

Adsorption Bed Reactor using Polyvinyl Alcohol and Polyethylene Glycol

¹K. Anitha, ²V. Shanmugavadivu
¹Assistant Professor, ²Assistant Professor
 Mahendra Engineering College

Abstract - Industrial waste water and their harmful issues are the threatening factors of this technological and industrial world. This waste water when released into the natural water ways affects the soil quality as well as the aquatic life to a greater extent. The heavy metals in these waste waters are haunting the irrigation also. Hence treatment of these water is necessary and urgent. Polyvinyl Alcohol and Polyethylene Glycol polymer is referred for the removal of the heavy metals from this water especially from the effluents of sago and textile industry. These membranes are used in a Reverse Osmosis system and on the basis of 18 electron rule heavy metals can be adsorbed successfully in this adsorption bed reactor using Polyvinyl Alcohol and Polyethylene Glycol. Thus the treated water can be used for industrial purpose as well as for aquatics in a least expensive but effective process

keywords - Polyvinyl Alcohol , Polyethylene Glycol, Heavy metal removal

1. Introduction

Adsorption is the adhesion of atoms, ions or molecules from a gas, liquid or dissolved solid to a surface. In other words the process of taking up substances from solution on surface is called adsorption. This process creates a film of the adsorbate on the surface of the adsorbent. This process differs from absorption, in which a fluid (the absorbate) is dissolved by or permeates a liquid or solid (the absorbent), respectively. Adsorption is a surface-based process, while absorption involves the whole volume of the material. The term adsorption encompasses both processes, while desorption is the reverse of it. Adsorption is a surface phenomenon.

Poly vinyl alcohol:

Polyvinyl alcohol (PVA), which is essentially made from polyvinyl acetate through hydrolysis, is easily degradable by biological organisms and in water is a solubilised crystalline structure polymer. PVA is an artificial polymer that has been used during the first half of the 20th century worldwide. It has been applied in the industrial, commercial, medical, and food sectors and has been used to produce many end products, such as lacquers, resins, surgical threads, and food packaging materials that are often in contact with food. Polyvinyl alcohol (PVA), which is essentially made from polyvinyl acetate through hydrolysis, is easily degradable by biological organisms and in water is a solubilised crystalline structure polymer. This polymer is widely used by blending with other polymer compounds, such as biopolymers and other polymers with hydrophilic properties; it is utilized for various industrial applications to enhance the mechanical properties of films because of its compatible structure and hydrophilic properties. Some man-made polymers, which are made from non-renewable and non-biodegradable sources, such as PVA, are available. Polymers that are biologically decomposable originate from petroleum-based synthetic materials, which decompose naturally under aerobic (composting) or anaerobic (landfill) conditions. PVA is a widely used thermoplastic polymer that is benign to living tissues, harmless, and nontoxic. This polymer is widely investigated because of its use in cross-linked products and nano fillers. PVA is a biodegradable polymer, and its degradability is enhanced through hydrolysis because of the presence of hydroxyl groups on the carbon atoms. PVA is a major artificial polymer that has been available for more than nine decades. PVA is synthesized through the saponification process of poly(vinyl acetate) and has long been used by blending with other natural polymers because of its film-forming features. The complete dissolution of PVA in water is bound by its intrinsic properties, which require the water temperature to be at $\sim 100^{\circ}\text{C}$ with a holding time of 30 min. All PVA grades are hydrophilic and depend on certain factors, such as molecular weight, element dimensions of distribution, and particle crystal structure. The resulting gel properties have been reported in literature.

Chemical Structure of PVA:

The properties of polyvinyl acetate depend on the extent or degree of its hydrolysis, specifically whether it is full or partial, which in turn dictates its categorization into two groups, namely, (a) partially hydrolyzed and (b) fully hydrolyzed. The molecular weights obtained for PVA products may vary (20,000–400,000), depending on the length of the initial vinyl acetate polymer, the level of hydrolysis to eliminate the acetate groups and whether it occurs under alkaline or acidic conditions. Figure 2 shows the structure of PVA. Hydrolysis levels vary from what is considered a typical value of 80% to reach more than 99%. Nearly fully hydrolyzed forms result in forming PVA hydrogels with tuneable properties through cross linking of the linear polymers, which subsequently result in polymer (gel) - fluid (sol) species. Polymer contents affect the physical status of the resulting material: low polymer content results in a soft material because the fluid moves freely through the matrix, whereas a higher polymer content results in considerable stiffening and strengthening of the material's matrix. Studies on the diffusive permeability of solutes in PVA gel membranes and the application for separation have been delineated because of chemical stability, particularly on film-forming, and hydrophobicity.



Fig 1.1 PVA Polymer



Fig 1.2 PEG Polymer

Polyethylene Glycol:

Polyethylene glycol (PEG) is a polyether compound with many applications from industrial manufacturing to medicine. PEG is also known as polyethylene oxide (PEO) or polyoxy ethylene (POE), depending on its molecular weight. The structure of PEG is commonly expressed as $H-(O-CH_2-CH_2)_n-OH$.

PEG, PEO, and POE refer to an oligomer or polymer of ethylene oxide. The three names are chemically synonymous, but historically PEG is preferred in the biomedical field, whereas PEO is more prevalent in the field of polymer chemistry. Because different applications require different polymer chain lengths, PEG has tended to refer to oligomers and polymers with a molecular mass below 20,000 g/mol, PEO to polymers with a molecular mass above 20,000 g/mol, and POE to a polymer of any molecular mass. PEGs are prepared by polymerization of ethylene oxide and are commercially available over a wide range of molecular weights from 300 g/mol to 10,000,000 g/mol.

PEG and PEO are liquids or low-melting solids, depending on their molecular weights. While PEG and PEO with different molecular weights find use in different applications, and have different physical properties (e.g. viscosity) due to chain length effects, their chemical properties are nearly identical. Different forms of PEG are also available, depending on the initiator used for the polymerization process – the most common initiator is a mono functional methyl ether PEG, or methoxy poly(ethylene glycol), abbreviated mPEG. Lower-molecular-weight PEGs are also available as purer oligomers, referred to as monodisperse, uniform, or discrete. Very high purity PEG has recently been shown to be crystalline, allowing determination of a crystal structure by x-ray diffraction. Since purification and separation of pure oligomers is difficult, the price for this type of quality is often 10–1000 fold that of poly disperse PEG.

PEGs are also available with different geometries.

