1.1 Introduction

The toxic nature of many metals, especially Uranium is one of the most hazardous heavy metals because of its chemical toxicity and radioactivity. Excessive amounts of uranium have entered into the environment through the activities associated with the nuclear industry (Benedict et al., 1981) [1]. There have been extensive studies for development of various technologies for measurement and removal of uranium from wastes produced from nuclear power programs and nuclear fuel reprocessing activities such as The Egyptian Fuel Manufacturing Pilot Plant, FMPP which is a new facility, producing an MTR-type fuel elements, enriched to 19.7% ± 0.2 U^{235}, which are required for the Egyptian Second Research Reactor (ETRR-2).

The large volume of legacy wastes poses one of the most urgent needs for the nuclear industry and governments. The presence of long-lived radionuclides in aqueous wastes significantly increases the complexity and cost of treating the waste for disposal [2]. Incidental wastes resulting from processes utilizing nuclear fission may contain radionuclides (especially cesium and strontium) or lanthanide elements (Ce, Sm, Eu, for example) that require remote handling of the waste and process equipment. Other wastes that contain actinide elements (U, Np, Pu, *Am* or Cm) require, at the minimum, extensive contamination controls, if not limited shielding to handle waste is present.

Separation of the major radioactive elements from the waste allows downstream processing the bulk of non-radioactive fraction of the waste to be performed in less expensive equipment and facilities with hands-on operation and maintenance. Separation technologies also concentrate the radionuclides destined for geologic disposal into a smaller volume. This lowers capital and operating costs of treatment facilities as well as final storage and disposal costs.

Toward this end, an array of robust separation technologies are either in use or are in various stages of development around the world. Among such technologies, liquid-liquid extraction, ion exchange, sorption, reverse osmosis, electrodialysis techniques, which are efficient but expensive [3,4] and precipitation continue to dominate the nuclear industry. Chemical precipitation can be envisaged, but the generation of precipitated bulky hydroxides and colloidal particles is often a major disadvantage. The search for an effective and economical method for removing radioactive elements ions from waste solutions requires the consideration of unconventional materials and processes that might have potential in this field.

One of the efficient methods is the adsorption by an effective chelating polymer. Polymeric substances with the ability to complex metal ions from solution are very common. Both natural and industrial sources found useful applications and are of great interest from the scientific and technological points of view. Chelating resins represent an important category of synthetic polymers with wide applicability to selectively removing metal ions. Several reviews cover many examples of the vast number of chelating groups that were incorporated into polymer networks are reported [5-8].

The selective complexation of a targeted metal ion by a given ligand is an important objective for many applications, including catalytic [9] chromatographic separation [10], and metal ion recovery processes [11]. The desirable properties of chelating polymers are high capacity for the metals of interest, high selectivity, and fast kinetic-rapid equilibration with metal containing in solution.

Polymer chelating resins containing the amidoxime functional groups are good candidate for investigation. Literature data mentioned that the amidoxime groups form stable complexes with different metal ions and, consequently, the polymers with the amidoxime groups can be successfully used as adsorbents for the preconcentration of trace metals from aqueous solutions [12-16]. The most important applications reported the recovery of U(VI) ions from seawater [17-20]. And the recovery of U(VI), Pu(VI) and Pu(IV) ions from weakly-basic aqueous carbonate solutions [21]. For this reason, many research studies were focused on the synthesis of new chelating polymer structures with amidoxime groups by the radiation-induced grafting and by chemical initiation of acrylonitrile (AN) onto starch and the subsequent amidoximation of polyacrylonitrile [22].

Another efficient method for removal of toxic material from waste solutions is the adsorption process based on the use activated carbon because it is inexpensive, widely applicable, efficient, and creates relatively little sludge [23-29]. Activated carbon has been widely used in various industries for water purification [30-35]. There are different varieties of activated carbon. Its efficiency, capacity and tendency to specific metallic ionic species or molecules are basically dependent on the precursor for preparation of the activated carbon and the way it is chemically or physically treated. However, in commercial activated carbons, these functional groups cover only a small portion of the carbon's surface [36-38].

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To enhance the capacity of charcoal to adsorb heavy metal, surface modification have been introduced. These include chemical activation using zinc chloride.

1.2. Separation methods

Separation or recovery of a selected species from various matrices (natural and waste water,. geological, biological and industrial materials, substances of high purity and radioactive waste solution), especially at trace levels, is one of the most difficult and complicated tasks

There are various treatment methods available for the removal and recovery of heavy metals from wastewater. Some of these are well-established methods that have been in practice for decades: others are of more recent innovations. The most commonly used methods are precipitation, solvent extraction, ion exchange, membrane, and adsorption technique.

These separation techniques are classified according to the significant difference in at least one of their chemical or physical properties of the different species to be separated. Table (1.1) provides a partial list of some separation techniques based on the chemical and physical properties of the species.

Table (1.1): Classifying Separation Techniques

Basis of Separation	**Separation Technique**
Size	filtration dialysis size-exclusion chromatography
Mass and density	Centrifugation
Complex formation	Masking
Change in physical state	distillation sublimation recrystallization
Change in chemical state	precipitation ion exchange electrodeposition volatilization
Partitioning between phases	extraction chromatography

In the following , it is a brief outline on separation methods of interest to the present work;

1.2.1 Precipitation

In chemical reactions, precipitation is the phenomenon that occurs when a dissolved substance in a liquid passes out of solution into solid form as the result of a chemical reaction.

The completion of reactions in the coagulation or precipitation processes is almost instantaneous after the chemicals are dissolved fully. The precipitates first formed by the chemical reactions are crystals of molecular size. The initial growth or increase in size of these colloidal crystals and coagulated solids is caused by charge reduction and Brownian movement. Additional growth is a result of gentle but turbulent stirring of the suspension flocculation [39].

Precipitation is employed for the removal of heavy metals from wastewaters. Heavy metals are generally precipitated as hydroxide through the addition of lime or caustic to a pH of minimum solubility. However, several of these compounds are amphoteric and exhibit a point of minimum solubility.

