

Preparation of Poly-Acrylamide Graft Copolymer and Its Application in Waste Water Treatment

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ABSTRACT: Waste water is any water that has been adversely affected in quality by anthropogenic influence. Wastewater can originate from a combination of domestic, industrial, commercial or agricultural activities, surface runoff or storm water, and from sewer inflow or infiltration. Here we are developing a system which is used for the waste water management.

KEYWORDS: Grafted copolymers, Pandan leaves; Flocculant, COD, Reactive black 5.

I. INTRODUCTION

Developmental activities such as construction, transportation and manufacturing not only deplete the natural resources but also produce large amount of wastes that leads to pollution of air, water, soil and oceans; global warming and acid rains. Human activities directly or indirectly affect the environment adversely. Industrial waters and even natural waters are often contaminated by toxic or sometimes carcinogenic impurities causing ecological disequilibrium and sever public health problems. The facilities to treat waste water are not adequate in any city in India. Presently, only about 10% of the waste water generated is treated; the rest is discharged as it is into our water bodies. The pollution of water resource due to the disposal of heavy metal ions has been an increasing worldwide concern for the last few decades. For instance, heavy metal contamination in water is a serious crisis due to toxicity, long persistence, and bioaccumulation and bio magnifications in food chain of heavy metals. The most common hazardous metals found in industrial wastewater are copper, cadmium, lead, nickel, chromium, zinc and mercury etc. Not only cationic but also anionic impurities may cause environmental hazard e.g. arsenic, pesticide and organic dyes or in larger amounts the phosphates. This kills fish and, when found in drinking water, can kill young children. Water can also be polluted by a number of organic compounds such as oil, plastics and pesticides, which are harmful to humans and all plants and animals in the water. Therefore there is a need for removal/separation of toxic or ion from seawater or aqueous waste solution by using adsorbent.

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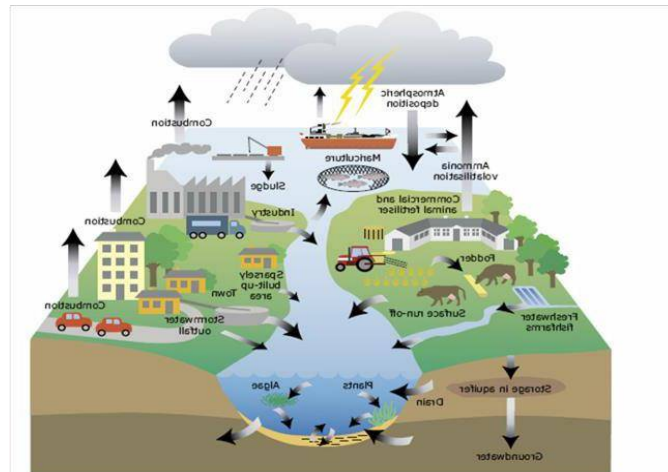


Fig. 1.1. Sources of sink of heavy metals

Cobalt has long been used as the unique binding agent of carbides in hard-metal production. The exposure of Cobalt arises from their applications in industry and nuclear medicine. Occupational exposure of Cobalt occurs principally in the refining of Cobalt, in the production of alloys and in the tungsten carbide hard metal industry.

Cobalt may cause a skin allergy. If allergy develops, very low future exposure can cause itching and a skin rash. Exposure to Cobalt dust can irritate the skin, eyes, nose and throat. Cobalt may cause an asthma-like allergy. Future exposure can cause asthma attacks with shortness of breath, wheezing, cough, and/or chest tightness. Cobalt may affect the heart, thyroid, liver and kidneys. Cobalt may be a carcinogen in humans since it has been shown to cause cancer often muscle (only at the injection site) in animals. Many scientists believe there is no safe level of exposure to a carcinogen. Cobalt may damage the male reproductive system and affect male fertility in animals.

According to OSHA workplace exposure limits for cobalt permissible exposure limit (PEL) is 0.1mg/m³ averaged over an 8-hour work shift. High exposure levels have been reported, with a concentration of up to 79 mg/m³ in a plant where cobalt nitrate was calcined. Adverse respiratory effects have been reported at concentrations between 0.1 and 0.2 mg/m³. The threshold limit value and time weighted average (TLV-TWA) for Co metal, dust and fume (as cobalt) is 0.05 mg/m³ as a tentative value.

Therefore, many methods are used to remove cobalt from water systems, conventional methods have been used as chemical precipitation, coagulation, ion exchange, solvent extraction and filtration, evaporation and membrane methods. Adsorptions of heavy metals on conventional adsorbents have been used widely in the chemical, biological, analytical, and environmental fields. Adsorption is the most effective technique for controlling the extent of pollution due to heavy metal ions from aqueous solution. The important aspect of the adsorption process is easy regeneration ability and less operational cost, simple design, easy operation and free or less generation of toxic substances. The adsorption process at solid/liquid interface has been extensively employed for several reasons, mainly due to its efficiency and economy. Physical adsorption because of its low cost, high efficiency, easy handling, wide variety of adsorbents and high stabilities toward the adsorbents, has become the most widely used methods for the elimination of heavy metal ions from wastewater.

II. OBJECTIVES

1. The objective of the proposed system is given below
2. We are proposing method which is used for the waste water management

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Vol. 6, Issue 8, August 2017

III LITERATURE SURVEY

At a worldwide level, around 80% of wastewater created is released into nature untreated, causing boundless water pollution.[4]:2 There are various procedures that can be utilized to tidy up wastewaters relying upon the sort and degree of tainting. Wastewater can be dealt with in wastewater treatment plants which incorporate physical, compound and organic treatment forms. Metropolitan wastewater is dealt with in sewage treatment plants (which may likewise be alluded to as wastewater treatment plants). Agrarian wastewater might be dealt with in horticultural wastewater treatment forms, while mechanical wastewater is dealt with in modern wastewater treatment forms.

