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Research Article

Natural Polysaccharides Based Adsorbents for Industrial Effluent Treatment

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Abstract

Herein we report the flocculation characteristics of some amylopectin based graft copolymers developed in the laboratory in a paper mill wastewater and Municipal sewage water. Colour removal study of an industrial textile dye effluent is also carried out by the sulphated amylopectin based graft copolymer, dextrin based graft copolymer/SiO_2 nanocomposite and katira gum based hydrogels. Their performances are also compared in the same textile dye effluent. Surface properties of all the developed materials are also evaluated by BET method. The results show that natural polysaccharide based adsorbents are highly effective for the industrial effluent treatment.

Keywords: Katira gum; Dextrin; BET isotherm; Flocculation; Adsorption

Introduction

Water, which is vital for sustaining life in our environment, serves as the livelihood of living systems. Access of safe drinking water is essential for maintaining a healthy lifestyle. Surprisingly, despite the Earth's surface being covered by 75% water, one in three peoples worldwide still lacks access to safe drinking water [1,2]. This scarcity of potable water and the water for domestic use has become a pressing and persistent issue, caused by the continuous growth of the global population. One of the major causes of water pollution is the mixing of heavy metals, coal dust, poisonous dyes, clays, fragrant molecules, silica, suspended particles, etc. discharged by the industries to the water bodies without proper treatment [3,4]. The untreated release of these pollutants into water bodies cause significant harm to aquatic life [5,6] and mammals also. Suspended colloidal particles are greatly responsible for water pollution. From the discharge by the several industries like paper, iron, mining etc. the suspended pollutants like kaolin clay, iron ore slime, coal and silicon dioxide are coming to the water system. Excess presence of kaolin clay in the water bodies causes (5.0 micrograms) health issues of human and aquatic life also [7]. Presence of iron ore and coal particulates cause water pollution [8,9].

Several industries like textiles, beauty, leather, plastics, printing use synthetic dyes like Congo Red (CR), Methylene Blue (MB), Malachite Green (MG), etc. Disposal of these dyes into the water bodies leads to severe water pollution and distress aquatic life [10,11]. Most of the Commercial dyes utilized in these industries have complex structures containing the azo-bonds (-N=N-) which make them stable and are not degraded easily by micro-organisms [12,13]. These dyes cause many severe diseases in living organisms like allergy, disordering of the central nervous system, dermatitis, bladder cancer, and more [14,15]. Water containing azo dyes affects photosynthesis as they prevent the penetration of sunlight into the water system [16,17].

Hence polluted water should be freed from contaminants like suspended solid particles, toxic organic dyes, and toxic heavy metal ions to protect the environment and the ecosystem. In the last few decades, many conventional techniques like precipitation, coagulation, oxidation process, membrane filtration, evaporation, and ion exchange process have been developed to treat the polluted water [18-24]. But these processes are not technically and economically efficient enough. However, recent attention has been directed to the treatment and recycling of effluent through various eco-friendly efficient techniques like flocculation and adsorption processes [25].

Flocculation is the process in which small particles present in a liquid suspension are combined into larger clusters known as flocs, achieved by adding small number of chemical substances, referred to as flocculants [26-28]. Extensive utilization of polymeric flocculants is observed for the following reasons: they have minimum impact on the pH of the medium and can be employed in small quantities. Also, in the case of polymeric flocculants, bigger and stronger flocs are also formed [29]. Adsorption is a process by which toxic dyes, heavy metal ions, and other adsorbates can be separated from a solution. There are many advantages of the adsorption technique like cost-effectiveness, easy availability, easy regeneration, and more.