When treating industrial wastewaters containing metals, it is frequently necessary to pretreat the wastewaters to remove substances that will interfere with the precipitation of the metals, if present.

1.2.2. Solvent extraction

Solvent extraction [40.41] involves contacting the aqueous solution containing the metal ions with an organic liquid extractant which is insoluble in water. The extractant is capable of forming complexes or ion exchange with the metal ion. Upon mixing, the metal ions are transported to the organic phase. The phases are allowed to separate, and the metal ions are stripped from the loaded organic phase with an appropriate solution. The concentrated metal ion solution can then be purified or disposed.

Solvent extraction offers the advantages of fast kinetics, high capacities, and selectivity for target metal ions [42]. The finite aqueous solubility of the extractants, solvents, and modifiers is, however, a significant disadvantage. This not only adds to the cost of the procedure through loss of reagents, but contaminates the water with potentially toxic organics. There is also loss of the organics through evaporation and entrainment. In addition, solvent extraction is not recommended for dilute metal ion solutions due to the large volumes of extractants needed [43].

1.2.2.1 Membrane Processes

Membranes are materials that selectively stop or slow the passage of particular types of molecules. They may consist of dry solids, solvent swollen gels, or immobilized liquids and for practical purposes can be considered to be constructed of polymers. In general, membranes of interest have a highly porous structure, although the pores may be as small as 10 A in size. Pore shape is generally irregular, although certain gel membranes have both a highly regular and highly uniform diameter. Basic mechanisms of selectivity by uncharged membranes are based on sieving, diffusion, .and solubility effects. Charged membranes also select by ion exchange and therefore can be used as ion-exchange systems,

The classical membrane process is osmosis. Here the potential of two solutions separated by a membrane is different because of a difference in salt concentrations. Water diffuses through the membrane until the chemical potential is equal on both sides. There is an interaction between the pressure potential and the chemical potential caused by the concentration gradient, which results in balance being made by a combination of the two. The osmotic process can be reversed [i.e.. reverse osmosis (RO)] by increasing the pressure on the saline side of the membrane. A similar result can be achieved by introducing an electrical potential across the membrane (electrodialysis).

Selectivity of a given membrane is strongly affected by the method of manufacture. For example, cellulose acetate membranes are normally about 100 µm thick with a 0.2 µm thick surface skin that is much denser than the core, i.e., less porous or with smaller pores. This skin is formed during casting by exposing the surface to air. At this stage of manufacturing, the skin allows permeation of sodium chloride. Further treatment of the membrane by an annealing process increases the density of the skin and greatly decreases the permeability to sodium chloride [44, 45].

1.2.3. Ion Exchange

Ion exchange can be used for the removal of undesirable anions and cations from a wastewater. Cations are exchanged for hydrogen or sodium and anions for hydroxyl ions.

Ion-exchange resins operate on the similar principles as solvent extraction. The resins contain functional groups are capable of ion exchange or complex the metal ions. The resin is contacted with the contaminated solution, loaded with metal ions, and stripped with an appropriate eluent. Because the functional group interacting with the metal ion is covalent bound to an insoluble polymer, there is no loss of reagent into the aqueous phase. The resins can be regenerated and reused for next processes [46]. A disadvantage of ion-exchange resins can be the slower kinetics compared to solvent extraction. However, increasing the porosity of the resin or decreasing the bead size or crosslinking can help improving the kinetics by increasing the accessibility of the metal ions to the polymer-supported ligands.

The selectivity of ion-exchange resine for targeted metal ions is of great importance in the separation of the metals from complex solutions.

Ion exchange resins consist of an organic or inorganic network structure with attached functional groups. Most ion exchange resins used in wastewater treatment are synthetic resins made by the polymerization of organic compounds into a porous three-dimensional structure. The degree of crosslinking between organic chains determines the internal pore structure, with higher crosslink density giving smaller pore sizes. From a kinetic viewpoint, a low degree of crosslinking would enhance diffusion of ions through larger pores. However, physical strength decreases and swelling in water increases as crosslink density is lowered. The functional ionic groups are usually introduced by reacting the polymeric matrix with a chemical compound containing the desired group. Exchange capacity is determined by the number of functional groups per unit mass of resin.

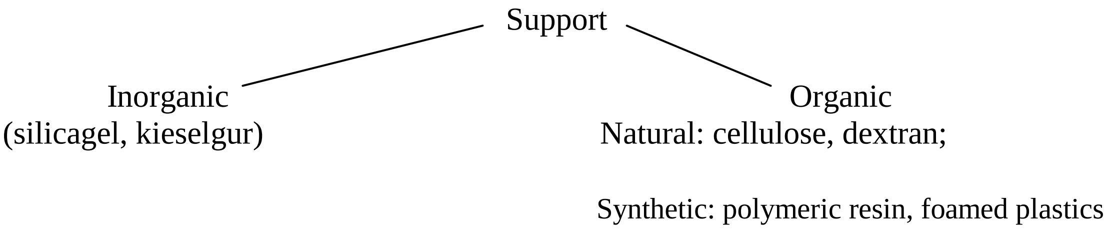
Ion exchange resins are called [cationic] if they exchange positive ions and [anionic] if they exchange negative ions. Cation exchange resins have acidic functional groups. such as sulfonic, whereas anion exchange resins contain basic functional groups, such as amine. Ion exchange resins are often classified by the nature of the functional group as strong acid, weak acid, strong base, and weak base. The strength of the acidic or basic character depends upon the degree of ionization of the functional groups, similar to the situation with soluble acids or bases. Thus. a resin with sulfonic acid groups would acts as a strong acid cation exchange resin.

The most common strong acid ion exchange resin is prepared by copolymerizing of styrene and divinyl benzene followed by sulfonation of the copolymer. The degree of crosslinking is controlled by the fraction of divinyl benzene in the initial mixture of monomers [47]. There are three basics types of resins: cationic, anionic and mixed.