For civil wastewater the utilization of septic tanks and other On-Site Sewage Facilities (OSSF) is broad in some country territories, for instance serving up to 20 percent of the homes in the U.S.[5] One kind of vigorous treatment framework is the initiated ooze process, in light of the support and distribution of a mind boggling biomass made out of miniaturized scale living beings ready to ingest and adsorb the natural issue conveyed in the wastewater. Anaerobic wastewater treatment forms (UASB, EGSB) are likewise broadly connected in the treatment of modern wastewaters and organic slop. Some wastewater might be exceedingly regarded and reused as recycled water. Built wetlands are likewise being utilized.

Wastewater can originate from:

- Human excreta (dung and pee) regularly blended with utilized tissue or wipes; this is known as blackwater in the event that it is gathered with flush toilets
- Washing water (individual, garments, floors, dishes, autos, and so forth.), otherwise called greywater or sullage
- Surplus produced fluids from residential sources (drinks, cooking oil, pesticides, greasing up oil, paint, cleaning fluids, and so forth.)
- Urban overflow from expressways, streets, carparks, rooftops, walkways/asphalts (contains oils, creature excrement, litter, gas/petroleum, diesel or elastic deposits from tires, soapscum, metals from vehicle depletes, de-icing specialists, and so on.)
- Storm channels (may incorporate waste)
- Manmade fluids (illicit transfer of pesticides, utilized oils, and so on.)
- Industrial squander
- Industrial site seepage (sediment, sand, soluble base, oil, concoction deposits);
- Industrial cooling waters (biocides, warm, sludges, sediment)
- Industrial process waters
- Organic or biodegradable waste, including waste from abattoirs, creameries, and frozen yogurt produce
- Organic or non bio-degradable/hard to-treat squander (pharmaceutical or pesticide producing)
- Extreme pH squander (from corrosive/antacid assembling, metal plating)
- Toxic squander (metal plating, cyanide creation, pesticide fabricating, and so forth.)
- Solids and emulsions (paper producing, foodstuffs, greasing up and water powered oil fabricating, and so on.)
- Hydraulic cracking
- Produced water from oil and gaseous petrol generation
- Agricultural contamination, immediate and diffuse

Wastewater can be weakened or blended with different sorts of water as:

- Seawater entrance (high volumes of salt and organisms)
- Direct entrance of stream water
- Rainfall gathered on rooftops, yards, hard-standings, and so on (for the most part clean with hints of oils and fuel)
- Groundwater penetrated into sewage

After it has experienced some treatment, the "treated wastewater" remains, e.g.:

- Septic tank release
- Sewage treatment plant release

IV. PROPOSED SYSTEM

This work deals with the development of starch grafted copolymer with acrylamide by chemical initiation method. The synthesis of grafting of Am onto starch characterized by the technique of FTIR and FESEM is used to study the changes in the properties of the material caused by the grafting. Also to study of swelling behavior on starch-g-Am at different pH of solution and contact time. The synthesized materials have been examined for the adsorption and adsorption isotherm metal ion Co(II) in waste water as function of effect of pH, effect of concentration of Co(II) and contact time.

Fourier transform infrared spectroscopy (FTIR):

Infrared (IR) spectroscopy is one of the most common spectroscopic techniques used by organic and inorganic chemists. In an IR spectrophotometer, infrared radiation of successively increasing wavelength is passed through the sample and the percent transmittance is measured. An infrared spectrum is the graph of percent transmittance versus either increasing wavelength or decreasing frequency. The position of an infrared absorption band is specified in frequency units by its wavenumber (cm⁻¹).

The Fourier transform infrared (FTIR) spectroscopy works by allowing the transmitted or reflected beam to combine with the reference beam after the path difference has been introduced. The interference pattern so produced is Fourier transformed to produce the spectrum of the material. The resulting spectrum represents the molecular absorption and transmission, creating a molecular finger prints of the sample. Like a finger print no two unique molecular structures produce the same infrared spectrum. The FT-IR spectra of the graft copolymer were compared with the standard data confirming the formation of the copolymer. The FT-IR spectra of the copolymer were recorded in the region 4000-400 cm⁻¹ on FT-IR 8400 Shimadzu using KBr.

Different chemical functional groups can be identified by infrared spectroscopy. Every functional group absorbs some characteristic IR radiation. The absorption of infrared (IR) radiation (at wavelength above ~ 1 μm) distorts the dipole in the molecule, including molecular vibrations with energy shifts of an order of magnitude smaller in electronic absorption spectra. For a molecule to absorb IR, the vibrations or rotations within a molecule must cause a net change in the dipole moment of the molecule. The alternating electric field of radiation interacts with fluctuations in the dipole moment of the molecule.

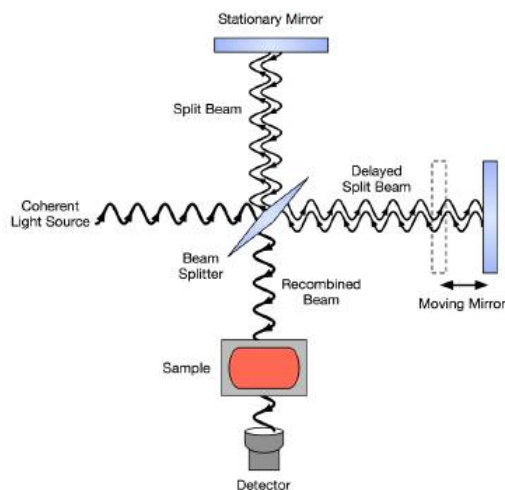


Fig 1:-Schematic diagram of FTIR

If the frequency of the radiation matches the vibrational frequency of the molecule then radiation will be absorbed, causing a change in the amplitude of molecular vibration. These molecular vibrations are mainly of stretching and bending type. Thus, the FTIR analysis confirms the formation of a compound gives further information about the interaction and the nature of binding initially.

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1.2.Sorption mechanisms

The first major challenge for the adsorption field is to select the most promising types of sorbent from an extremely large pool of readily available materials. The next real challenge is to identify the sorption mechanisms. In general, there are three main steps involved in pollutant sorption onto solid sorbent:

1. The transport of the pollutant from the bulk solution to the sorbent surface;
2. Adsorption on the particle surface;
3. Transport within the sorbent particle.
4. The sorption mechanism of polysaccharide based materials is different from

In liquid-phase adsorption, it is commonly known that adsorption capacities of an adsorbent is attributed to many factors and the adsorbate-adsorbent interaction play an important role as well as that between adsorbate and water. Many studies have been made on the possibility of adsorbents using activated carbon, silica, fly ash, clay etc. Physical adsorption plays little role in the interaction between adsorbent and pollutants because beads have a small surface area. The pH may also affect the speciation of metal ions, and changing the speciation of the metal may result in turning the chelation mechanism into the electrostatic attraction mechanism.