- Branched PEGs have three to ten PEG chains emanating from a central core group.
- Star PEGs have 10 to 100 PEG chains emanating from a central core group.
- Comb PEGs have multiple PEG chains normally grafted onto a polymer backbone.

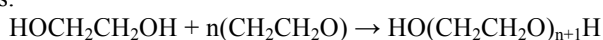
The numbers that are often included in the names of PEGs indicate their average molecular weights (e.g. a PEG with $n = 9$ would have an average molecular weight of approximately 400 daltons, and would be labeled PEG 400.) Most PEGs include molecules with a distribution of molecular weights (i.e. they are polydisperse). The size distribution can be characterized statistically by its weight average molecular weight (M_w) and its number average molecular weight (M_n), the ratio of which is called the polydispersity index (M_w/M_n). M_w and M_n can be measured by mass spectrometry.

PEGylation is the act of covalently coupling a PEG structure to another larger molecule, for example, a therapeutic protein, which is then referred to as a PEGylated protein. PEGylated interferon alfa-2a or -2b are commonly used injectable treatments for hepatitis C infection. PEG is soluble in water, methanol, ethanol, acetonitrile, benzene, and dichloromethane, and is insoluble in diethyl ether and hexane. It is coupled to hydrophobic molecules to produce non-ionic surfactants. PEGs potentially contain toxic impurities, such as ethylene oxide and 1,4-dioxane. Ethylene Glycol and its ethers are nephro toxic if applied to damaged skin.

Polyethylene glycol (PEG) and related polymers (PEG phospholipid constructs) are often sonicated when used in biomedical applications. However, as reported by Murali et al., PEG is very sensitive to sonolytic degradation and PEG degradation products can be toxic to mammalian cells. It is, thus, imperative to assess potential PEG degradation to ensure that the final material does not contain undocumented contaminants that can introduce artifacts into experimental results. PEGs and methoxy polyethylene glycols are manufactured by Dow Chemical under the tradename Carbowax for industrial use, and Carbowax Sentry for food and pharmaceutical use. They vary in consistency from liquid to solid, depending on the molecular weight, as indicated by a number following the name. They are used commercially in numerous applications, including as surfactants, in foods, in cosmetics, in pharmaceuticals, in biomedicine, as dispersing agents, as solvents, in ointments, in suppository bases, as tablet excipients, and as laxatives. Some specific groups are lauromacrogols, nonoxynols, octoxynols, and poloxamers. Macrogol, used as a laxative, is a form of polyethylene glycol. The name may be followed by a number which represents the average molecular weight.

Production:

The production of polyethylene glycol was first reported in 1859. Both A. V. Laurence and Charles Adolphe Wurtz independently isolated products that were polyethylene glycols. Polyethylene glycol is produced by the interaction of ethylene oxide with water, ethylene glycol, or ethylene glycol oligomers. The reaction is catalyzed by acidic or basic catalysts. Ethylene glycol and its oligomers are preferable as a starting material instead of water, because they allow the creation of polymers with a low polydispersity (narrow molecular weight distribution). Polymer chain length depends on the ratio of reactants.



Depending on the catalyst type, the mechanism of polymerization can be cationic or anionic. The anionic mechanism is preferable because it allows one to obtain PEG with a low poly dispersity. Polymerization of ethylene oxide is an exothermic process. Overheating or contaminating ethylene oxide with catalysts such as alkalis or metal oxides can lead to runaway polymerization, which can end in an explosion after a few hours. Polyethylene oxide, or high-molecular weight polyethylene glycol, is synthesized by suspension polymerization. It is necessary to hold the growing polymer chain in solution in the course of the poly condensation process.

The reaction is catalyzed by magnesium-, aluminium-, or calcium-organo element compounds. To prevent coagulation of polymer chains from solution, chelating additives such as dimethyl glyoxime are used. Alkaline catalysts such as sodium hydroxide (NaOH), potassium hydroxide (KOH), or sodium carbonate (Na₂CO₃) are used to prepare low-molecular-weight polyethylene glycol.

Health effects

PEG is generally considered biologically inert and safe. However, studies of clinical safety are generally based on adults, not children. The FDA has been asked to investigate the possible effects of PEG in laxatives for children. Also, a minority of people are allergic to it. Allergy to PEG is usually discovered after a person has been diagnosed with an allergy to an increasing number of seemingly unrelated products, including processed foods, cosmetics, drugs, and other substances that contain PEG or were manufactured with PEG.

Cellulose Acetate

Cellulose acetate is the acetate ester of cellulose. It was first prepared in 1865. Cellulose acetate is used as a film base in photography, as a component in some coatings, and as a frame material for eyeglasses, it is also used as a synthetic fiber in the manufacture of cigarette filters and playing cards. In photographic film, cellulose acetate replaced nitrate film in the 1950s, being far less flammable and cheaper to produce.

Characteristics

Acetate is a very valuable manufactured fiber that is low in cost and has good draping qualities. Acetate is used in fabrics such as satins, brocades, and taffetas to accentuate luster, body, drape and beauty.

- cellulosic and thermoplastic
- selective absorption and removal of low levels of certain organic chemicals
- easily bonded with plasticizers, heat, and pressure
- acetate is soluble in many common solvents (especially acetone and other organic solvents) and can be modified to be soluble in alternative solvents, including water
- hydrophilic: acetate wets easily, with good liquid transport and excellent absorption; in textile applications, it provides comfort and absorbency, but also loses strength when wet
- acetate fibers are hypoallergenic and high surface area
- made from wood pulp, a renewable resource and can be composted or incinerated
- can be dyed, however special dyes and pigments are required since acetate does not accept dyes ordinarily used for cotton and rayon (this also allows cross-dyeing)
- resistant to mold and mildew
- easily weakened by strong alkaline solutions and strong oxidizing agents.