-The cationic group includes		**- The anionic resins include**	
$R\text{-}S0_3H$	sulfonic	$R - NH_2$	primary amine
$R\text{-}OH$	phenolic	$R - R^1NH$	secondary amine
$R\text{-}COOH$	carboxylic	$R - R_2{}^1N$	tertiary amine
$R - PO.H_7$	phosphonic	$R - R_3{}^1N^+ OH^-$	quaternary amine

Where in each case R indicates a hydrocarbon polymer and R' indicates a specific group, for example, CH_2 The mixed - bed resins are combinations of these two types. The salts of these resins can serve as the exchange medium and actually more commonly do. A particular example is the use of the sodium salt in water softening because of the feature of simple recharging. A note should be made that this results in a product water with high sodium concentration, which is not recommended for cardiac patients.

The importance of separation and concentration techniques involving chelating sorbents in the trace level has risen substantially. Pre-treatment of radioactive sample by the sorption technique not only increases the ion concentration to a detectable level but also eliminates its harmful effects. The use of chelating sorbents can provide a concentration factor up to several hundred folds, better separation of interference ions, high efficiency, and the possibility of combining with different recycling methods. A chelating sorbent essentially consists of two components: the chelate forming functional group and the polymeric matrix or the support; the properties of both components determine the features and the applications of the respective material. The selectivity and capacity, of the sorbents is determined mainly by the chelating group (the nature of the functional group and / or donor atom able to form complexes with metal ions). Other properties of the sorbents, namely the kinetic features, mechanical and chemical strength and regeneration depend on the polymeric matrix. Different polymeric materials are used for supporting chelating groups immobilization. In a simple classification these materials are either of inorganic or organic orgin



1.2.4 Adsorption

Adsorption is one of the physico-chemical treatment process for wastewater. This process gaining prominence as a means for producing good quality water effluents in low in concentration of dissolved matters. This process exploiting the ability of certain solids preferentially to concentrate specific substances from solutions onto their surfaces and the affinity of the dissolved substances to be sorbed onto the solid surfaces [48].The adsorption process generally depends on;

i- Adsorbent properties [49]

a- Surface area per unit weight must be high to increase the ability to adsorb much more amount of the adsorbate.

b- The adsorbent must posses certain engineering properties depending upon the application to which they are applied.

c- They must have adequate strength and hardness so as not to be reduced in size during handling or crushed in supporting their own weight in beds of the required thickness.

d- They must be not expensive.

ii- Adsorbate properties [48]

a- Substances of high molecular weight are easily adsorbed.

b- They must have the affinity to condensate on the surface of the adsorbent or to interact with it.

1.2.4.1 Types of adsorption

There are two types of adsorption:

i- Physical Adsorption; Which is reversible and is a result of intermolecular forces of attraction between molecules of the solid (adsorbent) and the molecules of the substance adsorbed (adsorbate). The adsorbate may penetrate to the pores of the solid if it present. The reversibility of this process is very important in industrial field for recovery of the adsorbent, recovery of the adsorbate, or for the fractionation of mixtures.

ii- Chemical Adsorption; Chemisorption or activated adsorption, is the result of chemical interactions between the solid and the adsorbed molecules. The strength of the chemical bond very considerably, and identifiable for chemical compounds, but the adhesive force is generally much greater than that found in physical adsorption. It form monomolecular layer of the adsorbate on the surface through forces of residual valence of the surface molecules [50]. The heat liberated during chemisorption is usually large, of the order of the heat of chemical reaction. The process is frequently irreversible, and on desorption the original substance will often be found to have undergone a chemical change.

1.2.4.2 Adsorption equilibria

The common manner to depict the adsorption equilibrium between the two phases is to express the amount of substance adsorbed per unit weight of adsorbent, $\mathbf{q_e}$ as a function of the residual equilibrium concentration, $\mathbf{C_e}$, of substance remaining in the solution phase. An expression of this type, termed an adsorption isotherm, defines the functional equilibrium distribution of adsorption with concentration of adsorbate in solution at constant temperature. Commonly the amount of adsorbed material per unit weight of adsorbent increases with increasing concentration, but not in direct proportion. Experimental isotherms are useful for describing adsorption capacity to facilitate evaluation of the feasibility of this process for a given application, for selection of the most appropriate adsorbent, and for preliminary determination of adsorbent dosage requirements [51].

1.2.4.3. Equilibrium adsorption models

Most equilibrium data follow one of the following models:

1- Langmuir Adsorption Isotherm

The Langmuir isotherm is valid for monolayer adsorption on a surface containing a finite number of identical sites .The model assumes uniform energies of adsorption on the surface, and the adsorption occurs on localized sites with no transmigration of adsorbate in the plane of the surface and no interaction between adsorbate molecules, and the maximum adsorption occurs when the surface is covered by a monolayer of adsorbate [52].

The langmuir expression is represented by the following equation :

$$q_e = \frac{abc_e}{(1+bc_e)} \qquad (1.1)$$

Where:

q_e is the amount of heavy metal ions adsorbed per unit mass of adsorbent in mg/g,.

C_e is the equilibrium concentration of heavy metal ions in mg/l.