Various physical and chemical techniques have been designed for removing wastewater that contains heavy metal ions and dyes, including chemical precipitation [30], Ion exchange [31], photochemical degradation [32], coagulation and flocculation [33], physical adsorption [34], Bioremoval [35] and others. Each method has its advantages and limitations, and the selection of the appropriate technique depends on their efficiency, expense, and environmental impact. The adsorption approach is frequently employed to remove dyes and heavy metal ions from contaminated water because of its wide range of adsorbents, high efficiency, ease of operation, cost-effectiveness, regeneration, and reuse of the adsorbents [36]. Activated carbon is employed as an adsorbent more frequently, because of its significant surface area and excellent adsorption capacity. However, the limitations of activated carbon are lack of selectivity and regeneration process is expensive and complex. The researchers have been searching various low-cost materials as alternatives to activated carbon; for adsorption applications, particularly for the removal of toxic dyes and metal ions from polluted water, including Banana Pith [37], Cotton waste [38] and bentonite clay [39].

In the past few years, significant attention has been given to the adsorbent development by utilizing natural polysaccharides. This is mainly due to their several beneficial characteristics, such as biodegradability, cost-effectiveness, and stability under shear stress. However, the biodegradable nature of the polysaccharides can lead to reduce adsorption capacity and shorter storage life. On the other hand, synthetic polymers as adsorbents suffer from drawbacks like shear instability and non-biodegradability. To overcome these limitations, a novel class of adsorbents has emerged, involving grafting of the synthetic polymeric chains onto the backbone of natural polysaccharides. This innovative approach combines the benefits of both biodegradability and shear stability because of the presence of polysaccharide backbone [36]. Graft copolymers made from natural polysaccharides and several acrylic monomers like acrylic acid, methyl acrylate, acrylamide, N-methyl acrylamide are used effectively for the adsorption of organic pollutants from waste water. Lots of researchers used graft copolymers as an adsorbent for adsorption of organic pollutants from waste water because of their low toxicity, high adsorption capacity, and regeneration efficiency [40-42].

In recent years, dyes and heavy metal ions have been removed from their aqueous solutions using hydrogels based on natural polysaccharides. Hydrogels are hydrophilic polymeric networks that are crosslinked in a three-dimensional structure. They have the capability of absorbing water because of the presence of hydrophilic functional groups such as Amino ($-NH_2$), Hydroxyl (-OH), Carboxylic (-COOH), and Sulfonic Acids ($-SO_3H$). However, despite their water-absorbing properties, hydrogels remain insoluble under physiological conditions, including specific temperature ranges, pH levels, and ionic strength of the surrounding environment. Hydrogels are extensively utilized in various applications, such as drug delivery, wastewater treatment, tissue engineering, and the production of cosmetics, owing to their unique and specific properties [43-45]. Hydrogels have attracted significant research interest as adsorbents for pollutant removal from wastewater because of their remarkable properties, including high adsorption capacity, low toxicity, and the ability to be regenerated for multiple uses. These properties make them promising materials for sustainable and effective wastewater treatment methods.

In more recent times, with the advancements of nanoscience and nanotechnology, researchers have identified that modifying polymers with nanoscale fillers can significantly enhance the adsorption efficiency. This improvement is attributed to their enhance characteristics, such as higher hydrodynamic volume, enhanced thermal stability, abundant active sites, and improved mechanical resistance. Monodisperse silica nanoparticles have attracted significant interest as nanoscale fillers, primarily because of their remarkable capacity to enhance surface flexibility [46]. Again, there has been growing interest in utilizing carbon-based materials like Graphene Oxide (GO), Reduced Graphene Oxide (RGO) for synthesizing polymer composites and employing them as an effective adsorbent for organic molecules [47-49]. These materials possess remarkable properties, like large specific surface area, exceptional electron mobility, high thermal conductivity, and impressive mechanical strength, which make them highly appealing for various applications.

The katira gum [50] is a viscous polysaccharide extracted from the bark of the plant. Katira gum is a pale, semi-transparent substance that is insoluble in water but swells into a pasty, transparent mass when exposed to water. Katira gum can act as a stabilizer and emulsifier, making it useful in food and pharmaceutical industries. Katira gum is sweet, thermogenic, anodyne, sedative and effective in cough, diarrhoea, dysentery, pharyngitis, gonorrhoea, syphilis, and trachoma. The gum polysaccharide consists of equimolecular proportion of L-Rhamnose, D-Galactose and D-Galacturonic Acid, together with traces of a Ketohexose [50]. Katira gum contains Hydroxyl groups that can be used as reactive sites for crosslinking/grafting reactions. Swelling, thermal, mechanical, and other physic-chemical properties of katira gum can be improved by copolymerizing, crosslinking, and grafting with monomers of synthetic origin, or by the addition of nanoparticles to the hydrogel network [51].

