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EDX AND XRD, FT-IR SPECTRA, ANALYSIS CONTAINING HEXAVALENT CHROMIUM METAL ION ADSORPTION PRESENT IN AQUEOUS SOLUTION ON TO PHOSPHORIC ACID (H_3PO_4) ACTIVATED *MIMUSOPS ELENGI LEAVES* CARBON

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ABSTRACT

Adsorption studies were carried out by observing the effects of various experimental parameters removal of Chromium from Aqueous solution. Morphology of adsorbent due to adsorption has been analyzed P^H, FT-IR spectra, EDX and XRD analysis. Adsorption interactions of hexavalent chromium metal ion onto PTMAC and STMAC from aqueous solution. Using FT-IR spectra, and XRD techniques.and EDX studies revealed that the possibility of partial chemisorption though maximum adsorption is physical in nature. EDX showed the morphological observations of loaded and unloaded adsorbents. XRD studies exhibited the crystalline nature of unloaded adsorbent compared with loaded adsorbent.

Keywords: P^H, FT-IR spectra, EDX and XRD analysis, PTMAC, STMAC.

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1. INTRODUCTION

Freshwater ecosystems are home to numerous organisms such as fishes, amphibians, aquatic plants and invertebrates. When water is contaminated it causes illness and disease. About 80% of human diseases are related to water. If water is precious, water quality is more precious. Poor water quality continues to pose major threat to the human health. Improvements in existing strategies and the innovation of new techniques supported by strong science and technology base will be needed to eliminate the pollution of water resources, to improve the water quality and to treat the waste water to acceptable limits. [1-2]

1.1 Chemicals and other contaminants

Contaminants may include organic and inorganic substances.

1.2 Organic water pollutants are

- Detergents.
- Disinfectant by- products such as chloroform.
- Food processing waste which includes oxygen-demanding substances, fats andgrease.
- Insecticides and herbicides, a huge range of organo halides and other http://en.wikipedia.org/wiki/Chemical_compoundschemical compounds.
- Petroleum hydro carbons including fuels (gasoline, diesel fuel, jet fuels and fuel oil), lubricants (motor oil) and fuel combustion byproducts.
- Volatile organic compounds (VOCs) such as industrial solvent, from improper storage.
- Various chemical compounds found in personal hygiene and cosmetic products.

1.3 Inorganic water pollutants are

- Acidity caused by industrial discharges, Ammonia from food processing waste.

- Chemical waste as industrial by-products.
- Fertilizers containing nutrients, nitrates and phosphates which are found in storm
- Water runoff from agriculture as well as commercial and residential use.
- Heavy metals from motor vehicles via urban storm water runoff, acid mine drainage and metal plating unit effluents.
- Silt (sediment) run off from construction sites, logging, slash and burn practices or land clearing sites[3].

1.4 Heavy metal

Heavy metal pollution occurs directly by effluents from industries, refineries and waste treatment plants and indirectly by the contaminants that enter the water supply from soils/ground water systems and from the atmosphere via rain water. Modern industry is responsible for the larger extent in contamination of the environment [4]. Metals are notable for their wide environmental dispersion from industries, their tendency to accumulate in select tissues of the human body, and their overall potential to be toxic even at relatively minor levels of exposure. Today, heavy metals are abundant in our drinking water, air and soil due to our increased use of these compounds. Under certain environmental conditions, metals may accumulate to toxic levels and cause ecological damage [5]. Of the important metals, mercury, lead, cadmium, arsenic and chromium (VI) are regarded as toxic, whereas, others such as copper, nickel, manganese and zinc are not toxic, but their extensive usage and increasing levels in the environment is of serious concern [6-8]. Heavy metals are present virtually in every area of modern consumerism from construction materials to cosmetics, medicines to processed foods, fuel sources to agents of destruction, appliances to personal care products. It is very difficult for anyone to avoid exposure to any of the many harmful heavy metals that are so prevalent in our environment.

1.5 Drinking water quality

In general, water is considered to be fit for drinking, only when it possesses certain characteristics as itShould be colorless, odorless and tasteless in nature

- Should be free from turbidity and suspended impurities
- Should be free from pathogenic and micro organisms
- Should possess pH values between 7 and 8.5
- Hardness value should fall between 50 to 100 mg/L
- Should be anti-corrosive and free from hazardous substances [9].