'a' is a Langmuir constant which is a measure of adsorption capacity expressed in mg/g,

'b' is also Langmuir constant which is a measure of energy of adsorption expressed in l/mg

Equation (1.1) may be rearranged to facilitate its application to experimental data, yielding the linear form :

$$\frac{1}{q_e} = \frac{1}{a} + \frac{1}{abC_e} \qquad (1.2)$$

A plot of $(1 / q_e)$ against $(1 / C_e)$ gives a straight line of slope (1 / ab) and an intercept (1 / a)

In equation (1.1), *(b)* represents the monolayer coverage of the adsorbent particle in terms of gm of heavy metal/gm of adsorbent and is related to the Langmuir equilibrium constant. K_L - by equation:

$$\mathbf{K_L = ab} \qquad (1.3)$$

Equation (1.1) can be written now as follows;

$$q_e = \frac{k_L C_e}{1 + \frac{k_L C_e}{a}} \tag{1.4}$$

The essential characteristics of the Langmuir isotherm can be described by a equilibrium constant (R_L) which is defined by the following relationship:

$$R_L = \frac{1}{1 + bC_i} \tag{1.5}$$

The parameter indicates the shape of the isotherm accordingly:

R_L ----------------------type of isotherm

$R_L > 1$ ----------------Unfavorable

$R_L = 1$ -----------------Linear

$0 < R_L < 1$----------------Favorable

$R_L = 0$ -----------------Irreversible

2- Freundlich Adsorption isotherm

The Freundlich isotherm is an exponential model, it empirically relates the isotherm data and has been found to fit many adsorption system in dilute solutions. The equation is of the form:

$$\mathbf{q_e = K_f\, C_e^{\,1/n}} \tag{1.6}$$

Where:

K_f Freundlich constant, gm of metal/gm of adsorbent

n Freundlich exponent, gm of adsorbent/ liter

Taking the logarithm of both sides, the equation will be in the linear form as follow

$$Log(q_e) = Log(K_f) + \tfrac{1}{n} Log(C_e) \tag{1.7}$$

When the data from the laboratory test are plotted, the best straight line connecting the points is the isothermal relationship between contaminant concentration and adsorbent equilibrium capacity. The magnitude of the exponent (n) gives an indication of the favorability and capacity of the adsorbent adsorbate system.

3- BET adsorption Isotherm

Brunauer, emmett, and Teller [53] extended the Langmuir model to include multi-layer adsorption phenomena. The essential assumptions of the Brunayer-Emmett-Teller (BET) model are that any given layer need not be complete before subsequent layers can form, that the first layer of molecules adhere to the surface with an energy comparable to the heat of adsorption for monolayer attachment, and that subsequent layers are essentially condensation reactions. If the layers beyond the first are assumed to have equal energies of adsorption the BET equation takes the form:

$$\frac{X}{M}=\frac{AC_eX_m}{\left(C_{st}-C_e\right)\left(1+\frac{(A-1)C_e}{C_{st}}\right)} \tag{1.8}$$

Where:

X$_m$: solid phase concentration corresponding to complete coverage of available sites, or the limiting adsorption capacity, (gm of adsorbet/gm of adsorbent).

C$_{st}$: saturation concentration(solubility limit) of the solute,(gm of adsorbet /liter).

A: constant expressive of the energy of interaction between the solute and the adsorbent surface such that .

$$A=\left(\frac{d_2A_1}{d_1A_2}\right)\left(e^{\frac{E_1-E_2}{RT}}\right) \tag{1.9}$$

Where:

E_1: the average heat of adsorption of the first layer

E_2: the heat of condensation

($d_2\ A_1$ / $d_1\ A_2$) the ratio of evaporation condensation coefficients for the adsorbed layers and often is nearly equal to unity [53,54].

The BET equation can be 1inearized as:

$$\frac{C_eM}{C_{st}-C_e}=\frac{1}{AX_m}+\frac{(A-1)C_e}{AX_mC_{st}} \tag{1.10}$$

That is to facilitate its application. BET isotherm has some characteristics such as

-More than one layer thick on the surface of the adsorbent.

-Uniform, localized sites of the solid surface to adsorb.

-Adsorption at one site does not affect adsorption at neighboring sites.

-Energy of adsorption holds the first monolayer but condensation energy is responsible for adsorption of successive layers.

1.3. Grafting techniques

Considerable work has been done on techniques graft co-polymerization techniques of different monomers polymeric backbones. These techniques include chemical, photochemical, plasma induced techniques, enzymatic grafting and radiation techniques.

1.3.1 Chemical grafting technique

Chemical means of grafting can proceed along two major paths, viz. free radical and ionic modes. In the chemical process, the role of initiator is very important as it determines the path of the grafting process. Apart from the general free-radical mechanism, grafting in the melt and atom transfer radical polymerization (ATRP) are also interesting techniques to carry out grafting

1.3.1.1 Grafting by free radical using chemical technique

In the chemical process, free radicals are produced from the initiators and transferred to the substrate to react with monomer to form the graft co-polymers. In general, one can consider the generation of free radicals by indirect or direct methods. An example of free radicals produced by an indirect method is the production through redox reaction, viz. Mn^{2+}/H_2O_2, persulphates [55-59]. An alternate view is that persulphates reacts directly with the polymeric backbone (e.g. starch) to produce the requisite radicals. Free-radical sites may be generated on a polymeric backbone by direct oxidation of the backbone by certain transition metal ions (e.g. Ce^{4+}, Cr^{6+} , V^{5+} and Co^{+3}). The redox potential of the metal ions is the important parameter in determining the grafting efficiency. In general, metal ions with low oxidation potential are preferred for better grafting efficiency. The proposed mechanism for such a process has been ascribed to the intermediate formation of a metal ion-polymer chelate complex, viz. ceric ion is known to form a complex with hydroxyl groups on a polymeric backbone, which can dissociate via one electron transfer to give free radicals [60-66]. Apart from the above initiator, benzoyl peroxide (BPO) and azoisobutyronitrile (AIBN) are also effective in grafting reactions [67-68].This is important to note that the grafting efficiency is low with BPO and AIBN, compared with that obtained using one-electron transfer agents. For example, not all of the radical species contribute towards grafts of poly(methyl acrylate) on cellulose and vinyl acetate on starch. Moreover, between the two, BPO is more reactive than AIBN, since the effects of resonance stabilization reduce the efficiency of the primary radical (I) from AIBN in generating active sites on the backbone [67-69]