Dextrin, a significant member of water-soluble polysaccharides, is produced when starch is hydrolysed into sugars through processes like pyrolysis, involving dry heat under acidic conditions, or enzymatic action, such as by amylases. Both dextrin and starch share a general formula, $[C_a(H_2O)_b]_n$ (where b=a-1), where in glucose units are typically linked head-to-tail. Hence, D-glucose units are linked by α-(1-4) and α-(1-6) glycosidic linkages. Dextrin is also biodegradable in nature differs from starch as it possesses shorter chains, making it a smaller and less complex molecule [52]. Biodegradable in nature differs from starch as it possesses shorter chains, making it a smaller and less complex molecule [52].

Amylopectin is a water-soluble polysaccharide found in plant and consists of α-glucose units. It is one of the two components of starch; the other one is Amylose [53,54]. The monosaccharide present in amylopectin is glucose, they are joined together by the (1,4)-α-glycosidic linkages to each other. The amylopectin is also biodegradable in nature. Amylopectin offers several advantageous features that make it a suitable substance for preparing graft copolymers. These include its branched structure, natural availability, hydrophilicity, biodegradability, structural versatility, and biocompatibility. Hence, in the present research work amylopectin is chosen as the polysaccharide for preparing graft copolymers that are to be used as flocculating, metal, and dye adsorbing agents.

Experimental

Materials

Paper mill effluent is collected from Emami Paper mill located in Dhanbad, Jharkhand, India. The municipal sewage water is collected from the main drain of Egra municipality, East Midnapore, West Bengal, India. Textile effluent is obtained from Impact Jeans Factory, Indore, Madhya Pradesh, India. Magna floc 1011, Hydropol OC and Organopol 6425 are procured from BASF, Mumbai, India. AP-g-poly(AM-co-NMA), h-dext-g-PMA/SiO_2 , Polyacrylamide (PAM), AP-g-PAM, Sulfated AP, Sulfated AP-g-PAM, Sulfated AP-g-PDMA , KG-cl-poly(AM-co-NMA) and KG-cl-poly(AA-co-NVI) hydrogel are synthesised in the authors' laboratory. Malachite Green (MG) and Methylene Blue (MB) are procured from Loba Chemic, Mumbai, India.

Synthesis of materials

Graft copolymers of amylopectin are prepared by grafting a mixture of acrylamide and N-Methyl acrylamide, only acrylamide and only N, N-dimethyl acrylamide separately by free radical graft copolymerization process using $K_2S_2S_8$ as an initiator in water medium to obtain AP-g-poly(AM-co-NMA), AP-g-PAM and AP-g-PDMA respectively. Sulphated AP-g-PAM, AP-g-PDMA and only AP were synthesised by sulfation reaction of the individual polymer with chlorosulfonic acid. Partially hydrolysed dextrin-g-polymethyl acrylate/SiO_2 nanocomposite is prepared by first hydrolysing dextrin-g-PMMA with aqueous alkali partially followed by the composite formation with tetraethyl orthosilicate. The graft copolymer dextrin-g-PMMA is prepared by $K_2S_2S_8$ initiated graft copolymerization process between dextrin and MA. Katira gum based hydrogels are prepared by grafting a mixture of AA and NVI, AA and NMA onto KG backbone separately by free radical copolymerization technique using KPS as initiator and MBA as a cross linking agent in water medium. The synthetic details of all the graft copolymers are communicated in our previous reports [55-59].