1.3.Material used for removal of heavy metals:

The choice of adsorbents used in this study was motivated by the following rationale. Starch, an agricultural biopolymer, is more attractive for industrial use because of its renewability, biodegradability, and low unit cost. Native starch is one of the most abundant biopolymers on earth and is present in living plants as energy storage material. Starches are mixtures of two polyglucans, amylopectin and amylose, but they contain only a single type of carbohydrate, glucose. The excellent adsorption behavior of polysaccharides is mainly attributed to:

High hydrophilicity of the polymer due to hydroxyl groups of glucose units;

Presence of a large number of functional groups

High chemical reactivity of these groups;

Flexible structure of the polymer chain.

One of the most important and useful feature of starch is their good chemical reactivity. They possess a large number of reactive groups (hydroxyl groups) present at the 2-, 3-, and 6-positions in the glucose unit. From the polymer chemist's point of view, the modification of polysaccharides offers enormous opportunities. Through chemical reactions, in particular grafting reactions, polysaccharides can give interesting macromolecular superstructures, e.g. gels and hydrogels networks, polymeric resins, beads, membranes, fibers or composite materials. Considerable research and technical work has reported so far, and the chemical modification of starch via vinyl monomers graft copolymerization constitutes the most important field for improving the properties of starch, enlarging the range of its utilization. It is known that starch generated graft copolymer with many vinyl monomers. Active vinyl monomers such as acrylates, acrylamide and acrylonitriles were easily grafted polymerized on to starch.

1.4.Reaction Kinetics of graft copolymerization:

Grafting is one polymer modification technique in which a polymer is linked to the backbone of a parent polymer, the substrate, by chemical linkages.

1.4.1. Why grafting?

It allows surface modification such that bulk properties of the substrate remain unchanged while new modified properties are acquired from the polymer, which is grafted.

Graft copolymers possess mechanical properties, solution properties different than linear polymers due to the branched nature of the polymer as a result of grafted chains.

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Vol. 6, Issue 8, August 2017

1.4.2. How grafting is achieved?

There are various methods of graft copolymerization. In general grafting is achieved by creating active sites on the backbone of the substrate polymer initiating polymerization of the monomer to be grafted on the polymer backbone. Creation of active sites and initiation of the polymerization can be achieved by using a free radical initiator, an ionic initiator, irradiation or enzymes. Most common method of graft copolymerization is free radical chemical initiation. Free radicals are produced from the initiator and transferred to the substrate to react with monomer to form the graft copolymer. General mechanism of free radical grafting:

Dissociation of the initiator by heating to form free radicals:



The radical transfers an electron to the monomer to initiate polymerization



This step may lead to homopolymerization



or to grafting of a chain of given size onto the substrate



Or

A radical site is created on the polymer backbone which transfers an electron to the monomer and grafted chain grows on the polymer backbone



Termination by radical combination or H abstraction

1.4.3. Advantages of chemical grafting:

It is simple and relatively inexpensive.
It can be carried out in aqueous solution under mild conditions.

1.4.4. Disadvantages

By this method generates simultaneous homopolymer.

During grafting degradation of the chain backbone is possible.

There may be a heterogeneous distribution of grafting sites and grafted chain size.

1.5. Present work:

From the foregoing discussion and the available literature, it can be said that in most of the cases, the preferred choice has been the chemical method for initiation of polymerization. The grafting of Acrylamide with starch has been extensively studied.

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Vol. 6, Issue 8, August 2017

2.5.2. Field Emission Scanning Electron Microscopy (FESEM):

In FE-SEM a field-emission cathode in the electron gun provides narrower probing beams at low as well as high electron energy. This special arrangement over SEM results in to improved spatial resolution and minimized sample charging and damage. In FE-SEM, under vacuum, electrons generated by a field emission source are accelerated in a field gradient. The accelerated electron beam passes through electromagnetic lenses, focusing onto the specimen. As a result of this bombardment different types of electrons are emitted from the specimen. The detector catches the secondary electrons and an image of the sample surface is constructed by comparing the intensity of these secondary electrons to the scanning primary electron beam. This process results in to image construction and this image is displayed on a monitor.

FE-SEM produces clearer, less electrostatically distorted images with spatial resolution own to 1 1/2 nm. That is 3 to 6 times better than conventional SEM. Smaller area contamination spots can be examined at electron accelerating voltages compatible with Energy Dispersive X-ray Spectroscopy. Reduced penetration of low kinetic energy electrons probes closer to the material surface. High quality, low voltage images are obtained with negligible electrical charging of samples and conducting coatings on insulating materials is virtually eliminated in FE-SEM.