1.3.1.2 Grafting through living polymerization

In recent years, methods of' living polymerization' have developed to provide a potential for grafting reactions. In the view of Szwarc [70], the most plausible definition of a living polymer is that retains their ability to propagate for a long time and grow to a desired maximum size while their degree of termination or chain transfer is still negligible. Controlled free-radical polymerizations combine features of conventional free-radical and ionic polymerizations. Conventional free-radical polymerization requires continuous initiation, with termination of the growing chain radicals in coupling or disproportionation reactions, and as a result leads to unreactive (dead) polymers and essentially time invariant degrees of polymerization and broad molecular weight distribution. In case of a living polymerization, it provides living polymers with regulated molecular weights and low polydispersities [71-76]. Controlled free-radical polymerization may be effective through ATRP. ATRP of styrene and various methacrylates has been reported, using various catalytic systems [77,78]. In that method, dormant chains are capped by halogen atoms, which are reversibly transferred to metal complexes in the lower oxidation state. This generates the transient growing radicals and complexes in the higher oxidation state. Grafting from polymers including poly(vinyl chloride) (PVC), polyisobutene, polyethylene, and ethylene- co-vinyl acetate co-polymer has also reported through ATRP [79- 82]. Sonmez et al. [83] reported acrylamide grafting by ATRP; the initiation appears to take place via radical formation in a redox reaction of chlorosulfonamide groups with CuBr.

1.3.1.3 Ionic grafting using chemical technique

Grafting can also proceed through an ionic mode. Alkali metal suspensions in a Lewis base liquid, organometallic compounds and sodium naphthalenide are useful initiators in this purpose. Alkyl aluminum (R_3A1) and the backbone polymer in the halide form interact to form carbonium ions along the polymer chain, which leads to copolymerization. The reaction proceeds through cationic mechanism. Grafting can also proceed through an anionic mechanism. Sodium- Ammonia or the methoxide of alkali metals form the alkoxide of polymer, which reacts with monomer to form the graft co-polymer.

1.3.2 Photochemical grafting technique

When achromophore on a macromolecule absorbs light, it goes to an excited state, which may dissociate into reactive free-radicals, whence the grafting process is initiated. If the absorption of light does not lead to the formation of free-radical sites through bond rupture, this process can be promoted by the addition of photosensitizers, e.g. benzoin ethyl ether, dyes, such as Na-2,7 anthraquinone sulphonate or acrylated azo dye, aromatic ketones (such as benzophenone, xanthone) or metal ions UO_2^{+2} . That means the grafting process by a photochemical technique can proceed in two ways: with or without a sensitizer [84,85]. The mechanism without sensitizer involves the generation of free radicals on the backbone, which react with the monomer free radical to form the grafted co-polymer. On the other hand, in the mechanism with sensitizer', the sensitizer forms free radicals, which can undergo diffusion so that they abstract hydrogen atoms from the base polymer, producing the radical sites required for grafting. Uchida et al. [86] reported a novel method in which oxygen removal from polymerization mixture was not required, for the graft polymerization of acrylamide (AM) on the surface of poly (ethylene terephthalate) (PET) film, with simultaneous UV-irradiation without a photosensitizer. In that method, the addition of $NaIO_4$ plays a crucial role in the removal of any oxygen present in the aerated monomer solution, as oxygen is the strong inhibitor of radical polymerization. The periodate ion present in an aqueous solution containing $NaIO_4$ generally exists in the hydrated forms $H_4IO_6^-$and $H_2IO_5^-$ and $H_4IO_6^-$ may produce OH^- and IO_3^-.

1.3.3. Plasma radiation induced grafting technique

In recent years, the plasma polymerization technique has received increasing interest. Plasma conditions attained through slow discharge offer about the same possibilities as with ionizing radiation [87, 88]. The main processes in plasmas are electron-induced excitation, ionization and dissociation. Thus, the accelerated electrons from the plasma have sufficient energy to induce cleavage of the chemical bonds in the polymeric structure, to form macromolecule radicals, which subsequently initiate graft co-polymerization.

1.3.4. Enzymatic grafting technique

The enzymatic grafting method is quite new. The principle involved is that an enzyme initiates the chemical / electrochemical grafting reaction [89]. For example, tyrosinase is capable of converting phenol into reactive o-quinone, which undergoes subsequent non-enzymatic reaction with chitosan. Enzymatic grafting on a poly(dicarbazole-Nhydroxysuccinimide) film was reported by Cosnier et al. [90], thionine and toluidine blue have been irreversibly bound to the Poly(dicarbazole) backbone and the grafting of polyphenol oxidase (PPO) on polydicarbazole has been reported.

1.3.5. Grafting initiated by radiation technique

The iradiation of macromolecules can cause homolytic fission and thus forms free radicals on the polymer. Also, radiation grafting can proceed through an ionic mode, with the ions formed through high-energy irradiation. Thus, high energy MeV range proton beams have been successfully applied as ionizing radiation to induce graft polymerization of acrylonitrile to prepare midoxime type adsorbents on PE film substrates [91,92]. The hydrogen molecules liberated in a polymer film irradiated with an ion beam leave chemically active tracks in the substrate. A variety of carbon radicals, C=C bonds, C-C bonds and cross-linking are formed in the chemically active track. One unique advantage of high linear energy transfer (LET) with short stopping ranges irradiation, is the possibility to develop a radical distribution with a spatial variation of the order of nano-meter, whereas for low LET (e.g. γ-rays, e-beams), relatively uniform formation of the radical is expected for a specimen with a thickness of the order of millimeter. Radiation induced grafting differs from chemical initiation in many aspects. In a mechanistic way, as in a radiation technique the initiator is not required, free radical formation is on the backbone polymer/ monomer whereas in a chemical method, a free radical forms first on to the initiator and then it is transferred to the monomer/polymer backbone. Unlike the chemical initiation method, the radiation-induced process is free from contamination, so that the purity of the processed products may be maintained. Chemical initiation is limited by the concentration of the initiator, and it may be difficult to determine an accurate concentration of the initiator in pure form. Chemical initiation often brings about problems arising from local heating of the initiator, an effect that is absent in the formation of free-radical sites by radiation, which is only dependent upon the absorption of high-energy radiation. Due to large penetrating power of higher energy radiation, methods using radiation initiation provide the opportunity to carry out grafting at different depths of the base polymer matrix. Moreover, the molecular weight of the products can be better regulated in radiation techniques, and these are also capable of initiation in solid substrates. Regarding its limitation, nuclear radiation energy is usually expensive in comparison with chemical reactions. The length of irradiation time and setting up the optimum conditions present limitations of the radiation technique. Moreover, it should be well known whether the polymer is stable in the radiation range of interest.