Characterization of the materials

Size exclusion chromatography (SEC): Size Exclusion Chromatography (SEC) [model 2414 by Water (1) Pvt. Ltd., USA] is used to determine the molecular weight distribution and molecular weight of the graft copolymers and dextrin. The analysis is carried out with the column temperature set to 30 °C and a constant flow rate of 0.6mlmin^{-1}. An aqueous SEC apparatus with an HSPgel™ column of 6.0x150mm is used for the measurement process. The two columns are linked in series to measure the molecular weight distribution and molecular weight. The molecular weight of the synthesised polymers and dextrin are determined by calibrating the SEC instrument using dextran and poly (sodium salt of styrene sulfonic acid) as standards. Following each polymer's solution passing through the column, the elution volume is determined, and log M is plotted against the elution volume to create a distribution curve from which the Mw are determined. The various molecular weight parameters Mz+1, Mz, Mw, Mn, and MP are listed in Table 1. Additionally, the corresponding plots are shown in Figures 1-3 Several other characterization techniques like NMR, FTIR spectroscopy, XRD analysis, FESEM and Thermal analysis are discussed in our previous communication [55-58].

Table 1: Different molecular weights of the synthesised graft copolymers. M_z, M_{z+1}=higher average molecular weights, M_w=weight average molecular weight, M_n=number of average molecular weight, and M_p=mode of the molecular weight distribution/molecular weight of highest peak.

Polymer	M_{z+1} (Dalton)	M_z (Dalton)	M_w (Dalton)	M_n (Dalton)	M_p (Dalton)
AP	5476800	5164888	4856634	4567602	4298632
AP-g-PAM	5533842	5003147	9484029	4343287	4016312
AP-g-PDMA	4782551	4094215	9857498	2941159	2567650
AP-g-poly (AM-co-NMA)	46824586	40983542	34574984	28456721	26614578
Sulfated AP	7769154	5356452	5478658	5014237	4857943
Sulfated AP-g-PAM	6053652	5332453	9756452	4845268	4233574
Sulfated AP-g-PDMA	6430254	5843564	9987485	5041236	5542513
Dextrin	88394	76635	59256	52324	72062
h-Dext-g-PMA	2306542	2186245	1969325	1764652	2120439