1.6 Metal ions as pollutants

Waste water contains organic, inorganic and toxic pollutants. Most of the metals (Cd, Cr, Co, Cu, Zn, Pd, Hg, Ni and Ag) and metalloids (Se, As and Sb) causes hazard. Inorganic Pollutants are consists of metal compounds and mineral acids. They may toxic and disturb the bio-chemical processes. In the 20th century, there is a requirement large quantity of various metals, so the usage of metals is increased with the increase pollution too. Metal pollutants are primarily disturbed in the atmosphere, water, soil and sediments. Atmospheric metal pollution arises mainly from the mining, smelting and refining of metal ores. High metal concentrations have rendered 9.5% of Japanese rice and paddies which are incapable of producing consumable products. Some of the major metal pollutants include Lead, Mercury, Cadmium, Arsenic, Copper, Chromium and Iron [10].

1.7 Metal Source Diseases

Lead: Industries from Glass, Ceramic and Lead storage batteries, Hypertension, reproductive disorders, neurological and metabolic problems.

Mercury: Mining and Refining Industries, Fungicides, Central Nervous System damage and kidney failure [11].

Arsenic: Insecticides, Pesticides, Coal Combustion, Metal Smelling and

Roasting and causes Cancer [12].

Cadmium: Burning of fossil E fuels and industrial waste, Kidney damage and Hypertension.

Copper: Excess of Cu (470 mg) in human body is toxic and causes hypertension, sporadic fever, uremia, coma and even death. Cu also produces pathological changes in brain tissue.

2. EXPERIMENTAL

2.1 Preparation of Activated Carbon

Preparation of adsorbent using H_3PO_4

20 g of the crushed and ground *Mimusopss* elengi leaf powder were soaked in 100 ml of 60% H_3PO_4 solution. Theliquid/solid mixture was stirred continuously at ambient temperature for 2 h and left to soak for 12 h for thoroughpenetration of H_3PO_4 into the leaf powder of *Mimusopss* elengi [13]. After the stipulated soaking time, the slurry was keptin muffle furnace at 600°C for 2 h, for activation purpose [14, 15]. The samples were cooled and washed with colddeionized water until phosphate ions were no longer detected by the lead nitrate test. The product was finally air dried at105°C for 3 h, after which it was ground and sieved to get the particle size between 73 µm and 150 µm. The carbon was designated as Phosphoric Acid Treated *Mimusops elengi* Activated Carbon (PTMAC).

2.2 Preparation of activated carbon

Preparation of adsorbent using H_2SO_4

The dried *Memsops elengi* leaf powder was carbonizedby treating with concentrated sulphuric acid in the weightratio of 1:1 (w/v). Thus obtained charred masses wereheated for 8 hours in a muffle furnace at 400°C tocomplete carbonization and activation. The resulting carbons were washed with distilled water until aconstant pH of the slurry was reached. Then the carbonwas dried for four hours at 100°C in a hot air oven. Thedried material was ground well to a fine powder andsieved well using the sieves of desired particle sizerange. The carbon obtained from the *Memsops eleng i*leaf powder was after this chosen as Sulphuric acidTreated *Memsops elengi* Activated Carbon (STMAC).

2.3 Adsorption experiments

The effect of adsorption parameters such as initial concentration of Cr (VI), ion adsorbent dose and contacttime was studied by batch mode technique because ofits cleanness. Fixed dose of the adsorbent was taken in250 mL iodine flask and 50 mL and fixed concentration of the Chromium solution was pour into the flask.Desired pH of the solution was brought by adding dropsof Con HCl or 6 N NaOH. Then the content of the flask was agitated using rotary shaker with 180 rpm for pre determined duration. Then adsorbents were then separated by centrifugation and the concentration of the solution was determined by ‘Diphenylcarbazide’ method.The percentage removal of the Cr (VI) from the solution was calculated by the mass balance association. Tostudy the effect of pH were brought to 2 to 10

2.4 Diphenyl carbozide method

1 mL of the sample solution was pipette out into 25 Ml standard flasks. To this 1 mL of 6 N H_2SO_4 was added followed by 1 mL of diphenylcarbazide (A 0.25% (W/V) solution of diphenylcarbozide was prepared in 50%(V/V) acetone) and the total volume was made up to 25mL using double distilled water. Concentration of Cr (VI) ion was estimated by measuring concentration of the reddish brown color developed due to complex configuration using Systronics Double Beam UV-visible Spectrophotometer: 2202 at the wave length of 540 nm [16, 17].