1.3.5.1 Ionic grafting initiated by radiation technique

Ionic grafting may be of two different types: cationic or anionic. The polymer is irradiated to form the polymeric ion, and then reacted with the monomer to form the grafted co-polymer. The potential advantage of the ionic grafting is high reaction rate. Thus, small radiation doses are sufficient to bring about the requisite grafting. The cationic grafting initiated from the backbone. An alternate cationic grafting mechanism can proceed through monomer radical cation, which subsequently forms a dimer. Charge localization in the dimmer occurs in such a way that the dimer radical cation reacts with the radical produced by the irradiation of the polymer.

1.3.5.2 Free-radical grafting initiated by radiation technique

In the radiation technique, the presence of an initiator is not essential. The medium is important in this case, e.g. if irradiation is carried out in air, peroxides may be formed on the Polymer. The lifetime of the free radical depends upon the nature of the backbone polymer. Grafting proceeds in three different ways: (a) pre-irradiation, (b) peroxidation and (c) mutual irradiation technique. In the pre-irradiation technique [93-97], the polymer backbone is first irradiated in vacuum or in the presence of an inert gas to form free radicals. The irradiated polymer substrate is then treated with the monomer, in liquid or vapor state or as a solution in a suitable solvent. In the peroxidation grafting method, the trunk polymer is subjected to high energy radiation in the presence of air or oxygen to form hydroperoxides or diperoxides, depending on the nature of the polymeric backbone and the irradiation conditions. The stable peroxy products are then treated with the monomer at higher temperature, whence the peroxides undergo composition to radicals, which then initiate grafting. The advantage of this technique is that the intermediate peroxy products can be stored for long periods before performing the grafting step. On the other hand, with the mutual irradiation technique, the polymer and the monomers are irradiated simultaneously, to form free radicals and subsequent addition [98,99]. **S**ince monomers are not exposed to radiation in the preirradiation technique, the obvious advantage is that the method is relatively free from homopolymer formation, which occurs with the simultaneous technique. However, the decided disadvantage of the preirradiation technique is scission of the base polymer due to its direct irradiation, which can result in the formation of block co-polymers. These processes are represented through the following simple mechanisms.

(a) Grafting (pre-irradiation)

$$P \longrightarrow P^{\bullet} + M \longrightarrow PM^{\bullet}$$

(b) Grafting (peroxidation)

$$P \xrightarrow{O2} P\text{-}O\text{-}O\text{-}H \text{ or } P\text{-}O\text{-}O\text{-}P$$

$$\longrightarrow P\text{-}O^{\bullet} + O\text{-}H^{\bullet} \text{ or } 2\,P\text{-}O^{\bullet}$$

$$P\text{-}O^{\bullet}+O\text{-}H^{\bullet} \text{ or } 2\,P\text{-}O^{\bullet} + M \longrightarrow P\text{-}O\text{-}M$$

(c) Grafting (mutual irradiation)

$$P+ M \longrightarrow P^{\bullet} + M^{\bullet} \longrightarrow P\text{-}M^{\bullet}$$

1.4. Determination methods.

A method is the application of a technique to a specific analyte in a specific matrix. The requirements of the analysis determine the best method. In choosing a method, consideration is given to some or all the following design criteria: accuracy, precision, sensitivity, selectivity, robustness, ruggedness, scale of operation, analysis time, availability of equipment, and cost. Some of these criteria is considered in more detail in the following sections.

1.4.1-Accuracy; is a measure of how closely the result of an experiment agrees with the expected result. Analytical methods may be divided into three groups based on the magnitude of their relative errors. When an experimental result is within 1% of the correct result, the analytical method is highly accurate. Methods resulting in relative errors between 1% and 5% are moderately accurate, but methods of low accuracy produce relative errors greater than 5%.

1.4.2-Precision; when a sample is analyzed several times, the individual results are rarely the same. Instead, the results are randomly scattered. **Precision** is a measure of this variability. The closer the agreement between individual analyses, the more precise the results.

1.4.3-Scale of Operation; another way to narrow the choice of methods is to consider the scale on which the analysis must be conducted. Three limitations of particular importance are the amount of sample available for the analysis, the concentration of analyte in the sample, and the absolute amount of analyte needed to obtain a measurable signal. The first and second limitations define the scale of operations, the last limitation positions a method within the scale of operations. For convenience, we divide analytes into major (>1% w/w), minor (0.01% w/w – 1% w/w), trace(10^{-7} % w/w – 0.01% w/w) and ultratrace (<10^{-7} % w/w) components, and we divide samples into macro (>0.1 g), meso (10 mg – 100 mg), micro (0.1 mg –10 mg) and ultramicro (<0.1 mg) sample sizes. As shown in Fig (1.1)