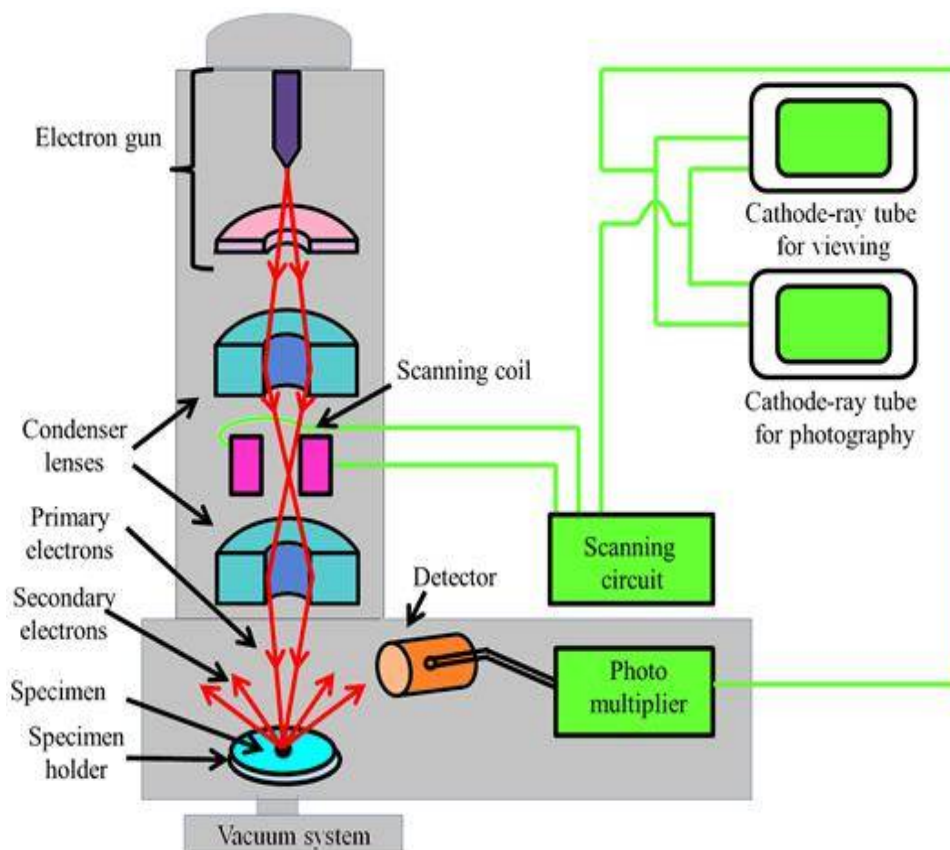


Fig.2.2 Schematic principle and instrument image of FE-SEM

2.5.3. Thermogravimetric analysis (TGA):

In this technique the change in sample weight is measured while the sample is heated at a constant rate (or at constant temperature), under air (oxidative) or nitrogen (inert) atmosphere. This technique is effective for quantitative analysis of thermal reactions that are accompanied by mass changes, such as evaporation, decomposition, gas absorption, desorption and dehydration. The TG was carried out on DTG 60-H. The heating rate was of 10 °C/min over the range

International Journal of Innovative Research in Science, Engineering and Technology

(A High Impact Factor & UGC Approved Journal)

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Vol. 6, Issue 8, August 2017

of 25–800 °C. The analysis was carried out under nitrogen flow; the flow rate was 50mL/min. Aluminum cup was used as a sample holder. The molecular formula for the complexes was fixed by comparing the expected and the weight loss obtained from the thermo gram.

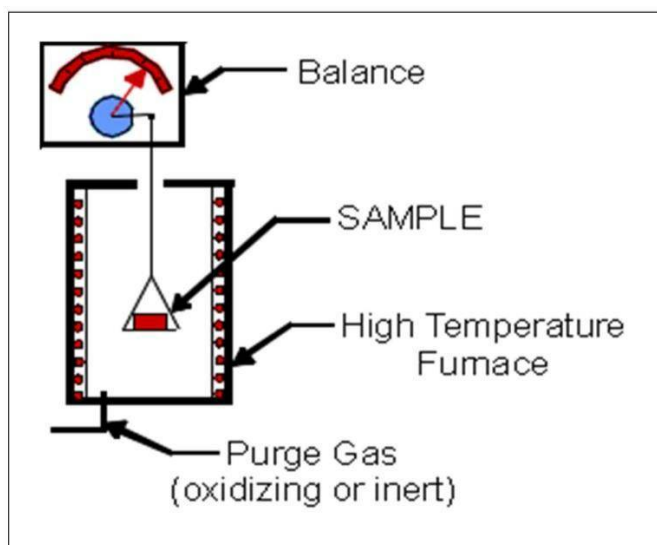


Fig.2.3 Schematic diagram of TGA

Result and discussion:

3.1. Spectroscopic characterization (FTIR):

The FTIR spectra for starch, Acrylamide, St-g-Am before extraction and St-g-Am after extraction are presented in figure 3.1.

In IR spectra, pure starch displays the O-H stretching absorption in the region of

3435 cm⁻¹ (broad, s), the C-H stretching at 2922 cm⁻¹ (m), C-O stretch at 1643 cm⁻¹ (s) and the peak at 1352 and 1107 cm⁻¹ for C-H rock and CH₂ bending respectively and the peak at 1305 cm⁻¹ for C-O-C stretch. The IR spectra of starch grafted acrylamide for both before and after extraction gives all peaks of starch. The additional peaks

found at 3321, 1668 and 1008 cm⁻¹ indicate the N-H stretching, the C=O stretching

and N-H bending of the amide bands respectively, which are characteristics of the – CONH₂ group containing in the acrylamide. The addition the peak at 1411 cm⁻¹ is for the C-N stretching and 765-710 cm⁻¹ for the weak band N-H out of plane bending. These are typical absorption bands of the amide. The IR spectra of starch grafted

Acrylamide after extraction shows decreases in the intensity of the bands at 1668 cm⁻¹ indicating C-O-C bond stretch which indicates removal of homopolymer was done effectively by soxhlet

International Journal of Innovative Research in Science, Engineering and Technology

(A High Impact Factor & UGC Approved Journal)

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Vol. 6, Issue 8, August 2017

Table 3.1 FTIR Spectra of Starch, acryl amide, St-g-Am before extraction and after extraction

Functional group	Wave number (cm ⁻¹)			
	Starch	Am	St-g-Am Before extraction	St-g-Am After extraction
OH stretching (broad)	3435	-	3321	3286
CH stretching (sharp)	2922	2989	2933	2921
carboxylic stretching	1643	1664	1668	1664
N-H stretching	-	3332	3321 (overlapped with -OH)	3286 (overlapped with -OH)
N-H bending of amide	-	1132	1008	1010

3.2. Thermal behavior:

The TGA analyses of grafted copolymer of St-g-Am were done in order to study the thermal stability. Figure 3.2 and table 3.2 shows TGA thermograms of the pure starch and grafted copolymer of acrylamide on starch. The thermal behavior of a polymer is important in relation to its properties as adsorbent.