3. RESULT AND DISCUSSION

Changes in the morphology of adsorbent due to adsorption have been analyzed with FT-IR spectra, EDX analysis and XRD patterns.

3.1 Fourier Transform Infrared Spectroscopy (FT-IR)

The instrumental evolution of the day makes non-destructive and quantitative and qualitative analysis possible, with significant accuracy and precision.Historically IR has been mostly used for qualitative analysis, to obtain structural information. The shift of the bands and the changes in signal intensity allow the identification of the functional groups involved in adsorption [18-20].

FT - IR for PTMAC and Cr (VI) ions loaded onto PTMAC

The FT – IR spectrum of PTMAC and the PTMAC loaded with Cr (VI) ions were shown in Figure 1a&b. It could be seen from the spectrum that almost there is no change in the spectral pattern before and after adsorption however there is a slight reduction of absorption bands. The four new peaks appeared at 1300cm^{-1},500cm^{-1}, 700 cm^{-1} and 3400 cm^{-1}showed that there is a formation of bond between carbon and dye. This clearly indicates that the alkene group present in the PTMAC might have involved in the bond formation with the Cr (VI) ions. This infers that the possibility of partial chemisorption though maximum of adsorption of Cr (VI) onto PTMAC adsorbent is by physical forces.

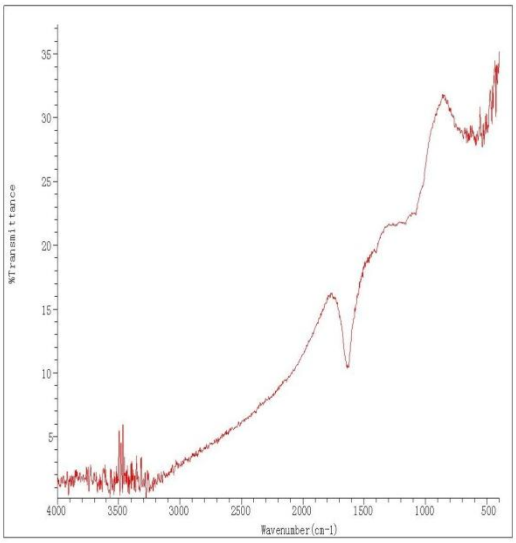

Figure 1(a): Before adsorption of Cr(VI) ions onto PTMAC

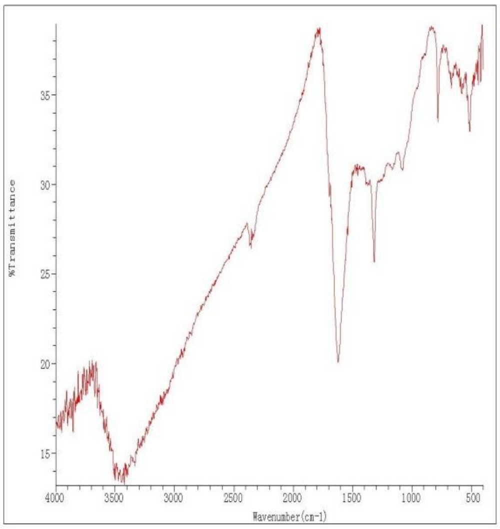

Figure 1(b): After adsorption of Cr (VI) ions onto PTMAC

FT - IR for PTMAC and Cr (VI) ions loaded onto STMAC

The FT – IR spectrum of STMAC and the STMAC loaded with Cr (VI) ions were shown in Figure 2.a&b. The two new peaks appeared at 1600cm^{-1} and 3400 cm^{-1}in the STMAC loaded with Cr (VI) ions showed that there is a formation of bond between carbon and dye. This clearly indicates that the alkene group present in the STMAC might have involved in the bond formation with the Cr (VI) ions. This infers that the possibility of partial chemisorption though maximum of adsorption of Cr (VI) onto STMAC adsorbent is by physical forces.