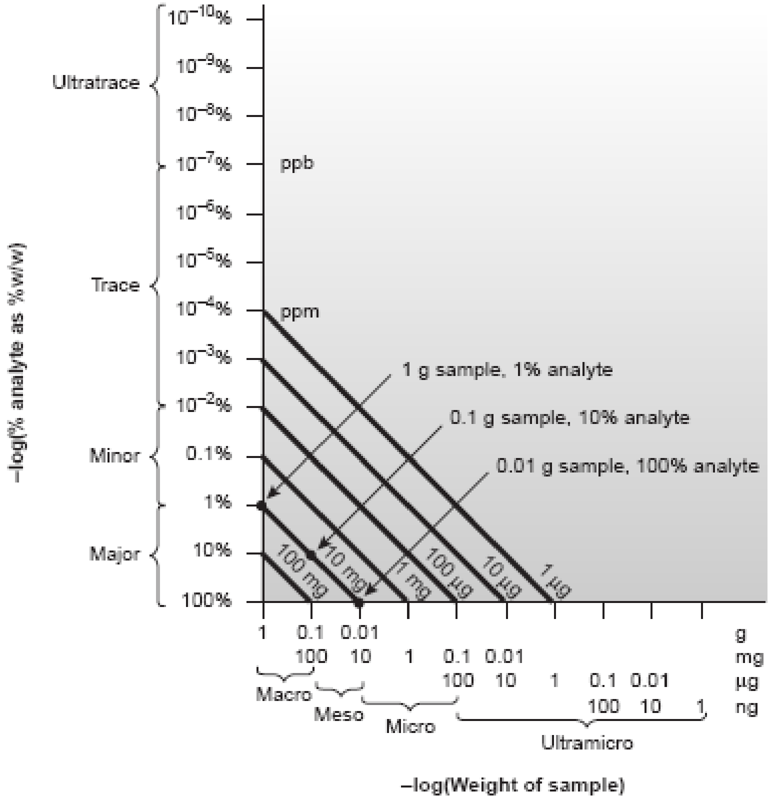


Fig (1.1): Scale of operation for analytical methods.

1.4.4-Sensitivity; the ability to demonstrate that two samples have different amounts of analyte is an essential part of many analyses. A method’s sensitivity is a measure of its ability to establish that such differences are significant. Sensitivity is often confused with a method’s detection limit. The detection limit is the smallest amount of analyte that can be determined with confidence. The detection limit, therefore, is a statistical parameter. Sensitivity is the change in signal per unit change in the amount of analyte.

1.4.5- Equipment, Time, and Cost; finally, analytical methods can be compared in terms of their need for equipment, the time required to complete an analysis, and the cost per sample. Methods relying on instrumentation are equipment-intensive and may require significant operator training. For example, the inductively coupled plasma atomic emission spectrometer(ICP-AES) method for determining uranium content in waste water requires a significant capital investment in the instrument and an experienced operator to obtain reliable results. Other methods, such as UV-Visible Spectrophotometer, require only simple equipment and reagents and can be learned quickly. The time needed to complete an analysis for a single sample is often fairly similar from method to method. This is somewhat misleading, however, because much of this time is spent preparing the solutions and equipment needed for the analysis. Once the solutions and equipment are in place, the number of samples that can be analyzed per hour differs substantially from method to method. This is a significant factor in selecting a method for laboratories that handle a high volume of samples. The cost of an analysis is determined by many factors, including the cost of necessary equipment and reagents, the cost of hiring analysts, and the number of samples that can be processed per hour. In general, methods relying on instruments cost more per sample than other methods.

1.4.6-Making the Final Choice; unfortunately, the design criteria discussed earlier are not mutually independent. Working with smaller amounts of analyte or sample, or improving selectivity, often comes at the expense of precision. Attempts to minimize cost and analysis time may decrease accuracy. Selecting a specific method requires a careful balance among these design criteria. Usually, the most important design criterion is accuracy, and the best method is that capable of producing the most accurate results. When the need for results is urgent, as is often the case in clinical labs, analysis time may become the critical factor.

The best method is often dictated by the sample’s properties. Analyzing a sample with a complex matrix may require a method with excellent selectivity to avoid interferences. Samples in which the analyte is present at a trace or ultratrace concentration usually must be analyzed by a concentration method. If the quantity of sample is limited, then the method must not require large amounts of sample.

It is important to show the best technique for measurement of the chemical analysis (trace elemental analysis) of our matrices, and the physical properties(particles size distribution) of our powder sample. There are many techniques for this targets such as inductively coupled plasma atomic emission spectrometer (ICP-AES) and UV-Visible Spectrophotometer this for trace elements analysis. Scanning Electron Microscope (SEM) and Sedigraph 5100 Micrometric Instrument (Analysis by X-ray Monitoring of Gravitational Sedimentation) this for particles size distribution analysis. And the choice is according to the previous data.

1.5. Literature survey

As a first sorbent, amidoxime sorbent; was choosen to be synthesized for removal of uranium from waste streams. The main approach for synthesis of this sorbent is based on polymerization of AN. Therefore, a recent literature survey on polymers based on AN is given in this section

Polymers that present nitrile groups display some uncommon features. It has been found that polymers network based on acrylonitrile (AN) were macroporous regardless of the crosslinker level, thus indicating importance of additional 'physical' crosslinks. Resin based on acrylonitrile is easy to prepare and presents a reactive pendant group (nitrile group), which can be modified differerent kinds of reagent through nucleophilic addition [100]. However, normally, the degree of modification is low due to poor accessibity of nitrile groups [101-106]. Hence, the aim of many works is to present simple way to enhance AN incorporation into resin structure and to introduce the amidoxime group by reaction with hydroxylamine.

Chelating filter papers with chemically bonded amidoxime groups were synthesized by radiation-induced grafting of acrylonitnie onto filter paper followed by chemical treatment with hydroxylamine. The effect of grafting conditions such as absorbed dose, dose rate, monomer concentration and filter paper thickness on the grafting yield was studied. It was found that the degree of grafting increases with increasing absorbed dose and dose rate, and then tends to level off at high doses. The order of the dependence of the initial grafting rate on the dose is found to be of 0.33. An increasing monomer concentration was accompanied by a significant increase in grafting. At high monomer concentration the initial rate of grafting is fast followed by a slow rate. The rate of grafting is controlled by the filter paper thickness and the diffusion of monomer into the interior of the filter paper . Mechanical properties of the prepared filter paper were improved over the ungrafted paper. The amidoxime filter papers were examined for adsorption of uranium concentration ranging between 10-100 ppm [107].

