Chapter VI

Summary And Outlook.
SUMMARY AND OUTLOOK

Water is one of the abundantly available substances in nature. It is a marvelous substance-flowing, swirling, seeping, constantly moving from sea to land and back again. About 80% of the earth is covered by water. A small percentage of the water is useful for drinking, agriculture, domestic and industrial consumption. The inordinate population growth, rapid industrialization, fast urbanization and modified agricultural operations have intensified the interaction of man with the environment. As a result, there is alarming increase in the pollution of air, water and soil.

Water is mostly used for industrial and municipal purposes. Each industry has its own water requirements and sometimes adequate supply of water may be very suitable for one industry but the same may be dangerous for the other. Human health is seriously affected by environmental and ecological disorder. The situation, if not controlled, would be a big threat to the survival of mankind on earth. Most rivers in our country are polluted in a lesser or a greater degree. The waste produced by industrial process is discarded in water resources in a dissolved state. Wastes from petrochemical industry, chemical industry, paper mills, sugar factories, steel industry and many other industries is discarded in water. These contain various metals like copper, zinc, mercury, lead and detergents as well as acids and other pollutants. These are lethal and disease of liver, kidneys, skin, reproductive system and nervous system in human can occur.

The textile industry, a major consumer of water for several of its wet processing operations, is also a major producer of effluent wastewater containing organic surfactants, salts, acids, alkalise, solvents and dyes as some of its main constituents. Dyes, though present in only small amounts are highly detectable and thereby are capable of causing serious problems of an aesthetic nature in the receiving waterbodies. India is the second largest exporter of dyestuffs and intermediates developing countries, after China. The presence of even very low concentrations of dyes in effluent is highly visible and degradation products of these textile dyes are often carcinogenic.
Dye removal has ecological and economical importance. Methods such as chemical coagulation, ozonization, membrane filtration, electrolysis, oxidation and bio-degradation have been widely used for the removal of dyes from water and wastewater. Adsorption has become one of the most effective and comparatively low cost methods for the colour removal of textile wastewater. Adsorption is by far the most effective and non-destructive technique that is widely used for the removal of dyes from aqueous solutions. It is attractive as the adsorbed dyes can be recovered with suitable regenerating agents. For removing the dye from water, polymeric hydrogels are used. Hydrogels are crosslinked macromolecular networks formed by hydrophilic polymers swollen in water or biological fluids. After polymerization, the hydrophilic gel is brought in contact with water, the network expands, the thermodynamically driven swelling force is counterbalanced by the retractive force of the crosslinked structure, two forces become equal at some point and equilibrium is reached.

TTEGDA (tetra ethylene glycol diacrylate)-, NN MBA (N,N'-methylene bis acrylamide)- and HDODA (1,6-hexane diol diacrylate)-crosslinked acrylic acid-N-vinyl pyrrolidone (AA-NVP) are the copolymeric hydrogels prepared by suspension polymerization. Crosslinked copolymers with monomers in the ratio of 1:1, 2:1 and 3:1 were synthesized.

Malachite Green (MG) is a basic dye. This chemical dye is primarily designed to be used as a dye for silk, leather and paper. It is deadly toxic to all marine and freshwater invertebrates, algae, plant life. Malachite Green has detrimental effects on liver, gill, kidney, intestine and gonads of aquatic organisms. When it was inhaled or ingested by human, it may cause irritation to the gastrointestinal tract and even cancer. Contact of Malachite Green with skin causes irritation with redness and pain. Intermediate products after degradation of MG are also reported to be carcinogenic. The dye Brilliant Blue G (BBG) which is also known as acid blue 90 and Coomassie BBG. Its ingestion can cause eye, skin and respiratory tract irritation. BBG is a hazardous dye used for dying silk, paper and leather. Its use is banned in many countries because of its toxic nature.
The work presented in this thesis aimed at the removal of hazardous dyes from water using polymeric hydrogels. Dye binding studies of 5-20 mol% HDODA-, NNMBA-, TTEGDA-crosslinked acrylic acid-N-vinylpyrrolidone-copolymers were carried out. The conditions for maximum binding were optimized by altering certain factors such as nature and degree of crosslinking, concentration of dye solution, amount of polymer added, swelling, pH and temperature.