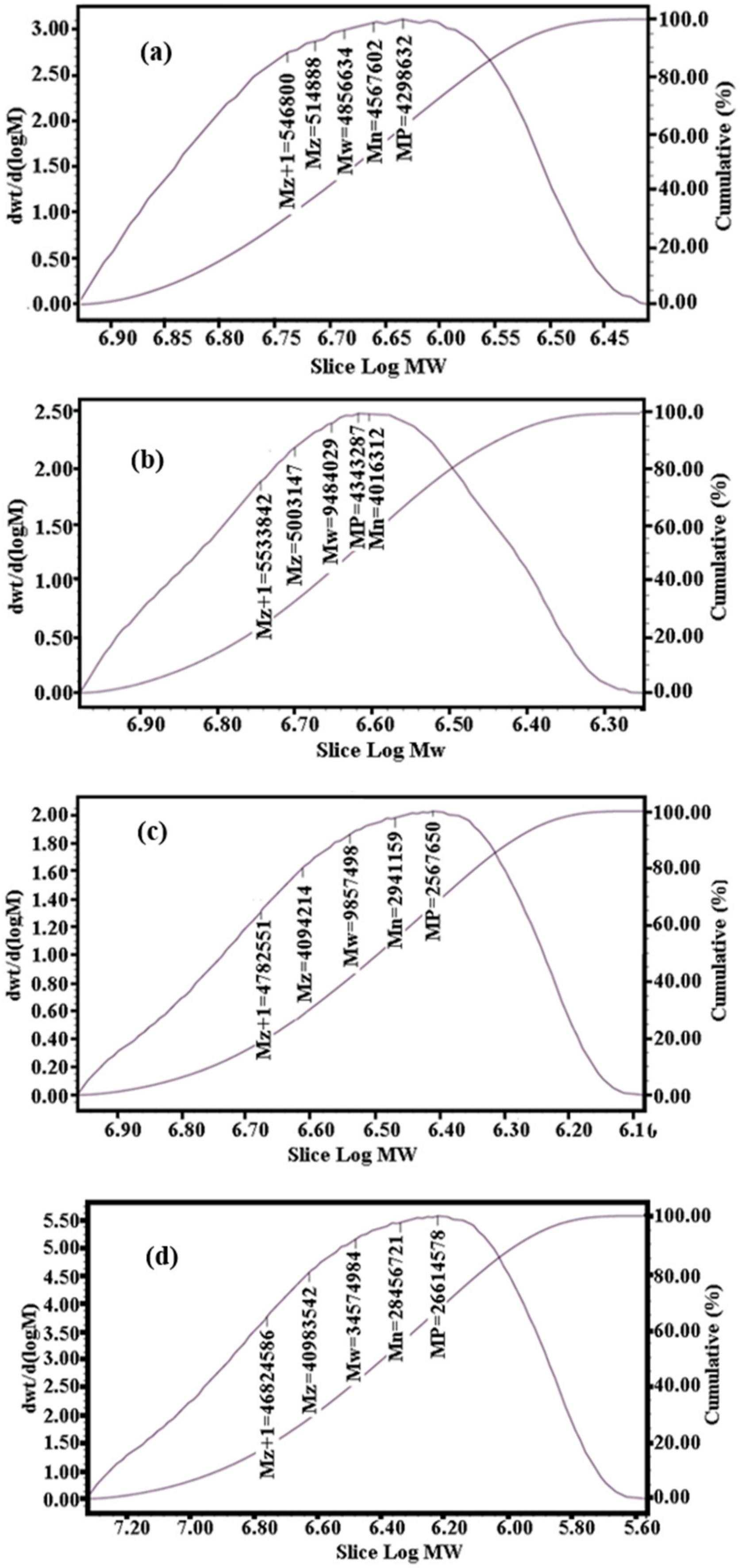


Figure 1: SEC plots of (a) AP, (b) AP-g-PAM, (c) AP-g-PDAM and (c) AP-g-poly (AM-co-NMA).