In order to observe thermal behavior of polymer, pure starch shows first degradation from 51⁰C to 107⁰C due to loss of OH group, and then it shows maximum degradation at around 304.6⁰C. In the TGA figure pure starch (St) and St-g-Am began to decompose at 51⁰C and 51.8⁰C respectively. The weight loss for starch was 39.61% at 304.6⁰C, while for St-g-Am 34.54% at 330.3⁰C. The total weight loss of starch was around 82.2% in heating process of up to 700⁰C. Similarly for St-g-Am the total weight loss was around 65.23% in the heating process of up to 700⁰C. From TGA curve it confirms that the thermal stability of St-g-Am is higher than that of starch because of grafting of monomer onto backbone chain. Thus, the thermodynamic property of starch is improved evidently by grafting with Am.

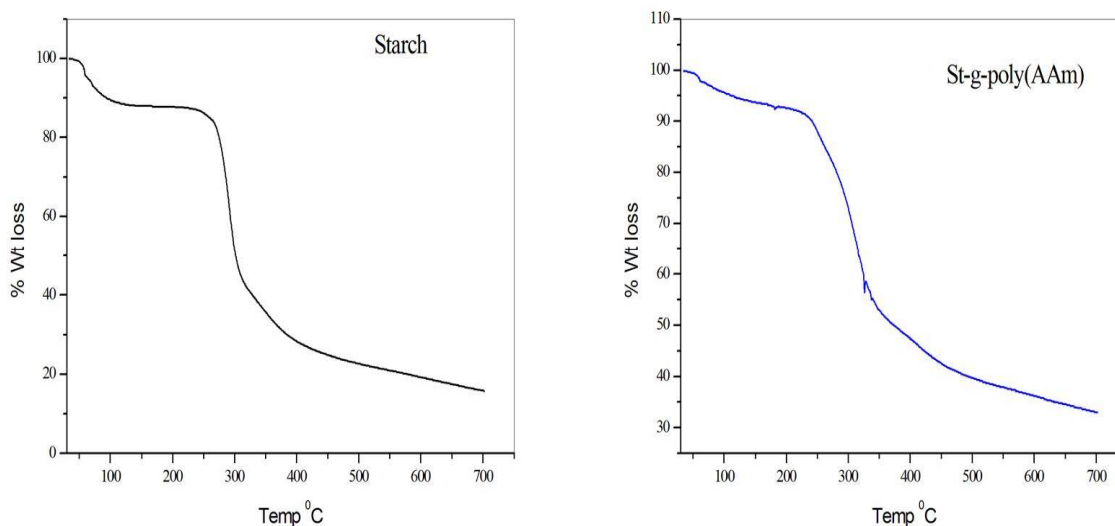


Fig. 3.2 TGA curve

Table.3.2 TGA data of Starch and St-g-Am

Sample	Temperature range (°C)	% Total weight loss
Starch	51-676	82%
St-g-Am	51.8-660	65%

3.3. Surface morphology of Acrylamide grafted copolymer of starch:

The surface appearance of the pure starch and graft copolymer were viewed by FESEM as shown in figure 3.3 In order to elucidate the topological changes in to the graft copolymer structure, pure starch has an irregularly oval shape with smooth surface whereas St-g-Am possesses complex and porous surface texture, which reveals successful grafting of acrylamide on to starch. It is supposed that these pores are the region of water permeation and interaction sites of external stimuli with the hydrophilic groups of the graft copolymer.