Production

The Federal Trade Commission definition for acetate fiber is "A manufactured fiber in which the fiber-forming substance is cellulose acetate. Where not less than 92 percent of the hydroxyl groups are acetylated, the term triacetate may be used as a generic description of the fiber." Acetate is derived from cellulose by initially deconstructing wood pulp into a purified fluffy white cellulose. To manufacture a good product, special qualities of pulps, such as dissolving pulps, are used. The uneven reactivity of cellulose presents a common problem affecting the quality of the cellulose acetate product. The cellulose is reacted with acetic acid and acetic anhydride in the presence of sulfuric acid. It is subjected to a controlled, partial hydrolysis to remove the sulfate and a sufficient number of acetate groups to give the product the desired properties. The anhydroglucose unit is the fundamental repeating structure of cellulose and has three hydroxyl groups which can react to form acetate esters. The most common form of cellulose acetate fiber has an acetate group on approximately two of every three hydroxyls. This cellulose diacetate is known as secondary acetate, or simply as "acetate". After it is formed, cellulose acetate is dissolved in acetone, forming a viscous solution for extrusion through spinnerets (which resemble a shower head). As the filaments emerge, the solvent is evaporated in warm air via dry spinning, producing fine cellulose acetate fiber.

Disposal and Degradation

The global production of CA materials was over 800,000 tonnes (790,000 long tons; 880,000 short tons) per year in 2008. Many products are disposed of as [litter](#) or into compost. While it was initially believed that CA was virtually non-[biodegradable](#), it has been shown that after initial partial deacetylation the polymer's cellulose backbone is readily biodegraded by [cellulase](#) enzymes. In biologically highly active [soil](#), CA fibers are completely destroyed after 4–9 months. Photo degradation is optimal with 280 nm or shorter wavelength UV-irradiation and enhanced by [TiO₂](#) pigment. CA cigarette filters take years to be broken down in the open.

PVA – PEG Polymer

PVA-PEG graft co-polymer is a synthetic branched co-polymer consisting of a main backbone of PEG and two to three side chains of PVA. The co-polymer is manufactured by grafting polyvinyl acetate chains onto the PEG backbone which are then hydrolysed to form the PVA side chains. The final co-polymer consists of approximately 75% PVA units and 25% PEG units on a weight basis. PVA-PEG graft co-polymer is primarily intended for use as a film coating on food supplement products. Specifically, the sponsor is requesting that the co-polymer be considered for use as a glazing agent, binder for tablets and

stabilizer in food supplements at a level not to exceed 10% in the food supplement. The sponsor indicates that the final co-polymer formulation may contain 0.3 to 0.5% colloidal silica to improve the flow of the co-polymer in powder form. Graft copolymers are a form of copolymer where the side chains are structurally different from the main chain. PVA-PEG graft copolymer is a synthetic branched graft co-polymer consisting of side chains of PVA on a main chain of PEG. The copolymer is made up of approximately 75% vinyl alcohol units (-CH₂CH₂(OH)-) and 25% ethylene glycol units (-CH₂CH₂O-). PVA-PEG graft copolymer is manufactured by forming polyvinyl acetate side chains onto a PEG backbone that has an average molecular weight of 6,000 Daltons. The polyvinyl acetate side chains are then hydrolysed to form PVA side chains. The sponsor indicates that the copolymer has an average of 2 to 3 PVA side chains per polyethylene glycol backbone, and an average molecular weight between 40,000 and 50,000 Daltons. Two CAS registry numbers are referenced for the polymer: 96734-39-3 and 121786-16-1. There is no definitive molecular formula for the PVA-PEG graft co-polymer. However, the following structural formula is representative of the copolymer.

| Physico-chemical properties | |
|---|--|
| Molecular weight | 45,000 Daltons |
| pH | 5-6 |
| K value (7% water) | 21-26 |
| Solubility | |
| Water | > 20% |
| 0.08 N HCl (pH 1.2) | > 20% |
| Phosphate buffer, pH 6.8 | > 20% |
| Water/Ethanol (1:1) | 20% |
| Organic solvents | Insoluble |
| Viscosity at 20 wt% (water) | 115 mPa.s |
| Oxygen permeability | 104 cm ³ /100 μm ² /d |
| Water vapor permeability | 510 cm ³ /100 μm ² /d |
| Elongation at break (film thickness 100 μm) | 100% @ 0.4% strain |
| Disintegration time (film thickness 100 μm) | 0.44 sec. @ pH 1.2, pH 6.8 |
| Dissolution time (film thickness 100 μm) | 1.20 min. @ pH 1.2, pH 6.8 |
| Surface tension, 23 °C | 10 wt% solution: 44 mN/m ² 20 wt% solution: 41 mN/m ² |
| PEG (free) | None |

Fig 1.4 Physico-Chemical properties

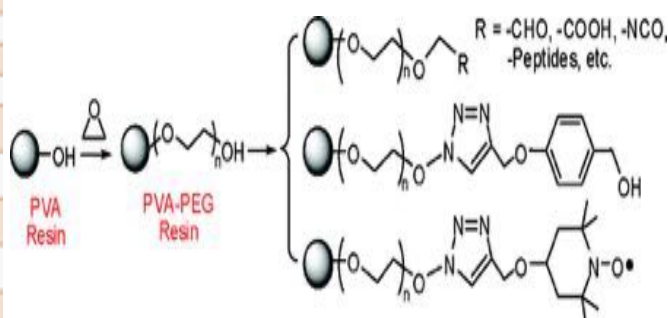


Fig 1.5 PVA-PEG Structure

Manufacturing Process

PVA-PEG graft co-polymer is synthesized by means of a two-step reaction process. In the first step, a polymerization reaction occurs whereby PEG and vinyl acetate are reacted together in the presence of a polymerization initiator in methanol to form PEG-graft poly (vinyl acetate) copolymer. In the second step, the PEG-graft-poly (vinyl acetate) copolymer is further reacted with sodium methoxide in methanol to form PVA-PEG graft copolymer and methyl acetate. No additional catalysts are used. The polymer solution is then purified by steam distillation.

Chemical characterization

Composition The co-polymer is characterized by an average molecular weight of 40,000 to 50,000 Daltons. The bulk material appears as a white to pale yellow free-flowing powder. The co-polymer is freely soluble in water, but is practically insoluble in undiluted ethanol, acetic acid, acetone, and chloroform. The co-polymer does, however, dissolve in dilute acids and dilute alkali hydroxides. The sponsor provided data on the analysis of the co polymer by means of infrared and nuclear magnetic resonance spectroscopic methods. **4.2 Impurities** The predominant impurities identified by the sponsor for the PVA-PEG graft copolymer are carry over impurities from the starting materials, residual solvents, reaction by products, and heavy metals. PEG-PVA is a hydrophilic freely water-soluble polymer, comprised of 25% PEG and 75% PVA, wherein the vinyl alcohol moieties are grafted on a polyethylene glycol backbone. PEG-PVA is a spray dried powder of a high flow ability recognizable by an angle of repose below 30°. The grafted PEG acts as a plasticizer, and hence provides a greater flexibility of films without additional plasticizers. PEG-PVA films with iron oxide red pigment are effective against transmission of light and meets the European pharmacopeia's requirement of coloured light protecting glass containers¹¹. The low viscosity of PEG-PVA even at higher solid contents in aqueous solutions, improves processing time and saves cost.

