# Adsorbents And Its Nature

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## Introduction

The nature of adsorbent depends mainly on the chemical composition of the adsorbent but the surface which is responsible for the adsorption is affected due to the presence of pores, edges, corners and cracks. In adsorption process, adsorbents are used usually in the form of spherical pellets, rods, moldings or monoliths with hydrodynamic diameters between 0.5 and 10 mm. They must have high abrasion resistance, high thermal stability and small pore diameters which results in higher exposed surface area and hence high surface capacity for adsorption. The traditional methods commonly used for removal of heavy metals from aqueous solution include ultrafiltration**,** evaporation**,** precipitation**,** solvent extraction, electrodialysis, reverse osmosis, ion exchange and adsorption. Among these techniques, adsorption is generally preferred due to its high efficiency, low-cost possibilities, easy handling, and also the availability of different types of adsorbents. Nowadays, among the various solid adsorbents, copolymers are widely used in the removal of metal ions due to their high adsorption capacities and selectively. To increase the efficiency for removal of heavy metal surface modification of copolymer can be done. The surface modified copolymer may be proved to be a very good adsorbents which can be successfully used for removal of toxic heavy metal from contaminated water and may which can have potential environmental applications.

## Literature Review

Balancer *et. al.* prepared formaldehyde based terpolymeric resin using salicylaldehyde/Biuret, characterized them using various physicochemical methods and studied their ion exchange properties as a function of pH and time. The resins were also was found to have semiconductor behavior.

Granule *et. al.* prepared 8-HQAF terpolymer resin based on the condensation polymerization of 8-hydroxyquinoline and adipamide with formaldehyde in the presence of 2M HCl as catalyst. The newly synthesized terpolymer resin was found to be soluble in DMF, DMSO and aqueous NaOH and insoluble in common organic solvents. From the elemental analysis, UV-visible, IR and 1HNMR spectral studies, they have proposed the tentative structure for the 8-HQAF terpolymer.

M. Karunakaran *et. al.* prepared terpolymer resin RTF-1 by the condensation of Resorcinol(R), Thiourea(T) and Formaldehyde(F) in the presence of 2M HCl as catalyst at 140+20C. The synthesized terpolymer resin has been characterized by FTIR, 1HNMR and gel permeation chromatographic techniques. An ion-exchange property of RTF-1 terpolymer resin was studied using 'Batch equilibrium technique.

## Materials and Methods

Mechanical sieving machine Mesh Sizes: Various sizes available to separate the adsorbents based on particle size Purpose: To obtain adsorbents of appropriate size for the process Digital Balance Accuracy: Weighs substances/compounds to the microgram level Purpose: Ensures precise measurement of the mass of materials. Micro Pipette Purpose: Accurately measures small volumes of solutions/liquids. Used for: Dispensing reagents or preparing solutions. (Fig.2.1) Presumably shows the Hot Air Oven. Likely depicts the Digital Balance. Probably illustrates the Micro Pipette. Note: The specific model numbers or additional details about the silver and pipettes might not be provided in the given text. Hot Air oven-TI-127C with temperature range 500C above ambient to 3000C manufactured by Tempo-Instrument Pvt. Ltd. Mumbai was used for drying process (Fig.2.2) The mechanical sieving machine manufactured by Jayanth Scientific Industries, Mumbai-2 with different mesh sizes was used for getting the appropriate size of the adsorbents. Digital balance was used for accurate weighing of the substances/compounds to the microgram level. Surface area is one of the main criteria in deciding the adsorption capacity of adsorbents. Generally larger the surface area higher the adsorption capacity of the material. Surface area is related to physical and chemical properties of the materials Water retention and movement, cation exchange capacity and adsorption are the properties are closely related to the specific surface area. It is usually expressed in square meters per gram (m2/g). The purpose of surface area measurements is commonly for determining the accessibility of internal surfaces of the materials to molecules or ions, which can be adsorbed there on. Suitable dye molecules can be used for determining the surface area of the absorbent material.