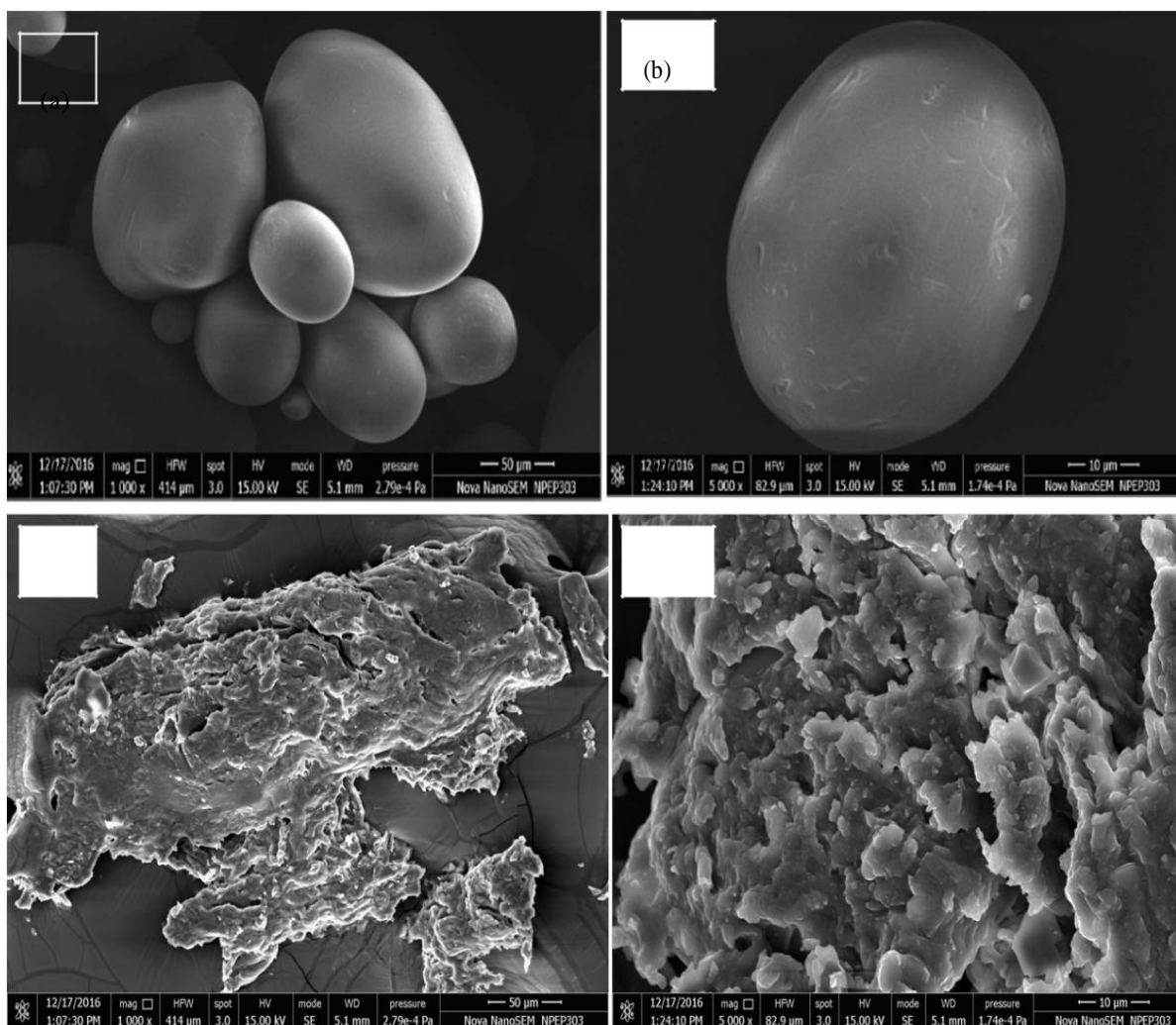


Fig.3.3 FE-SEM of (a)& (b) Starch, (c) & (d) St-g-Am

3.4. Swelling behavior

3.4.1.pH-dependent swelling:

The grafted copolymer shows different swelling behavior at various pH, so we investigated the effect of pH ranged from 3 to 10. Water absorbency of the optimized grafted copolymer was studied in various pH solutions that ranged from 3.0 to 10.0. To prepare the pH media, the stock NaOH (pH 10.0) and HCl (pH 3.0) solutions were diluted with distilled water to reach the desired basic and acidic pH, respectively. The maximum Ps of the grafted copolymer was obtained in the neutral medium (pH 7) whereas a lesser Ps was observed in the acidic and alkaline media shown in fig 3.4.

The lesser Ps in the acidic media was attributed to the fact that amide groups of Am were present along the macromolecular chains in the grafted copolymer was remaining unionized. In neutral medium, the degree of protonation in AAm increased and NH_2 ions get converted into NH_3^+ ions which resulted in a more hydrophilic polymer network and contributed to the higher water absorption capacity. In basic medium the swelling capacity also

International Journal of Innovative Research in Science, Engineering and Technology

(A High Impact Factor & UGC Approved Journal)

Website: www.ijirset.com

Vol. 6, Issue 8, August 2017

decreases that can be attributable to the complete dissociation of amide group and high concentration of Na^+ and OH^- ions leads to the reduction of Ps. The higher concentration of Na^+ ions acted as a screening bar and hence a lesser Ps was observed.

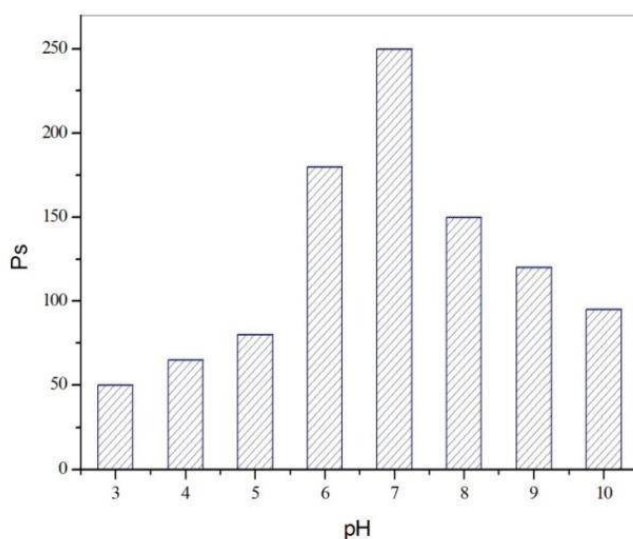


Fig. 3.4 Swelling behavior of St-g-Am as effect of pH

3.4.2. Effect of time on percentage swelling

Effect of swelling time on percent swelling was studied at different time intervals from 30min to 1080 min in neutral medium at room temperature shown in fig. 3.5. It can be seen that the Ps increased rapidly to 1330% up to 120 min whereas, swelling was found to be ceased with further increase in swelling time. Because after optimal swelling time the porous structure of copolymer got saturated and allowed no more accommodation for the water molecule. It also seems that the decrease in Ps at higher reaction time may be attributed to the reduction of all the consuming reactants. Furthermore, the increase in contact time results in the decrement of active free sites for grafting which in turn leads to the retardation of diffusion of reactants.

International Journal of Innovative Research in Science, Engineering and Technology

(A High Impact Factor & UGC Approved Journal)

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Vol. 6, Issue 8, August 2017

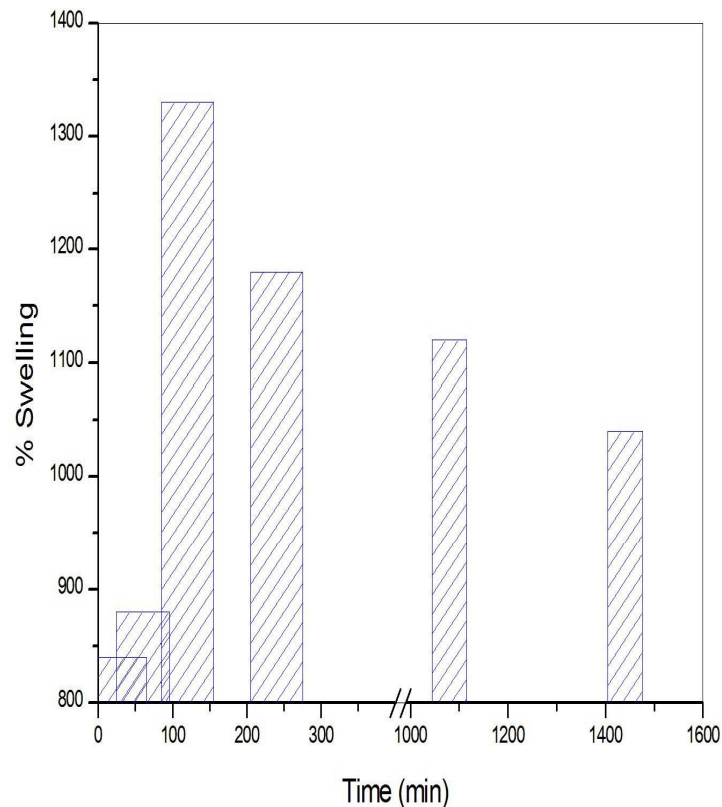


Fig. 3.5 Effect of time on percentage swelling 3.5. Removal of metal ion:

3.5.1.Effect of pH:

Performance of adsorption is dependent on the characteristics of the wastewater. In particular, uptake is strongly pH-dependent. The wastewater pH may be an important factor in the sorption of pollutants onto sorbents. The adsorption of metal ions on the surface of any adsorbent involves an ion exchange mechanism, whereby the charge on the surface of the adsorbent determines the possible interactions between the binding sites of the adsorbent

International Journal of Innovative Research in Science, Engineering and Technology

(A High Impact Factor & UGC Approved Journal)

Website: www.ijirset.com

Vol. 6, Issue 8, August 2017

and adsorbate molecules. In addition, most pollutants are weak electrolytes, for which the adsorption equilibrium depends on the solution pH. For this estimation, 0.01 g portions of sorbent St-g-Am was treated with 25 mL of Co^{2+} ion solution (1000 mg L^{-1}) at various pH values 2-7 using dilute 0.1 M HCl and 0.1 M NaOH solution. The effect of pH on the adsorption capacity was not investigated at higher pH because at pH values higher than 8, precipitation of Co^{2+} occurs, and the accurate interpretation of adsorption behaviour becomes difficult.

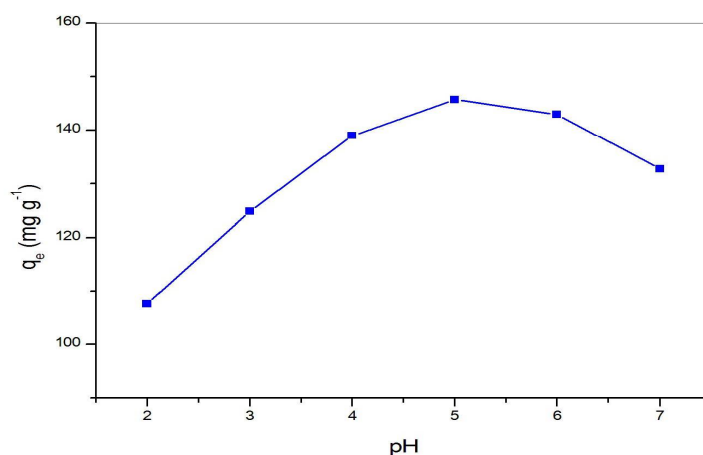


Fig. 3.6 Effect of pH

From fig.3.6 it observed that with increasing pH till pH 5, the protonated functional groups were deprotonated, and the electrostatic attraction between the negatively charged binding sites of the St-g-Am copolymer and the positively charged metal ions increased, enhancing the adsorption efficiency. The adsorption of Co^{2+} ions at pH 5 was observed to be maximum 145.75 mg g^{-1} as shown in fig. 3.6 Moreover, with increasing pH, the electrostatic repulsion between the neighbouring ionized groups increased, leading to an increase in the grafted chains inside the copolymer structure, this also contributed to the increased percentage removal. The uptake of metal ion is much higher in acidic solution than those in neutral and alkaline solutions. In acidic solutions i.e. at lower pH more protons will be available to protonate amine groups of

acrylamide, thereby increasing electrostatic attractions between metal and adsorption sites, which cause an increase in metal adsorption. This induces a competition between protons and metal ions for adsorption sites. It can be seen that the pH of aqueous solution plays an important role in the adsorption of metal ions onto St-g-Am copolymer.

3.5.2.Effect of concentration:

The adsorption behavior of Co^{2+} ion on St-g-Am copolymer was studied by varying the concentration of Co^{2+} ions at pH 5 as shown in fig.3.7, by employing batch experiment to such system, where Co^{2+} ion solution of different concentration (100 mg L^{-1} to 4000 mg L^{-1}) were added to a copolymer of definite weight (0.01 g) and then were allowed to equilibrate.

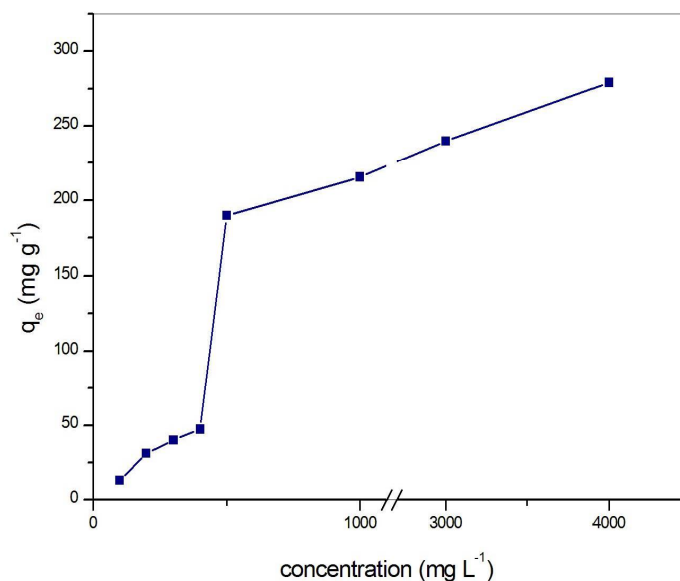


Fig. 3.7 Effect of concentration of Co²⁺ ion

It was found that the uptake of metal ions increases with increasing initial metal ion concentration but the rate of increasing becomes slowly after the concentration reached 500 mg/L which indicates there were few empty adsorption site on the adsorbent and suggested that the adsorption almost reached equilibrium. This was estimated due to the fact that with higher initial concentration, the driving force of the concentration gradient became stronger, thus being favorable for metal adsorption. This behavior mainly depends on their polarities, initial concentration, molecular structure, steric effects as well as their solubilities.