Spherical cross linked poly (vinyl alcohol) (PVA) beads with good mechanical stability were prepared by reverse-suspension polymerization, using dimethyl sulfoxide (DMSO) as a co solvent in an aqueous phase. Poly (ethylene glycol)s with varying chain lengths were grafted onto the PVA beads by anionic polymerization of ethylene oxide. The thermal behaviour, morphology, and swelling were evaluated for each of the new polymer matrices. High loading and good swelling in water and organic solvents were characteristic of the PEG-grafted PVA beads. The polymer beads also exhibited good mechanical and chemical stability and were unaffected by treatment with 6 N HCl and with 6 N NaOH. The hydroxyl groups of the PVA-PEG beads were converted into aldehyde, carboxylic acid, and isocyanate functions to provide scavenger resins and were extended by way of a benzyl alcohol in a Wang linker. The transglutaminase substrates dipeptides (Z-Gln-Gly) and heptapeptides (Pro-Asn-Pro-Gln-Leu-Pro-Phe) were synthesized on PVA-PEG₅, PVA-PEG₂₀, and the Wang linker-derivatized PVA-PEG resins. The cleavage of the peptides from the resins using MeOH/NH₃ mixture at different temperatures (0 °C and room temp) and 50% TFA/DCM provided, respectively, peptide methyl esters, amides, and acids in good yields and purity as assessed by LC-MS analysis.

2. Heavy Metals Removal by PVA-PEG Polymer

Batch experiments showed that the adsorption capacities of PEG and PVA polymers increased quietly as a result of molecular weight with increase in active surfaces of adsorbents. It is important to note that the adsorption capacities of the PEG

and PVA polymers presented in this paper vary, depending on the characteristics of the individual adsorbent, the extent of molecular weight, and the concentration of adsorbate. The maximum percentage removal with PEG of Cd, Cr, Cu, Pb, Zn, and Mo followed the order: Cu (96%) > Cr (94%) = Mo (94%) > Zn (74%) > Cd (70%) > Pb (11%), while the removal of Cd, Cr, Cu, Mo, Pb, and Zn with PVA adsorbents followed the order: Cu (95%) > Mo (93%) > Cr (91%) > Cd (84%) > Zn (78%) > Pb (>10%). Obviously, PEG and PVA polymers are suitable for industrial hazardous solid waste containing Cd, Cr, Cu, Mo, Pb, and Zn contaminations. The calculated singular indices including ecological risk factor showed that Cd should be considered a moderate potential ecological risk, while Cr, Cu, Pb, and Zn indicated a low ecological risk.

Leaching experiments:

Leaching experiments were conducted with polyethylene glycol (PEG) and polyvinyl alcohol (PVA) to determine concentrations of heavy metals that are released from PG to the aqueous phase. Four kinds of polymers with different weight average molecular weights were applied as follows: (PEG-1, MW = 10,000), polyethylene glycol (PEG-2, MW = 35,000), polyvinyl alcohol 80% hydrolyzed (PVA-1, MW = 9500), and polyvinyl alcohol 87–89% hydrolyzed (PVA-2, MW = 18,000). These polymers were obtained from Merck, Germany, and used without purification. Distilled water was used as dispersing medium. PEG and PVA were used as polymers. The reaction was carried out in an aqueous media at room temperature for 4 h. Total 2.2 g of PEG and PVA was used for leaching test. Masses of 0.5 g, 0.7 g and 1 g were weighed and volumes of 100 ml of distilled water were added to each experiment to produce surfactant solutions. The surfactant solution was then added followed by 2 g of PG for each test, assuring that the solid always remained in suspension. Important parameters, such as, room temperature of 30 C, leaching duration of 24 h, and liquid/solid (L/S) ratio influencing the leaching process, were investigated in order to obtain metal concentrations as high as possible or select optimal parameters for the leaching process. Finally, the mixing products of PG and surfactant solutions were then separated by centrifugation at 3000 rpm for 5 min. The extract was decanted and filtered through 0.45 μ m filter paper. The treated PG mass was dried overnight at 65 C, and then analyzed by AAS analysis.

The results of the present work suggested that the addition of PEG and PVA with different molecular weights could change the PG structure and properties to remove heavy metals. During batch experiments, because of the addition of PEG and PVA with increasing molecular weight and with increasing dosage, a decrease in mobility increases the heavy metals removal. The results of heavy metal removal from PG leachate with polymer methods consisting of PEG and PVA were approved. The batch experiments' result obtained showed that the removal of Cd, Cr, Cu, Pb, Zn and Mo in these samples ranged from 57% to 70%, 80% to 94%, 90% to 96%, 7% to 11%, 55% to 74%, and 81% to 94%, respectively for PEG, and from 70% to 84%, 80% to 91%, 89% to 95%, 7% to 10%, 55% to 78%, and 82% to 93%, respectively for PVA. The potential ecological risk factors (E_{ri}) showed that Cd should be considered a moderate potential ecological risk, whereas Cr, Cu, Pb, and Zn indicated a low ecological risk. The potential ecological risk indices (RI) considered that Cd, Cr, Cu, Pb, and Zn indicated pollution in all studied samples is less. These results indicated that Cd, Cr, Cu, Pb, and Zn content removal using PEG and PVA polymers would be of great importance in environmental applications, and they can be considered a very suitable safe use of PG in agriculture and soil amendment.

Removal of Heavy Metals by RO

Adsorption on new adsorbents

Sorption is transfer of ions from water to the soil i.e. from solution phase to the solid phase. Sorption actually describes a group of processes, which includes adsorption and precipitation reactions. Recently, adsorption has become one of the alternative treatment techniques for wastewater laden with heavy metals. Basically, adsorption is a mass transfer process by which a substance is transferred from the liquid phase to the surface of a solid, and becomes bound by physical and/or chemical interactions. Various low-cost adsorbents, derived from agricultural waste, industrial by-product, natural material, or modified biopolymers, have been recently developed and applied for the removal of heavy metals from metal-contaminated wastewater. In general, there are three main steps involved in pollutant sorption onto solid sorbent: (i) the transport of the pollutant from the bulk solution to the sorbent surface; (ii) adsorption on the particle surface; and (iii) transport within the sorbent particle. Technical applicability and cost-effectiveness are the key factors that play major roles in the selection of the most suitable adsorbent to treat inorganic effluent.