**Fig.2.1:- Systronic UV-Vis Spectrophotometer**

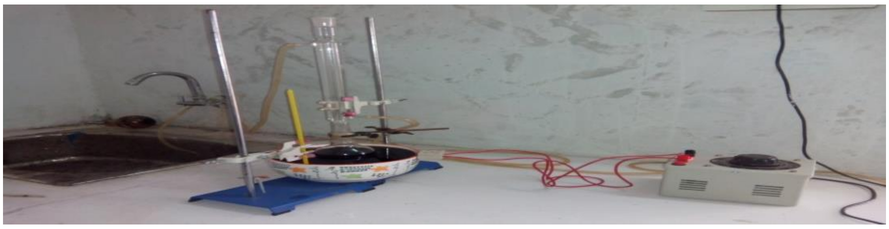

**Fig. 2.2:- Dimmer Stat with Oil Bath Assembly**

## Characterization of Newly Synthesized Materials

This chapter deals with characterization of newly synthesized copolymers/surface modified copolymers. The characterization specifically has as a goal to confirm the of the material. Many characterization techniques should ideally be linked to the desirable properties of the material such as strength, impermeability, thermal stability and optical properties. Characterization techniques are typically used to determine solubility, molecular weight, molecular structure, morphology, thermal properties and other important physical properties.

## 1h-Nmr

Nuclear Magnetic Resonance (NMR) spectroscopy involves transition of a nucleus from one spin state to another with the resultant absorption of electromagnetic radiation by spin active nuclei ( having nuclear spine not equal to zero) when they are placed in a magnetic field. The energy associated with NMR experiment is ncapable of disrupting even weakest chemical bond. Nuclear magnetic resonance spectroscopy pertains to nuclei and only one type of nucleus at a time( e.g.1H or 13C or 19F). When the frequency of the rotating magnetic field and that of the precessing nucleus become equal, they are said to be in resonance and absorption of energy by nucleus can occur. A plot of peak intensities versus the frequencies of absorption (expressed in Delta(δ) /Tau scale(τ)) constitutes an NMR spectrum. The 1H nucleus is most commonly studied in NMR spectroscopy because of its high natural butments (99.98%) and the fact that it is invariably present in the majority of organic compounds.

## Adsorption Studies and Experimental Techniques

pH is one of the very most important factor which influences almost all biological as well as chemical reactions. Therefore, it is one of most important factors to be considered for optimization. The experiment was carried out as per the procedure mentioned bellow Experiment Setup Adsorbing Cr(VI) from Solution Experiment Overview This experiment aims to study the adsorption of hexavalent chromium (Cr(VI)) from aqueous solutions using various newly synthesized adsorbents. Experimental Procedure Flask Preparation: A series of 250 mL conical flasks were prepared. Cr(VI) Solution: 100 mL of a Cr(VI) solution with an initial concentration (Co) of 25 mg/L was added to each flask Temperature Control: A constant temperature of 300 K (27 °C) was maintained throughout the experiment. pH Adjustment: The pH of the solutions was varied from 1 to 10 using 0.1 M sodium hydroxide or 0.1 M hydrochloric acid. Adsorbent Addition: Appropriate amounts of different adsorbents (RPHF-I, RPHF-II, RSF-I, RSF-II, CCRPHF-I, CCRPHF-II, CCRSF-I, and CCRSF-II) were added to each flask to achieve a concentration of 5 g/L. Flask Sealing: The flasks were stoppered to prevent evaporation and contamination. Experimental Goals To evaluate the adsorption capacities of the different adsorbents for Cr(VI) at various pH values. To determine the optimal pH for maximum Cr(VI) removal by each adsorbent. To compare the adsorption performance of the different adsorbents. The specific properties of the adsorbents (e.g., surface area, functional groups) will likely influence their adsorption capacities and pH dependence.