In my experiments, considering the effect of concentration on dyes, Malachite Green and Brilliant Blue G, dye binding plays an important role. In all cases, the weight of dye bound by the copolymer increased regularly with increasing concentration of dye solution.

But the dye MG and BBG binding decreased regularly, when high amounts of polymer are added. In the case of effect of temperature, the interaction between dye and polymer takes place through electrostatic interaction, the dye units are weakly bound to the polymer and heat of adsorption is very low. This results in a decrease of adsorption with increasing temperature. The lower dye uptake at higher temperature arises from the exothermicity of the uptake process. This leads to an overall decrease in the rate of uptake at lower affinity binding sites in preference to the high affinity binding sites. Sometimes, higher uptake at higher temperature taking place due to the endothermicity. Dye binding increases gradually as the temperature increases from 27-57°C due to the endothermic process (Polym Int, 2003, 52: 973-980 & J. Macromol Sci; Pure & Appl. Chem. 2006, 43, 689-694).

Considering the nature and degree of crosslinking, when the crosslinking is low, the polymer networks are flexible and not rigid enough to hold on the specific binding cavities leading to effective binding. At very high crosslinking, the highly crosslinked polymer is too rigid and reduces the accessibility of the dye into the cavities which also reduces effective binding. So each polymer requires an optimum crosslinking.

Effect of pH on binding of dyes MG and BBG was also studied. The experiments were carried out at different pH of phosphate buffer [Na₂HPO₄–KH₂PO₄ (0.025 M)] at room temperature. The extent of dye binding was found out
spectrophotometrically. The dye binding of NNMBMA-, TTEGDA- and HDODA-crosslinked AA-NVP polymers at different pH conditions were studied.

In most of the MG binding studies, considering the pH, basic systems are highly accessible for binding of dye and shows highest binding. At lower pH, the protonation of the polymer occurs resulting in the lower uptake. The complexation was more effective at the less protonated state and it increases up to the optimum pH. But in the case of BBG binding, dye binding is high at a lower pH. The reason behind is the interaction of ions in basic dye with ions at acidic pH.

The swelling characteristics of the polymers vary with the nature and extent of crosslinking agents. Since dye binding was carried out in aqueous media, the swelling studies of HDODA-, NNMBMA- and TTEGDA-crosslinked 5-20 mol% AA-NVP systems were followed in water. Here the water-intake by the HDODA-, NNMBMA- and TTEGDA-crosslinked systems increases. Availability of reactive sites for water molecules is increased for consecutive points. The swelling of HDODA-, NNMBMA- and TTEGDA-crosslinked AA-NVP system shows high value due to the increased flexibility and hydrophilic nature. In the case of dye bound systems, availability of reactive sites for water molecules is decreased, thereby decreasing the swelling characteristics.

Characterisation of copolymeric hydrogels and dye bound polymers were carried out by using FT-IR spectra, UV spectra, $^{13}$C NMR spectra and Scanning Electron Microscopy (SEM) studies. The incorporation of crosslinking agent and functional monomer in the polymer backbone was confirmed by $^{13}$C NMR spectra. FT-IR spectra provide the fundamental analytical basis for rationalizing the mechanism of interactions for selective binding site formation at the molecular level. The interaction between the functional monomer and the dye can be confirmed by the characteristic FT-IR absorption analysis. SEM is the most widely used technique to study the shape, size, morphology and porosity of polymers. The efficiency of a functional monomer is governed by the accessibility of the reactive functional groups anchored on it, which, in turn, depends upon the extent of swelling. The rate of diffusion of a reagent into the polymer matrix depends on the extent of swelling. The extent of swelling can be determined in terms of change in weight.
From the optimization of the condition of dye binding studies, it was clearly showed that hazardous dyes Malachite Green and Brilliant Blue G were easily and effectively removed from wastewater by using TTEGDA-, NN MBA- and HDODA-crosslinked AA-NVP copolymeric hydrogels.