Adsorption on modified biopolymers and hydrogels:

Biopolymers are industrially attractive because they are, capable of lowering transition metal ion concentrations to sub-part per billion concentrations, widely available, and environmentally safe. Another attractive feature of biopolymers is that they possess a number of different functional groups, such as hydroxyls and amines, which increase the efficiency of metal ion uptake and the maximum chemical loading possibility. New polysaccharide-based-materials were described as modified biopolymer adsorbents (derived from chitin, chitosan, and starch) for the removal of heavy metals from the wastewater. Also graft polymer PVA-PEG can be used as adsorbent in reverse osmosis process for the effective removal of heavy metals from industrial waste water.. There are two main ways for preparation of sorbents containing polysaccharides: (a) cross linking reactions, a reaction between the hydroxyl or amino groups of the chains with a coupling agent to form water insoluble cross linked networks (gels); (b) immobilization of polysaccharides on insoluble supports by coupling or grafting reactions in order to give hybrid or composite materials. Hydrogels, which are cross linked hydrophilic polymers, are capable of expanding their volumes due to their high swelling in water. Accordingly they are widely used in the purification of wastewater. Various hydrogels were synthesized and their adsorption behaviour for heavy metals was investigated. prepared poly(ethyleneglycol dimethacrylate-co-acrylamide) hydrogel beads with the following metals in the order Pb(II) > Cd(II) > Hg(II); The removal is basically governed by the water diffusion into the hydrogel, carrying the heavy metals inside especially in the absence of strongly binding sites. Maximum binding capacity increases with pH increase to >6.

Evaluation of heavy metals removal processes:

In general, physico-chemical treatments offer various advantages such as their rapid process, ease of operation and control, flexibility to change of temperature. Unlike in biological system, physico-chemical treatment can accommodate variable input loads and flow such as seasonal flows and complex discharge. Whenever it is required, chemical plants can be modified. In addition, the treatment system requires a lower space and installation cost. Their benefits, however, are outweighed by a number of drawbacks such as their high operational costs due to the chemicals used, high-energy consumption and handling costs for sludge disposal. However, with reduced chemical costs (such as utilizing of low-cost adsorbents) and a feasible sludge disposal, physico-chemical treatments have been found as one of the most suitable treatments for inorganic effluent.

In wastewater systems containing heavy metals with other organic pollutants, the presence of one species usually impedes the removal of the other. For instance, hydrometallurgy, a classical process to recover metals, is inhibited by the presence of organic compounds and a pre-treatment step, to remove or destroy organics, is generally required, pyrometallurgy which is able to decontaminate systems from organic pollutants and recover metals suffers from lack of controllability, demanding extremely high temperatures. The most promising methods to treat such complex systems are the photocatalytic ones which consume cheap photons from the UV-near visible region. These photo catalysts serve as electron relays, from the organic substrates to metal ions. Thus, they induce both degradation of organic pollutants and recovery of metals in one-pot systems, operable at traces of the target compounds (less than ppm). summarizes the main advantages and disadvantages of the various physico-chemical treatments presented in this study.

3. Textile Industries & Sago Industries

Water pollution caused by the textile industry is mainly by the release of waste streams coming out from wet processing operations like scouring bleaching, dyeing and printing etc. Due to this chemical pollution, the normal functioning of cell is disturbed and this in turn may cause alteration in physiology and biochemical mechanisms of animals resulting in impairment of important functions like respiration, osmoregulation, reproduction and even mortality. In the present investigation, the concentration of selected heavy metals and physicochemical characteristics of the effluent samples were evaluated to ascertain the efficiency of industry's waste water treatment process. Conventional methods were employed for determination of physicochemical parameters while, heavy metals in the effluent samples were analyzed using an atomic absorption spectrophotometer. The results obtained from the physicochemical analysis of all the samples of effluent indicated high temperatures, alkaline pH, and foul smell and were highly colored. The TSS values in all the samples and TDS values in some samples were also very high. All the samples except one sample have high microbial load which reflects in their high BOD values. The COD values of all the samples were very high indicating high degree of pollution. The results also showed elevated levels of inorganic metals. The concentration of heavy metals also has great variability. Thus textile effluent was a major source of water pollution which will affect the flora and fauna existing in such environments. This study anchors on the need for treatment textile effluent before they are discharged into the environment.

Table 3.1 : Metal Concentration In Effluents

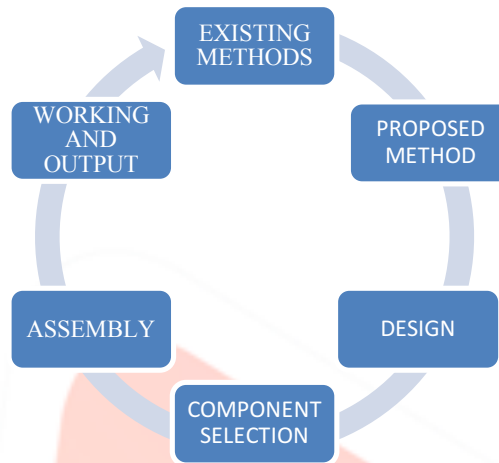
| METALS | CONCENTRATION(mg/l) |
|--------|---------------------|
| Na | 1395±342 |
| Ca | 35.12 ± 25.9 |
| Mg | 68.9 ± 22.2, |
| K | 46.46 ± 22.31 |
| Fe | 24.27 ± 9.96 |
| Ni | 1.186 ± 0.654 |
| Cr | 0.606 ± 0.184 |
| Pb | 1.74 ± 0.546 |
| Zn | 1.023 ± 0.8 |

HARMFUL EFFECTS:

With escalating demand for textile products, textile mills and their wastewater have been increasing proportionally, causing a major problem of pollution in the world. Many chemicals used in the textile industry cause environmental and health problems. Among the many chemicals in textile wastewater, dyes are considered important pollutants. Worldwide environmental problems associated with the textile industry are typically those associated with water pollution caused by the discharge of untreated effluent and those because of use of toxic chemicals especially during processing. The effluent is of critical environmental concern since it drastically decreases oxygen concentration due to the presence of hydro sulfides and blocks the passage of light through water body which is detrimental to the water ecosystem. Textile effluent is a cause of significant amount of environmental degradation and human illnesses. About 40% of globally used colorants contain organically bound chlorine, a known carcinogen. Chemicals evaporate into the air we breathe or are absorbed through our skin; they show up as allergic reactions and may cause harm to children even before birth. Due to this chemical pollution, the normal functioning of cells is disturbed and this, in turn, may cause alteration in the physiology and biochemical mechanisms of animals resulting in impairment of important functions like respiration, osmoregulation, reproduction, and even mortality. Heavy metals, present in textile industry effluent, are not biodegradable; hence, they accumulate in primary organs in the body and over time begin to fester, leading to various symptoms of diseases. Thus, untreated or incompletely treated textile effluent can be harmful to both aquatic and terrestrial life by adversely affecting the natural ecosystem and causing long-term health effects. Mills discharge millions of gallons of this effluent as hazardous toxic waste, full of color and organic chemicals from dyeing and finishing salts. Presence of sulphur, naphthol, vat dyes, nitrates, acetic acid, soaps, chromium compounds and heavy metals like copper, arsenic, lead, cadmium, mercury, nickel, and cobalt and certain auxiliary chemicals all collectively make the effluent highly toxic. Other

harmful chemicals present in the water may be formaldehyde based dye fixing agents, hydro carbon based softeners and non bio degradable dyeing chemicals. The mill effluent is also often of a high temperature and pH, both of which are extremely damaging. The colloidal matter present along with colors and oily scum increases the turbidity and gives the water a bad appearance and foul smell. It prevents the penetration of sunlight necessary for the process of photosynthesis. This interferes with the Oxygen transfer mechanism at air water interface. Depletion of dissolved Oxygen in water is the most serious effect of textile waste as dissolved oxygen is very essential for marine life. This also hinders with self purification process of water. In addition when this effluent is allowed to flow in the fields it clogs the pores of the soil resulting in loss of soil productivity. The texture of soil gets hardened and penetration of roots is prevented. The waste water that flows in the drains corrodes and incrustates the sewerage pipes. If allowed to flow in drains and rivers it effects the quality of drinking water in hand pumps making it unfit for human consumption. It also leads to leakage in drains increasing their maintenance cost. Such polluted water can be a breeding ground for bacteria and viruses. Impurities in water affect the textile processing in many ways.

4. Working Methodology



Components Used

- Water Storage Tank
- Sediment Filter
- Filter
- Membrane

Water Storage Tank

A water tank is a container for storing water. Water tanks are used to provide storage of water for use in many applications, drinking water, irrigation agriculture, fire suppression, agricultural farming, both for plants and livestock, chemical manufacturing, food preparation as well as many other uses. Water tank parameters include the general design of the tank, and choice of construction materials, linings.

Various materials are used for making a water tank: plastics (polyethylene, polypropylene), fibre glass, concrete, and stone, steel (welded or bolted, carbon, or stainless). Earthen pots also function as water storages. Water tanks are an efficient way to help developing countries to store clean water.

Sediment Filter

This is the prefilter stage of your reverse osmosis water purifier system. Each year you must change this sediment filter maintaining the regularity. This stage has been devised to remove the impurities such as silt, sediment, dirt from the drinking water. More importantly, this sediment filter has been designed to protect the RO membranes that are more delicate and easily get affected by dirt. If you do not change this sediment filter on a regular basis, the membranes of your RO system will get affected and become foul and choked.

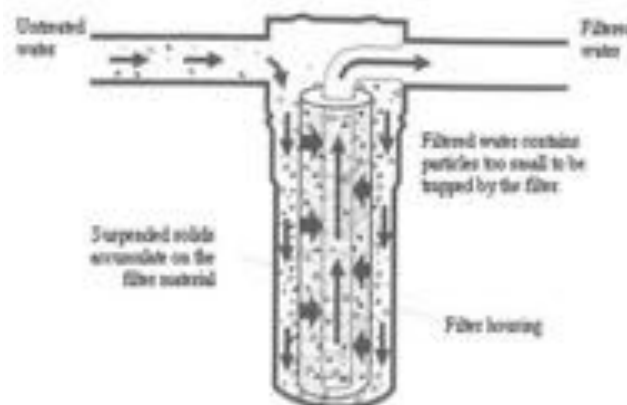


Fig 4.1- Sediment Filter

Virtually all cartridge-style sediment filters follow the "radial flow" pattern seen in the illustration. In a radial flow design, water flows through the wall of the filter into the inner core. This arrangement provides filtering surface that consists of

the entire length and circumference of the cartridge. The filter above is a "depth" filter. Pleated filters offer even more filtering surface.

In general terms, filters of this type are sieving devices. They are like nets that catch and hold particles that are too large to pass through the holes in their surface. There are large backwashing filters that perform this function. They use beds of natural media like sand, garnet, and anthracite to filter out unwanted particles like dirt or iron rust. The newer versions usually rely on specifically designed and manufactured media with brand names like Filter Ag, ChemSorb, or Micro Z to catch particles. When particles are trapped in the bed, the filter "backwashes" by running water backward through the media bed to wash the unwanted particles down the drain.

Filter

A water filter removes impurities from water by means of a fine physical barrier, a chemical process or a biological process. Filters cleanse water to various extents for irrigation, drinking water, aquariums, and swimming pools. Filters use sieving, adsorption, ion exchanges and other processes. Unlike a sieve or screen, a filter can remove particles much smaller than the holes through which the water passes.

Water polishing:

The term **water polishing** can refer to any process that removes small (usually microscopic) unwanted material from a portion of water. The process and its meaning vary from setting to setting: a manufacturer of aquarium filters may claim that its filters perform water polishing by capturing "micro particles" within nylon or polyester pads just as a chemical engineer can use the term to refer to the removal of magnetic resins from a solution by passing the solution over a bed of magnetic particulate. In this sense, water polishing is simply another term for water filtration.

Membrane

Membrane can be defined as essentially as a barrier; which separates two phases and restricts transport of various chemicals in a selective manner. Membrane is a heart of every purification process. The membrane can be made of an inorganic or organic, synthetic or biological product. Membrane of reverse osmosis system permeable for solvent and impermeable for solute. A membrane is a selective barrier that allows the passage of certain constituents and retains other constituents found in the liquid. The influent of a membrane is known as the feed-stream, the liquid that passes through the membrane is known as the permeate and the liquid containing the retained constituents is the retentive or concentrate.