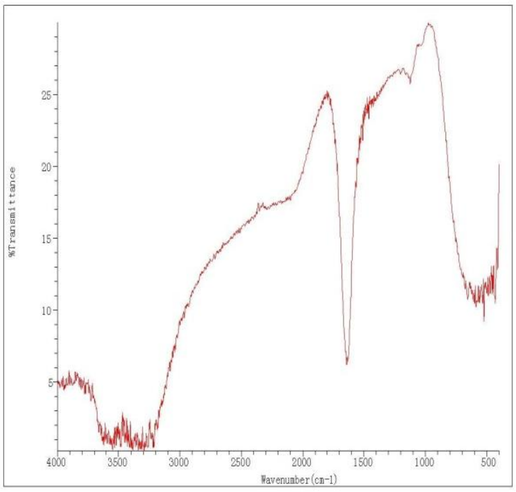

Figure 2(a): Before adsorption of Cr (VI) ions onto STMAC

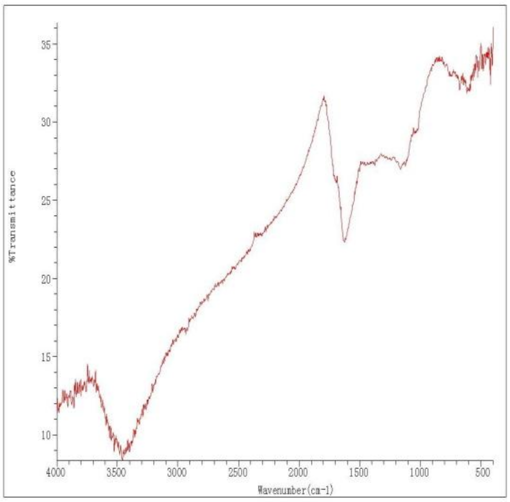

Figure 2(b): After adsorption of Cr (VI) ions onto STMAC

3.2 Energy Dispersive X-ray Spectroscopy (EDX)

Energy Dispersive X-ray Spectroscopy (EDX) is an analytical capability that can be coupled with several applications including Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM) and Scanning Transmission Electron Microscopy (STEM). EDX, when combined with these imaging tools, can provide elemental analysis on areas as small as nanometers in diameter. The impact of the electron beam on the sample produces x-rays that are characteristic of the elements present on the sample. EDX Analysis can be used to determine the elemental composition of individual points or to map out the lateral distribution of elements from the imaged area [21 – 22].

EDX studies for Cr (VI) ion loaded PTMAC

EDX analysis of Cr (VI) ion loaded PTMAC were shown in Figure 3.a. The well - defined peak of adsorbent loaded with Cr (VI) ion shows that Cr (VI) ion was bound onto the PTMAC surface. Peaks of certain Cr (VI) ions are very small which infers the surface adsorption through Vander Walls force.

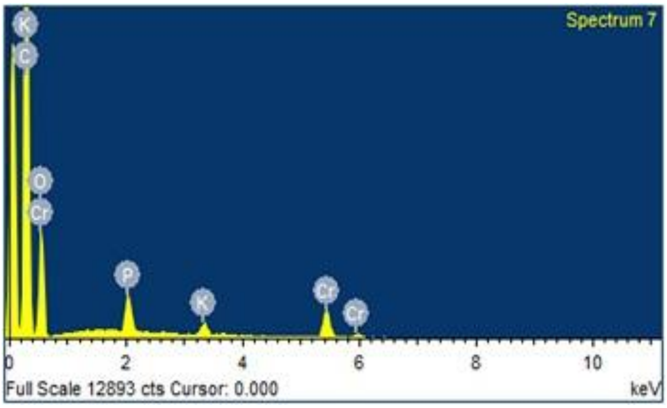

Figure 3(a): EDX studies for Cr (VI) ion loaded PTMAC

EDX studies for Cr (VI) ion loaded STMAC

EDX analysis of Cr (VI) ion loaded STMAC were shown in Figure 3.b. The well-defined peak of adsorbent loaded with Cr (VI) ion shows that Cr (VI) ion was bound onto the STMAC surface. Peaks of certain Cr (VI) ions are very small which infers the surface adsorption through Vander Walls force.

