002 g	Dilution ± 0.03 mL	$C_{Measured}$ ± 0.03 ppm	C ppm
30.0 \pm 0.2	0.3003	1/10	2.50	25.0 \pm 0.2
60.0 \pm 0.3	0.3006	1/10	5.07	50.7 \pm 0.3
100.0 \pm 0.3	0.3011	1/10	8.48	84.8 \pm 0.3
150.0 \pm 0.5	0.3020	1/10	12.74	12.7 \pm 0.5
250.0 \pm 0.7	0.3023	1/25	8.63	229.6 \pm 0.7
400.0 \pm 1.1	0.3035	1/50	7.27	378.6 \pm 1.1

$V_{solution}=30.0\pm 0.1$ mL, pH=5.00 \pm 0.01, t=7200.0 \pm 0.2 sec, T=25.0 \pm 0.1°C

Amount of adsorbed ions were calculated as described previously and results are given in Table 2.20.

Table 2.20. Effect of solution concentration on Cr(VI) adsorption of PAN

C_0 ppm	m_{PAN} ± 0.0002 g	C ppm	q mg Cr(VI)/g PAN
30.0 \pm 0.2	0.3003	25.0 \pm 0.2	0.50 \pm 0.03
60.0 \pm 0.3	0.3006	50.7 \pm 0.3	0.92 \pm 0.05
100.0 \pm 0.3	0.3011	84.8 \pm 0.3	1.52 \pm 0.07
150.0 \pm 0.5	0.3020	12.7 \pm 0.5	2.25 \pm 0.09
250.0 \pm 0.7	0.3023	229.6 \pm 0.7	3.41 \pm 0.11
400.0 \pm 1.1	0.3035	378.6 \pm 1.1	3.61 \pm 0.15

$V_{solution}=30.0\pm 0.1$ mL, pH=5.00 \pm 0.01, t=7200.0 \pm 0.2 sec, T=25.0 \pm 0.1°C

Results indicates maximum adsorption capacity of PAN as 3.61 \pm 0.15 mg Cr(VI)/g PAN at 400 ppm.

- Effect of solution concentration on Cr(VI) Adsorption of Cotton

Maximum adsorption capacity of Cotton was studied with solutions having different Cr(VI) concentrations (Table 2.21)

Table 2.21. Data for Cr(VI) adsorption on Cotton with concentration

C _o ppm	m _{PAN} ±0.0002 g	Dilution ±0.03 mL	C _{Measured} ±0.03 ppm	C ppm
30.0±0.2	0.3160	1/10	2.50	25.0±0.2
60.0±0.3	0.3090	1/10	5.17	50.7±0.3
100.0±0.3	0.3022	1/10	8.81	88.1±0.3
150.0±0.5	0.3031	1/10	13.48	134.8±0.5
250.0±0.7	0.3089	1/25	9.24	230.9±0.7
400.0±1.1	0.3028	1/50	7.61	380.5±1.1

V_{solution}=30.0±0.1 mL, pH=5.00±0.01, t=7200.0±0.2 sec, T=25.0±0.1°C

Adsorbed amount of Cr(VI) and uncertainties are given in Table 2.22.

Maximum adsorption capacity is observed to be almost equal to PET at 400 ppm.

Table 2.22. Effect of solution concentration on Cr(VI) adsorption of Cotton

C _o ppm	m _{PAN} ±0.0002 g	C ppm	q mg Cr(VI)/g PAN
30.0±0.2	0.3160	25.0±0.2	0.47±0.03
60.0±0.3	0.3090	50.7±0.3	0.80±0.05
100.0±0.3	0.3022	88.1±0.3	1.18±0.07
150.0±0.5	0.3031	134.8±0.5	1.50±0.09
250.0±0.7	0.3089	230.9±0.7	1.85±0.11
400.0±1.1	0.3028	380.5±1.1	1.93±0.15

V_{solution}=30.0±0.1 mL, pH=5.00±0.01, t=7200.0±0.2 sec, T=25.0±0.1°C

Amount of adsorbed Cr(VI) ions by 1 gram of adsorbent against to concentration is plotted and given in Figure 2.7.