The concept of a membrane has been known since the eighteenth century, but was used little outside of the laboratory until the end of World War II. Drinking water supplies in Europe had been compromised by the war and membrane filters were used to test for water safety. However, due to the lack of reliability, slow operation, reduced selectivity and elevated costs, membranes were not widely exploited. The first use of membranes on a large scale was with micro-filtration and ultra-filtration technologies. Since the 1980s, these separation processes, along with electro dialysis, are employed in large plants and, today, a number of experienced companies serve the market.

Material used For Membranes in RO

Membranes are prepared from almost every available material. In large-scale production commercial thermoplastic and cellulosic's are primarily used.

1. Cellulose acetate.
2. Aromatic polyamide
3. Polyamide

Modules Types for Reverse Osmosis System

The several forms of Reverse Osmosis membranes are sold packaged in devices to contain the steam pressure and to separate the feed and reject stream from the permeate streams. The device; usually called a module, is designed to control the feed stream-velocity and turbulence in order to reduce concentration polarization.

There are four types of modules related to the types of membrane

- a) Spiral wound
- b) Tubular
- c) Plate and frame
- d) hollow module membrane

Spiral Wound Module

A variation of the basic plate-and-frame concept is the spiral-wound module, which is widely used today in reverse osmosis, ultrafiltration, and gas separation. Its basic design is illustrated.

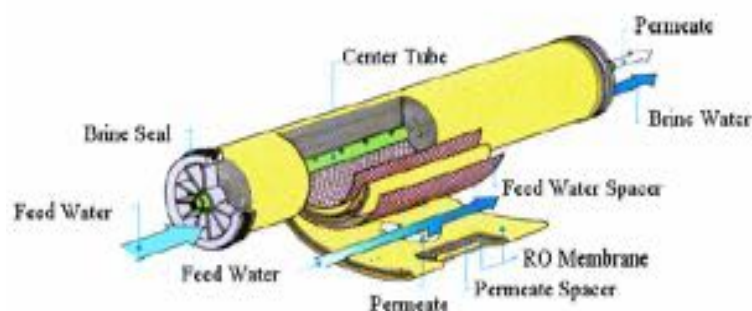


Fig 4.2: Spiral Wound Membrane Module

The feed flow channel spacer, the membrane, and the porous membrane support form an envelope which is rolled around a perforated central collection tube and inserted into an outer tubular pressure shell. The feed solution passes in axial

direction through the feed channel across the membrane surface. The filtrate is moves along the permeate channel and is collected in a perforated tube in the center of the roll. Small spiral wound units consist of just one envelope which limits the total membrane area that can be installed in one unit to about 1 to 2 m². The main reason for the limitation of the surface area which can be installed in a module containing one single envelope is the pressure drop encountered by the permeate moving down the permeate channel to the central collection tube. Because the channel in a practical unit is very narrow its length is limited to 2 to 5 m. A significantly longer path would result in an unacceptable pressure drop in the permeate channel.

Commercial spiral wound modules are about 1 meter long and have a diameter of 10 to 60 cm. The membrane area in a spiral-wound element is 3 and 60 m². Generally, 2 to 6 elements are placed in series in a pressure vessel. The spiral-wound module provides a relatively large membrane area per unit volume. The large scale production is quite cost effective and module costs per membrane area quite low. The major application of the spiral-wound module is in reverse osmosis sea and brackish water desalination. But it is also extensively used in ultra filtration and gas separation. However, the spiral-wound module is quite sensitive to fouling, and the feed channels can easily be blocked and particles or fibers should be removed from the feed solution by a proper pre treatment procedure.

Membrane preparation:

In general production method of PVA & PEG. Poly (vinyl alcohol) casting solution was prepared by dissolving 5wt. % (PVA) in water at 90°C with constant stirring until homogenous solution was obtained. After that add 0.001 wt% of the cross linking agent is malice acid. The resultant polymer solution was cast on a glass plate and the plate was subsequently placed in an oven at 50°C overnight and washed with distilled water before used. Also preparation of CA by the same technique then casting preparation. The solution was casted on a solid flat and horizontal surface of glass plate. Prior to the casting process, the glass plate was cleaned by vigorous scrubbing of the surface with a quiet liquid laboratory detergent, large volume of tap water followed by several rinse of distilled water.

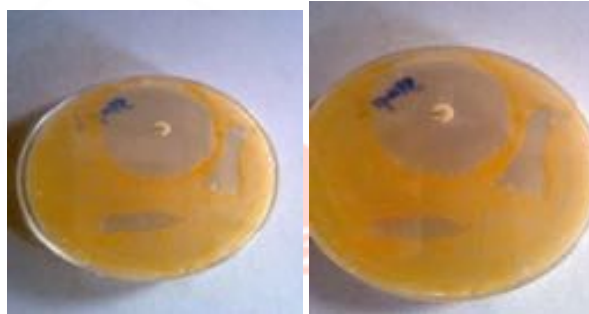


Fig 4.3 PVA & PEG membrane

The membrane was allowed to dry and the solvent was slowly evaporated in an oven at temperature 50°C for 18 hr. After drying, the membrane is floated off and the thickness of the film was determined by the thickness gauge. Applications of CA/PEG reverse osmosis membrane in desalination of saline water samples the selected CA/PEG reverse osmosis membranes were of composition 1:1 CA/PEG copolymer ratio at 100 μ membrane thicknesses. The selected membrane possesses good mechanical properties (tensile strength=63.5 M Pa and elongation=49.88%) and suitable Rs and JH2O for different feed concentrations. Three water samples were used. Two ground water samples (brackish, highly saline) and extremely saline water (sea water) were used. The waste (brine) water was recycled to maintain a constant concentration in the feed tank by adding distilled water.

Casting of the PVA film :

PVA solution (10% w/v) was prepared in Millipore water by heating it on a water bath at 85-90 °C under constant stirring. The desired quantity of maleic acid (dose varied from 10 to 60% w/w with respect to the weight of the polymer) was mixed with the solution with the help of a mechanical stirrer. The solution was cast in the form of film on glass substrates with the help of a casting blade. The film was dried at ambient temperature and subsequently cured in an oven by varying the curing time (30-120 min) and temperature (120-160 °C).

Working Principle

Our project consists of sediment filter, pre filter, post carbon filter, membrane (PVA&PEG), motor, and shut off valve.