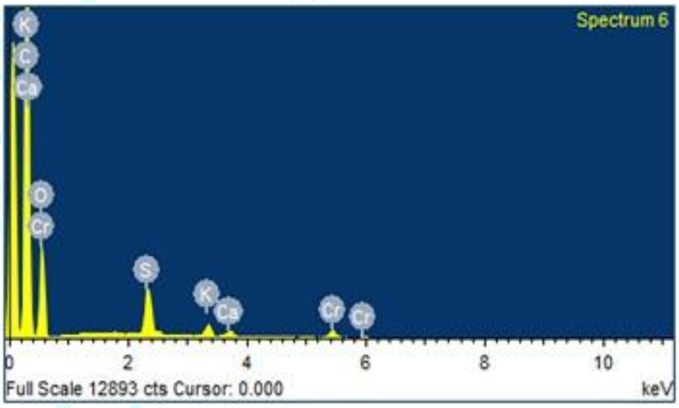

Figure 3(b): EDX studies for Cr (VI) ion loaded STMAC

3.3 X ray diffraction studies

XRD studies show changes in the crystallinity of the adsorbent well defined peaks show the crystalline nature and the hallow peak shows the non- crystalline amorphous nature of the carbon [23 – 25].

XRD pattern of Cr (VI) loaded PTMAC

XRD pattern of PTMAC and PTMAC loaded with Cr (VI) ions were shown in Figure 4.a&b. It is observed that the XRD pattern of PTMAC loaded with Cr (VI) ions have slightly changed when compared to unloaded PTMAC. This suggests that the Cr (VI) ions molecules diffuse into micropores and macropores and adsorb mostly by physisorption and partially by chemisorption by altering the structure of the carbon.