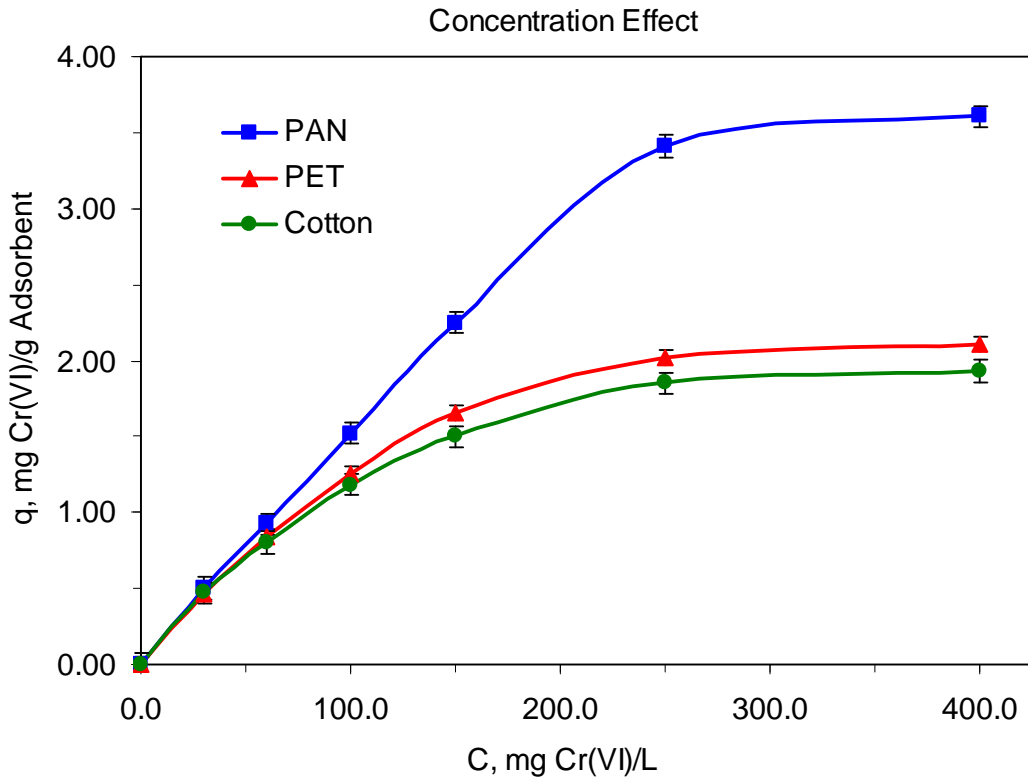


Figure 2.7. Variation in Cr(VI) adsorption with solution concentration

$$V_{\text{solution}}=30.0\pm 0.1 \text{ mL}, \text{pH}=5.00\pm 0.01, t=7200.0\pm 0.2 \text{ sec}, T=25.0\pm 0.1^{\circ}\text{C}$$

Figure shows that Cr(VI) adsorption increases with the increase in Cr(VI) concentration and reaches to a maximum at 300 ppm. Maximum adsorption capacity of PET is observed to be slightly higher than the capacity of cotton which both are around 2.0 mg Cr(VI)/g adsorbent. The highest maximum adsorption capacity (3.61 ± 0.15 Cr(VI)/g PAN) is obtained with PAN in 400 ppm.

3. CONCLUSION and EVALUATION OF THE RESULTS

In this study removal of Cr(VI) ions from aqueous solutions was studied by adsorption technique. The waste PET water bottles, PAN synthetic wool and cotton natural polymer were used as adsorbent. Obtained results showed that they can be used as adsorbents.

PET did not adsorb Cr(VI) as received. PET chains contain carbonyl groups which make a lot of hydrogen bonding. This makes PET a rigid material with a non-porous surface. NaOH treatment oxidizes PET surface into a porous surface, which enhances its metal adsorption.

Adsorption processes are pH dependent. Studies showed that low Cr(VI) adsorption at low pHs increases with pH. Maximum adsorptions were obtained at pH=5.0-5.5. Active sites on the adsorbents probably are protonated in acidic medium which decreases Cr(VI) adsorption. Hence, low adsorption values were obtained at low pH's. With the increase in pH protonated active sites ionize so that Cr(VI) adsorption becomes easier. Hence, Cr(VI) adsorption increases. However, in basic conditions the metal ion may precipitate. Therefore, in order to prevent the precipitation of chromium, adsorptions were carried out at pH=5.0.

Adsorption-time experiments showed that the initial rates of adsorptions are high. This indicates that Cr(VI) ions can be adsorbed easily with the empty active sites on the adsorbent. Most of Cr(VI) ions was adsorbed within 40-50 min. However, due to filling of the active sites the rate slows down and reaches to equilibrium at about 90-100 min.

Effect of initial solution concentration studies showed that PAN has the highest Cr(VI) adsorption capacity with 3.61 ± 0.15 mg Cr(VI)/g PAN in 400.0 ± 1.1 ppm solution, while the maximum adsorption capacity of PET and Cotton are 2.11 ± 0.15 g Cr(VI)/g PET and 1.93 ± 0.15 g Cr(VI)/g Cotton respectively.

Low adsorption capacity of PET may be attributed to its rigid structure and nonporous surface. Low adsorption of cotton may be due to insufficient amount of functional groups on cellulose chains. The higher Cr(VI) adsorption of PAN probably is due to the flexible chains which can bind Cr(VI) ions easily.

3.1. Evaluation for the Method

Applied technique is a sensitive method which very low metal ion concentrations can be measured. However, working with dilute solutions increases the probability of errors. Weighing small amount of compounds and preparation of dilute solutions causes high uncertainties in the results. Error can be decreased by using standard solutions. Standard solutions can be used in the preparation of the Cr(VI) solutions and in the calibration of AAS.

Used glasswares may also cause error. This type of errors could be decreased by using well calibrated glasswares.

Experiments were carried out at room temperature. Although, adsorption process is not affected with small changes in temperature, the calibration of the instruments and standard solutions may be affected which may cause error in the results.

3.2. Further Investigation

Results showed that PET, PAN and Cotton can be used in the removal of Cr(VI) ions from aqueous solutions. If their adsorption capacities can be increased they may become valuable adsorbents. NaOH treatment could be applied to PAN and Cotton also. Longer NaOH treatment at high temperatures may be effective. Acid treatment can be tried, also. Also, they may adsorb different metal ions higher than Cr(VI). Therefore, studying the adsorption of other metal ions may be helpful.

Desorption of ions should also be studied and developed. By this way;

- Waste plastic pollutants could be removed from our environment,
- Waste materials could be converted into valuable products,
- Toxic metal ions could be removed from polluted waters,
- By desorption adsorbed metal ions could be gained,
- Using adsorbents in the removal of heavy metals for several times would economically help to many manufacturers.

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