Initially water filled in a tank which is holding on top of the system. This water continuously flows to downward due to gravitational force.

Salt water feed into pre sediment filter with help of motor, first stage of process a sediment filter.

The cartridge in a sediment filter can be made from pleated polyester, cellulose fibre or porous ceramic materials.

If iron is present in the water, specialized iron removal equipment is usually required. Cartridge filters are rarely effective in solving iron staining problems.

next stage pre filter it has filtered nano particles of dust and increase the effectiveness of taste and odour removal depends on the length of time the water is in contact with the activated carbon. Excessive flow through small amounts of activated

Final stage membrane here we are using PVA (polyvinyl Alcohol) & PEG (polyethylene glycol) composite material used as membrane material. Whenever filtered water enters into membrane units it will absorb bacteria and other dust. Chemical reaction took place finally it removes unwanted bacteria.

After this process, water get drained and come out from the filter outlet pipe as salt water ones side and pure water other side.

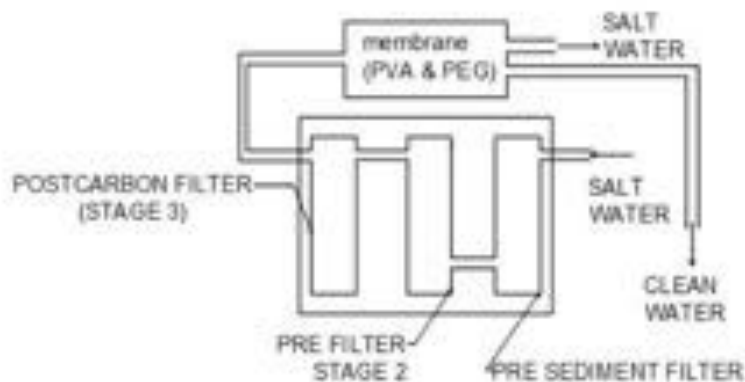


Fig 4.4- Reactor Layout

5. RESULTS

Textile Water Analysis- AAS Spectroscopy method

Atomic absorption spectroscopy (AAS) is a spectro analytical procedure for the **quantitative** determination of chemical elements using the absorption of optical radiation (light) by free atoms in the gaseous state.

Sago Water Analysis

| | |
|--------------------|---------------------|
| Sample name | Sago effluent water |
| Sample quantity | 1 L |
| Sample description | Turbid liquid |

Test Parameters

| Test parameters | Before Treatment (mg/l) | After Treatment (mg/l) |
|---|-------------------------|------------------------|
| Colour | 10 Hazen units | 4 Hazen units |
| Ph | 2.75 | 5.5 |
| Electrical conductivity ($\mu\text{S}/\text{cm}$) | 4910 | 2100 |
| Total dissolved solids | 3142 | 900 |
| Total solids | 5274 | 2770 |
| Total suspended solids | 2132 | 1372 |
| Chloride as Cl^- | 620 | 270 |
| Sulphate as SO_4 | 740 | 390 |
| Acidity as CaCO_3 | 15400 | 6900 |



Fig 5.1 Water Samples Before & After Treatment

Removal by PVA and PEG

| METALS | BY PEG | BY PVA |
|-------------|--------|--------|
| Copper | 96% | 95% |
| Chromium | 94% | 91% |
| Zinc | 74% | 78% |
| Cadmium | 70% | 84% |
| Phosphorous | 11% | 10% |

Conclusion

Thus by using PVA and PEG membrane in adsorption reactor heavy metals can be removed from effluents of textile industry. Also this reduces the organic load and acidity and such parameters from the effluents of sago industry. This method can also be employed for all kind of effluents from industries. Thus this provides a path way to use this method and the water

can be used for agricultural purposes. Though some effluent may not be a barrier for its usage in agriculture, it affects the aquaculture. This method will be cost effective and easy to use. Agriculture and its allied sectors will be benefited by this and this gives our future generation, effluent free water ways.

Reference

- [1] Bajpai, A.K., Vishwakarma, N., 2003, Adsorption of polyvinylalcohol onto Fuller's earth surfaces, Colloids and Surfaces, A: Physicochem. Eng. Aspects, 220 117-130.
- [2] Bajpai, A.K., and Vishwakarma, N., 2003, Colloids and surfaces, A: Physicochemical and Engineering Aspects, 220, 117-130. [4] Killmann, E., Maier, H., Baker, J.A., (1988), Hydrodynamic layer thickness of various adsorbed polymers on precipitated silica and polystyrene latex, Colloids Surf, 31, 51-71.
- [3] Chibowski, S., Paszkiewicz, M., Krupa, M., 2000, Investigation of the influence of the polyvinyl alcohol adsorption on the electrical properties of Al₂O₃-solution interface, thickness of the adsorption layers of PVA, Powder Technology, 107 (3), 251-255.
- [4] Emil, J., and Chibowski, S., 2005 Surface free energy and wettability of silyl layers on silicon determined from contact angle hysteresis, Advances in Colloid and Interface Science, 30, 121-131.
- [5] Hua Y, David W G. Journal of Applied Polymer Science, 1993, 49:1553-1563.
- [6] M'pandou, A., Siffert, B., 1987, Polyethylene glycol adsorption at TiO₂/H₂O interface: Distortion of ionic structure and shear plane position, Colloids and Surfaces, 24, 159-172. Rdziviolava, I.S., Ovchinnikova, G.P., Artemenko, S.E., Dmitrienko, T.G., 2004, Study of the thickness of polymer adsorption layer on the fibre surface, Fibre Chemistry, 36(2), 139-140.
- [7] Qdais, H. A., Moussa, H.: Removal of heavy metals from wastewater by membrane processes.
- [8] Sudilovskiy, P. S., Kagramanov, G. G., Kolesnikov, V. A.: Use of RO and NF for treatment of copper containing wastewaters in combination with flotation. Desalination 221, (1-3), 2008, pp. 192-201.
- [9] Sungyun Lee, Eunkyung Lee, Jinsung Ra, Byungcheon Lee, Suhan Kim, Seok Ho Choi, Sang Don Kim, Jaeweon Cho: Characterization of marine organic matters and heavy metals with respect to desalination with RO and NF membranes. Desalination, 221 (1-3), 2008, pp. 244-252.
- [10] Starov, V. M., Serguei R. K.; and Manuel, G. Velardey., 2000, J. Colloid Interface Sci, 227, 185-190.