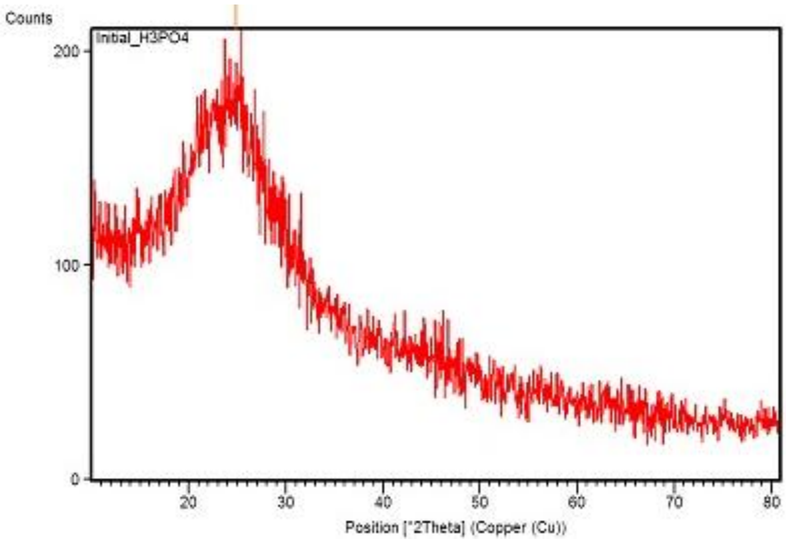

Figure 4(a): PTMAC before Adsorption

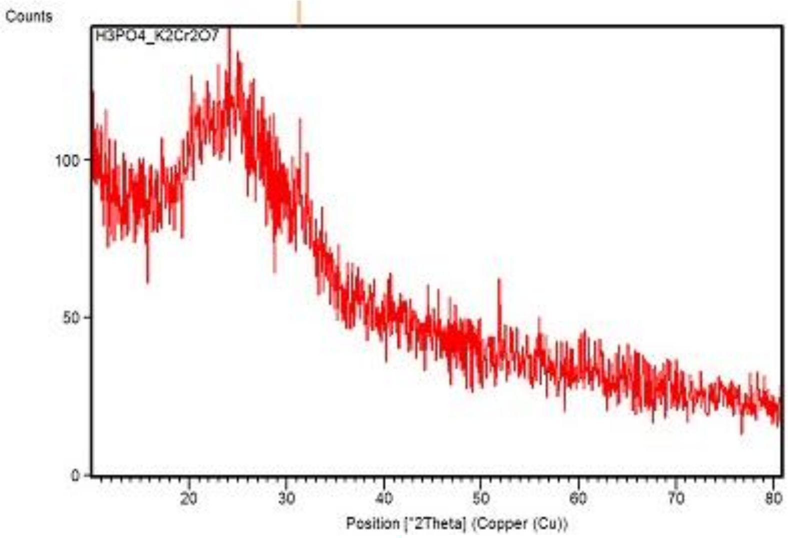

Figure 4(b): After Adsorption of Cr (VI) ions onto PTMAC

XRD pattern of Cr (VI) loaded STMAC

XRD pattern of STMAC and STMAC loaded with Cr (VI) ions shown in Figure 5a& b. It is observed that the XRD pattern of STMAC loaded with Cr (VI) ions have slightly changed when compared to unloaded STMAC. This suggests that the Cr (VI) ions molecules diffuse into micro pores and macropores and adsorb mostly by physisorption and partially by chemisorption by altering the structure of the carbon.