## Effect of Contact Time

Effect of contact time between the adsorbate and adsorbent particles is one of the most important parameters in the adsorption studies. This gives the equilibrium time i.e. minimum time required for maximum adsorption of Cr(VI) by the adsorbents. The experiment was carried out as per the procedure described below A series of 250 ml conical flasks were taken and 100 ml of metal solutions were added having the concentration of 25mg/lit and optimum condition such as pH and temperature were maintained. Each of the flasks was added with 5gm/lit of adsorbents and put on the rotary shaker for shaking at 500 rpm speed for different time intervals say 10, 20, 30, 40,---- 180 min. After agitation, samples were filtered throughout Whatman No. 42 filter paper. The filtrates were estimated for residual concentrations of metal ions. Percentage of Cr(VI) ion removal was calculated from the initial and final concentrations of metals ion in the flasks. Graphs were plotted by taking time (in min) on X-axis and percentage of Cr (VI) ion removal on Y-axis. From the graph, equilibrium time required for maximum adsorption was obtained and this value was considered in all further adsorption studies.

## Langmuir Adsorption Isotherm

Langmuir model is widely used for describing adsorption of various adsorbates on the surface of various adsorbents. Langmuir equation is related to the coverage (adsorption) of sorbate molecules on a solid surface (adsorbent) to concentration of a medium (solution) above the solid surface at a fixed temperature. This isotherm is based on following assumptions. Fixed number of adsorption sites: at equilibrium, at any temperature, adsorbed molecules occupy a fraction of the adsorbent surface site ($\theta$) and the rest ($1-\theta$) remain free There should be only one sorbent under consideration during isotherm application. A sorbate molecule under investigation can reacts with only one active site of adsorbents at a time. There is no chemical interaction between the sorbate species. A monolayer of sorbate is formed on the surface sorbent phase. By applying these assumptions and kinetic principle, Langmuir equation can be written in the following form.

$$\frac{C_e}{Q_e} = \frac{1}{Q_m b} + \frac{C_e}{Q_m}$$

Langmuir Isotherm: A Deeper Dive Building on the previous response, let's explore the Langmuir isotherm in more detail. The Langmuir Isotherm Equation The Langmuir isotherm, developed by Irving Langmuir in 1916, is a model that escribes the adsorption of molecules onto a solid surface. It assumes that the surface is homogeneous, and that each molecule adsorbed occupies a fixed number of sites preventing other molecules from adsorbing to those sites.

## Results and Discussion

The most important parameter influencing the sorption capacity is the pH of the desorption medium.200 The influence of pH on the percentage sorption of chromium has shown in Fig.5.1. The adsorption capacities of RPHF-I and CCRPHF-I towards Cr(VI) removal were determined using various pH values of the solution in the range 1.0 to 10. As the pH increased, there was little increase in the percentage of Cr(VI) removal and it was maximum at pH 5 for both the adsorbent materials under investigation i.e. RPHF-I, CCRPHF-I and the removal capacity at this pH was found to be 86.10 % and 92.37 % respectively. This indicates that both the adsorbents have same optimum pH value. The Cr(VI) ions exists in different forms in aqueous solutions and the stability of these forms is dependent on the pH of system. The positively charged surface of the adsorbent attracts negatively charged CrO4- ions, leading to stronger adsorption. Competition with OH- Ions: As the pH increases, the concentration of OH- ions in the solution also increases. These OH- ions compete with CrO4- ions for adsorption sites on the adsorbent surface. Decreased Adsorption: At higher pH values, the competition from OHions becomes more significant, reducing the adsorption of CrO4- ions. Implications for Adsorption Studies Optimal pH Selection: The optimal pH for Cr(VI) adsorption onto RPHF-I and CCRPHF-I is 5. Conducting adsorption experiments at this pH can ensure maximum removal efficiency. pH Control: Maintaining a pH of 5 during the adsorption process is crucial for achieving the desired results. Effect of pH on Adsorbent Surface Properties: The pH of the solution can influence the surface properties of the adsorbent, affecting its adsorption capacity and selectivity. Additional Considerations Adsorbent Properties: The specific properties of the adsorbents (e.g., surface area, functional groups) may also play a role in their adsorption behavior at different pH values. Cr(VI) Species: The speciation of Cr(VI) in solution (e.g., CrO42-, HCrO4-) can also influence adsorption. By understanding the relationship between pH and adsorption, researchers can optimize the conditions for Cr(VI) removal using these adsorbents.