Grafting of glycidyl methacrylate (GMA) and acrylonitrile (AN) on cellulose was carried out in U.V. and ceric salt (Ce^{4+})-initiation systems [108]. The U.V.-initiation system using hydrogen peroxide as a photoinitiator was characterized with a considerably low grafting rate compared to the Ce^{4+} initiation system. The resultant

GMA and AN-grafted celluloses were subjected to reactions with triethylenetetramine (Trien) and hydroxylamine, respectively, to compare the reactivity between the grafted samples (U.V.- and Ce^{4+} samples) prepared in the U.V.- and Ce^{4+} initiation systems. The U.V.-sample exhibited higher reactivity than the Ce^{4+} sample toward each reaction.

The samples containing Trien and amidoxime groups showed an ability to absorb cupric ion. Which was nearly equal among the two samples. The difference in the reactivity between the two samples was discussed in terms of the structure of grafted cellulose, which was characterized with average molecular weight and number of grafted chains and moisture regain of the sample.

Amidoxime resin containing functional group was prepeared by polyacrylonitrile (PAN) grafted on sago starch [109]. The PAN grafted copolyrner was obtained by free-radical initiating process using ceric ammonium nitrate as an initiator. Conversion of nitrile groups of the grafted copolymer into the amidoxime was carried out by treatment with hydroxylamine under alkaline solution. The chelating poly(amidoxime) resin was characterized by FT-IR spectra, TG and DSC analyses. The chelating behavior of the prepared resin was carried out by using some metal ions. A significant binding property of metal ions by the chelating resin was observed and the maximum copper capacity was 3.0 mmol g^{-1}at Ph 6. The sorption capacities of metal ions by the resin were pH dependent, and its selectivity towards the following metal ions is in the following order:

$Cu^{2+}>Fe^{3+}>As^{3+}>Zn^{2+}>Ni^{2+}>Cd^{2+}>Co^{2+}>Cr^{3+}>Pb^{2+}$.

The rate of exchange was rapid, i.e. $t_{1/2} < 9$ *min, bas*ed on the exchange of copper ion.

Chemical modification of cellulose powder is performed by successive reactions with acrylonitrile in an alkaline medium followed by aqueous hydroxylamine to prepare amidoximated cellulose. Due to complexation, the amidoxime groups immobilize heavy cations from buffered solutions at various pH values. The capacity of adsorption for Cu(II) and *C*r (III) ions is related to the amount of amidoxime groups in the support, and to the metal concentration of the polluted solution. The formation of a 1/1 complex is proved by the adsorption limit values. Desorption of the cations is possible by treatment with a stronger complexing agent such as ethylenediaminetetracetic acid [110].

As second sorbent, activated carbon; was choosen for removal of uranium from waste streams. The main approach for synthesis of this sorbent is based on chemical activation of charcoal. Therefore, a recent literature survey on activated carbon is given in this section.

Activated carbon cloths are used for adsorption of monocomponent solution of organics or metal ions[111]. However, to treat wastewaters with these materials, their performance has to be determined in multicomponent solution. Studies on adsorption competition between metal ions (Cu^2, Pb^2) and organic matter (benzoic acid) were reported[111]. The first part investigates adsorption equilibrium of monocomponent metal ions solution and shows the dependence of adsorption capacities on adsorbent porosity and metal ions chemical properties (molecular weight, ionic radius and electronegativity). The influence of the pH is also demonstrated. The second part of this work focused on adsorption competition between both metal ions (a decrease of adsorption capacities is observed, whose value is related to adsorption kinetic of metal ions) and between metal ions and organic matter, in solution or adsorbed onto the activated carbon cloth.

Low-cost activated carbon was prepared from Spartina alterniflora by phosphoric acid activation for the removal of Pb(II) from dilute aqueous solution[112]. The effect of experimental parameters such as pH, initial concentration, contact time and temperature on the adsorption was studied. The obtained data were fitted with the Langmuir and Freundlich equations to describe the equilibrium isotherms. The kinetic data were fitted with the Lagergren-first-order, pseudo-second-order and Elovich models. It was found that pH played a major role in the adsorption process. The maximum adsorption capacity for Pb(II) on S. alterniflora activated carbon (SAAC) calculated from Langmuir isotherm was more than 99 mg g^{-1}. The optimum pH range for the removal of Pb(II) was 4.8–5.6. The Freundlich isotherm model was found to best describe the experimental data. The kinetic rates were best fitted to the pseudo-second-order model. Thermodynamic study showed that the adsorption was a spontaneous exothermic process.

To increase the capacity of activated carbon to adsorb heavy metals, activated carbons were impregnated with the anionic surfactants sodium dodecyl sulfate (SDS), sodium dodecyl benzene sulfonate (SDBS), or dioctyl sulfosuccinate sodium (DSS) [113]. Surfactant-impregnated activated carbons removed Cd(II) at up to 0.198 $mmolg^{-1}$, which was more than an order of magnitude better than the Cd(II) removal performance of activated carbon without surfactant (*i.e.*, 0.016 $mmolg^{-1}$) even at optimal pH (*i.e.*, pH 6). The capacity of the activated carbon to adsorb Cd(II) increased in proportion to the quantity of surfactant with which they were impregnated. The kinetics of the adsorption of Cd(II) onto the surfactant-impregnated activated carbon was best described by a pseudo-second-order model, and was described better by the Freundlich adsorption isotherm than by the Langmuir isotherm. The surface charge of activated carbon was negative in all pH ranges tested (2–6). These results indicate that surface modification with anionic surfactant could be used to significantly enhance the capacity of activated carbon to adsorb cations.

Activated carbon was prepared from charcoal by chemical activation. The preparation process consisted of zinc chloride impregnation followed by carbonization [114]. The carbonization temperature ranges from 500 t0 700 ^{0}C for 1 h. Activated carbon produced from charcoal has been shown to be a good adsorbent for uranium from liquid radioactive wastes. The adsorption of uranium was studied as a function of pH, concentration of adsorbate, shaking time, particle size, amount of adsorbent and temperature.