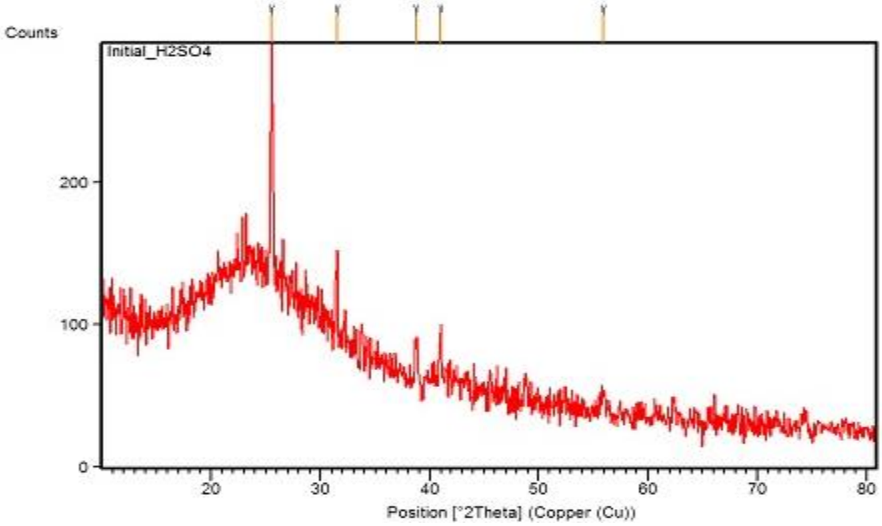

Figure 5(a): STMAC before Adsorption

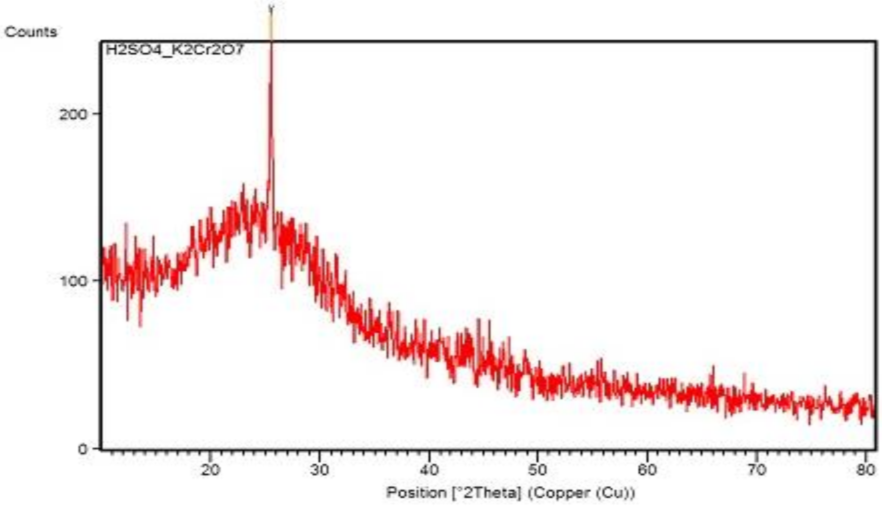

Figure 5(b): After Adsorption of Cr (VI) ions onto STMAC

4.0 Regeneration studies

The effect of pH on desorption of Cr (VI) ions are shown in Figure 6. When pH was varied from 1 to 12 the percentage of desorption of Cr (VI) ions was found to be increased from 25.2 % to 73.9 % for PTMAC and 23.2 % to 69.5 % for STMAC. Increase the pH of solution show significant increase in the percentage of desorption. The higher percentage desorption at basic pH suggest that OH$^-$ions might have replaced the HCrO$_4^-$ ions. This is in agreement with effect of pH study.

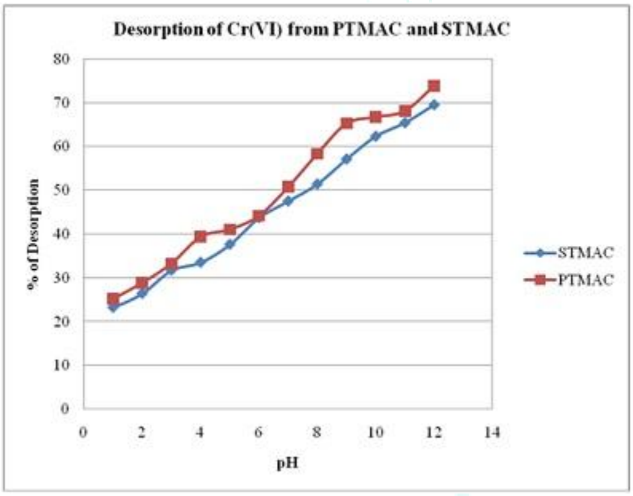

Figure 6: Desorption of Cr (VI) from PTMAC and STMAC

Table: 1 Desorption results for Cr (VI) on to PTMAC and STMAC.

[pH = 2; Dose = 20 mg/ 50 mL; Contact time = 180 min]

pH	% of Desorption	
	PTMAC	STMAC
1	25.2	23.2
2	28.9	26.4
3	33.3	31.7
4	39.4	33.5
5	41.1	37.6
6	44.2	43.7
7	50.8	47.5
8	58.4	51.4
9	65.3	57.1
10	66.8	62.3
11	68.2	65.4
12	73.9	69.5

5. CONCLUSION

Desorption studies inferred that pH 12.0 was the effective desorbing reagent for Cr (VI) ions where as hydrochloric acid solution (0.2 N). The FT-IR spectrums of PTMAC and STMAC unloaded and loaded adsorption of Cr (VI) indicated that the adsorption were physisorption.

The X-ray diffraction pictures of PTMAC and STMAC recorded unloaded and loaded adsorptions of Cr (VI) indicate that the adsorption was physisorption.

EDX analysis of Cr (VI) ion loaded PTMAC were shown in Figure 6.84. The well - defined peak of adsorbent loaded withCr (VI) ion shows those Cr (VI) ions were bound onto the PTMAC surface. Peaks of certain Cr (VI) ions are very small which infers the surface adsorption through Vander Walls force.

EDX analysis of Cr (VI) ion loaded STMAC were shown in Figure 6.87. The well-defined peak of adsorbent loaded with Cr (VI) ion shows those Cr (VI) ions were bound onto the STMAC surface. Peaks of certain Cr (VI) ions are very small which infers the surface adsorption through Vander Walls force.

The foregoing study demonstrated the evaluation of the low cost adsorbents prepared from the *Memsops elengi* leaves for the removal of Cr (VI), from aqueous solution. The values of equilibrium parameter constants, thermodynamic parameters show the feasibility of the adsorption of these selected metal ionand selected dye onto the prepared adsorbent. Yet additional research is needed to determine the useful capabilities and specific applications of these adsorbents with respect to other heavy metals, dyes and various real industrials waste water.

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