## Freundlich Isotherm

The Freundlich equation suggests multilayer adsorption. Sorption energy exponentially decreases on completion of the sorption centers of an adsorbent. Therefore, the parameters like $K_f$ and 'n' were estimated from the intercept and slope of the plots between log $Q_e$ against log $C_e$. Freundlich isotherms have shown in Fig.5.21 and Fig.5.22. The calculated parameters at 300C were presented in Table.5.2. The 30°C values of both the adsorbents i.e. RSF-I and CCRSF-I were found to 1.9453 and 2.944 mg/g respectively, which indicate the dominance of adsorption capacity. The Freundlich exponent 'n' were 2.631 and 2.881 for RSF-I and CCRSF-I respectively which again reflects the favourable adsorption. The values of R2 were found to be 0.985 and 0.987 for both the adsorbents i.e. RSF-I and CCRSF-I respectively, showed the well-fitting of Freundlich isotherm. These findings indicate that probably the sorption of Cr(VI) on RSF-I and CCRSF-I was a multilayer coverage.

## Effect of adsorbents dosage on Cr(VI) ion removal

The dependence of Cr(VI) sorption on adsorbent dosage was studied by varying the amount of RSF-II and CCRSF-II adsorbents from 0.5 to 10 gm/lit while keeping other parameters (pH of solution, contact time) optimum. The result is shown in Fig.5.27. It is observed that removal efficiency of the adsorbent generally improved with increasing dose. This is expected due to the fact that higher the dose of adsorbents in the solution the greater availability of exchangeable sites for the ions. RSF-II and CCRSF-II showed no further increase in adsorption after their certain dosages were added. At 25 mg/lit concentration of Cr(VI) ion, the maximum removal efficiency was about 91% for RSF-II at the dose of 7.0gm/lit. While CCRSF-II, it was 97.60% at the dosage 5.0 gm/lit. This suggests that after a certain dose of adsorbent the maximum adsorption gets set in and hence the number of ions bound to the adsorbent and number of free ions remains constant even after further addition of the dose of RSF-II and CCRSF-II. It is interesting to note that the saturation values of Cr(VI) (removal efficiency) for RSF-II and CCRSF-II adsorbents are different from one another due to the surface modification.

**Table 5.3 Langmuir Isotherm Parameters of adsorbents under studies**

| Adsorbents | Langmuir Isotherm Parameters | | | | | |
|---|---|---|---|---|---|---|
| | Cr(VI) | | | As(III) | | |
| | $R^2$ | b | $Q_m$ | $R^2$ | b | $Q_m$ |
| RPHF-I | 0.991 | 0.1768 | 08.84 | 0.980 | 0.1632 | 10.52 |
| CCRPHF-I | 0.989 | 0.2414 | 10.41 | 0.990 | 0.2727 | 15.15 |
| RPHF-II | 0.994 | 0.2148 | 09.90 | 0.991 | 0.2141 | 9.174 |
| CCRPHF-II | 0.991 | 0.2759 | 11.76 | 0.985 | 0.3314 | 11.24 |
| RSF-I | 0.993 | 0.1651 | 8.064 | 0.989 | 0.1757 | 9.433 |
| CCRSF-I | 0.991 | 0.2402 | 10.86 | 0.987 | 0.2500 | 15.38 |
| RSF-II | 0.992 | 0.2089 | 9.708 | 0.984 | 0.1892 | 11.36 |
| CCRSF-II | 0.987 | 0.301 | 15.15 | 0.981 | 0.3091 | 15.62 |

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