3.5.3. Effect of agitation time:

Fig. 3.8 shows effect of the agitation time on the percentage removal of the Co²⁺ ion using the St-g-Am copolymer. It was observed that the initial rate of metal ion uptake increased with increasing agitation time till 80 min with the adsorption capacity Co²⁺ ion 195.8 mg g⁻¹, after 80 min of agitation time there is decrease in adsorption capacity q_e. Moreover, it was also observed that the rate of metal ion uptake was initially very high and was reduced after a certain time interval, which showed that after the rapid adsorption of metal ions, the adsorption rate was further controlled by the mass transport in the grafted copolymer.

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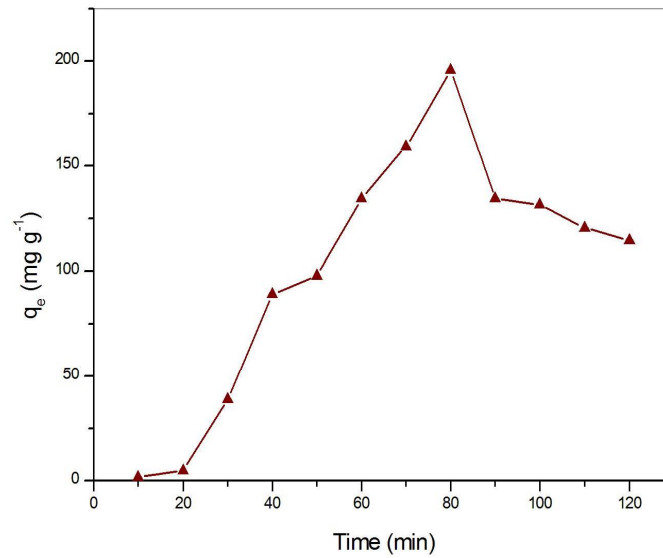


Fig.3.8 Effect of agitation time

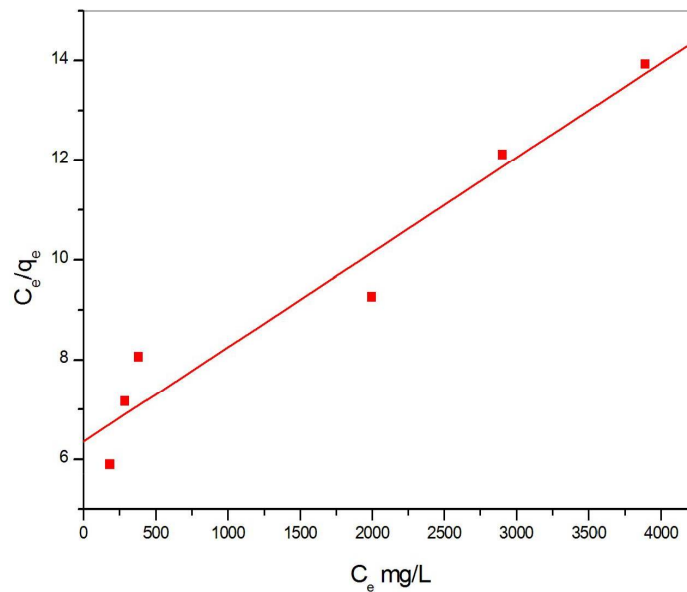


Fig. 3.9 Langmuir adsorption isotherm

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Vol. 6, Issue 8, August 2017

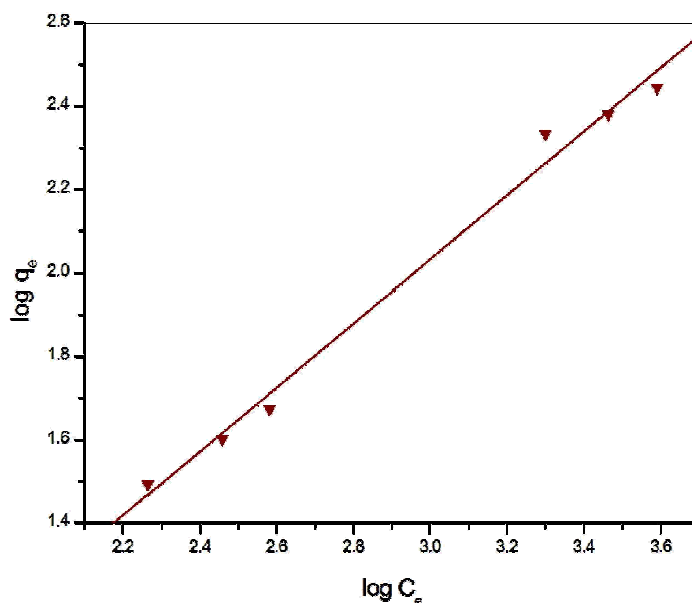


Fig. 3.10 Freundlich adsorption isotherm

Table 3.3 Langmuir and Freundlich constant for adsorption of Co(II)

Isotherm model	Parameter values			
	(L mg ⁻¹)	(mg g ⁻¹)		
Langmuir isotherm	2.989 × 10 ⁻⁴	526.31	0.971	0.887
Freundlich isotherm	(L g ⁻¹)			
	1.219	1.304		0.991

IV. CONCLUSION

The following conclusions can be made from the results obtained.

- The graft copolymer of Acrylamide with starch was synthesized chemical initiation method and polymer yield was observed 175.6%.
- Synthesis of acrylamide on starch was characterized by FT-IR, TGA and FESEM analysis.

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Vol. 6, Issue 8, August 2017

- Grafting of acrylamide with starch was confirmed with FTIR, which might have taken place at hydroxyl group.
- TGA studies revealed that the synthesized grafted copolymer were thermally more stable than pristine starch.
- FESEM micrographs showed complex and porous surface texture of St-g-AAm than starch, which confirmed successful grafting of acrylamide to starch.
- The study of swelling behavior is carried out by using solutions of different pH and agitation time.
- St-g-Am copolymer shows highest swelling percentage at pH 7. At pH 2 and pH 12 it shows minimum swelling percentage due to the ion-ion (cation-cation or anion – anion) interaction.
- The Co^{2+} adsorption capacity of St-g-AAm was studied as a function of time, pH and metal ion concentration.
- Maximum adsorption capacity was achieved up to 195.5 mg/g at pH 5 with 0.01g of adsorbate.
- Adsorption follows Freundlich isotherm $r^2=0.991$, indicating that adsorption takes place at specific heterogenous sites within the adsorbent.

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