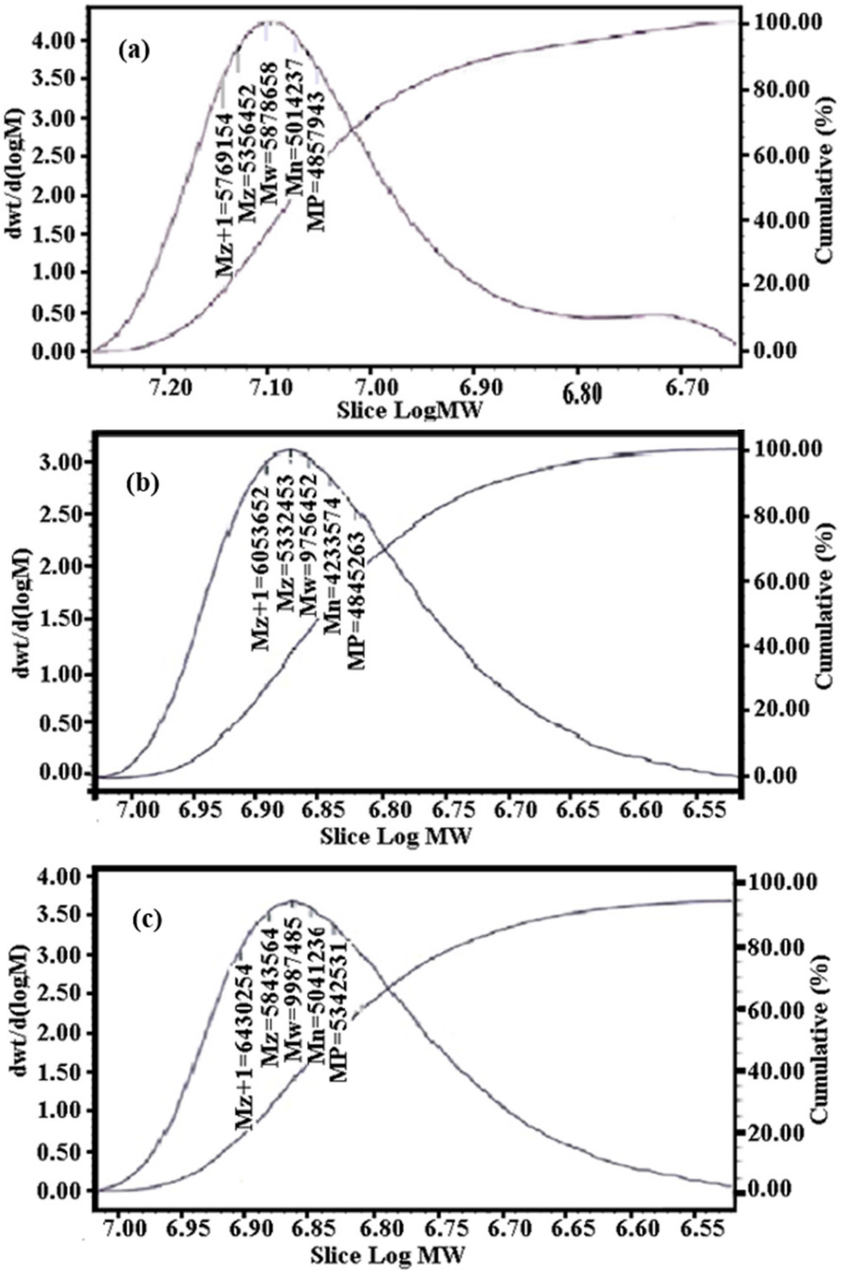
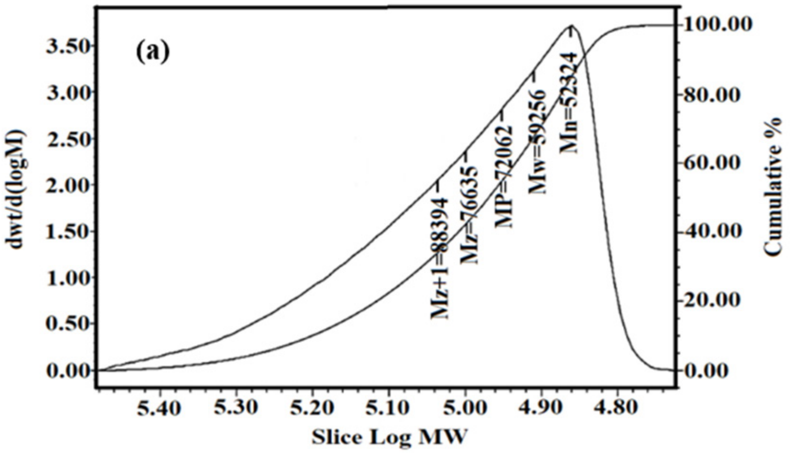


Figure 2: SEC plots of (a) Sulfated AP, (b) Sulfated AP-g-PAM and (c) Sulfated AP-g-PDMA.



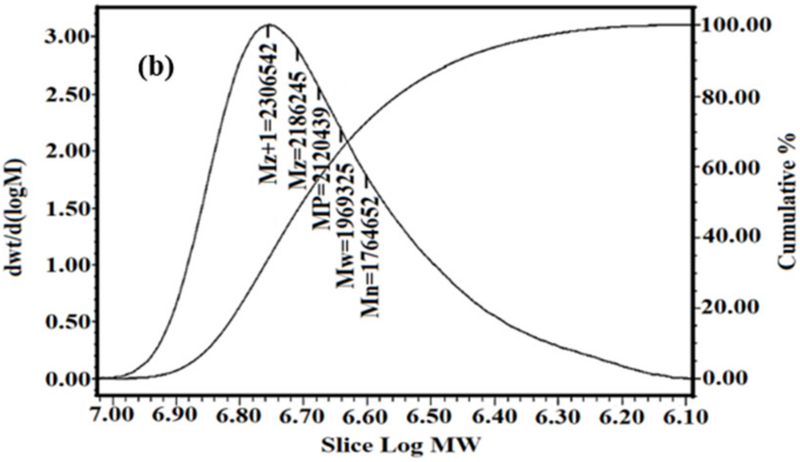


Figure 3: SEC plots of (a) dextrin and (b) h-Dext-g-PMA.

Flocculation studies

Flocculation study of a paper mill effluent: The flocculation performances of synthesised graft copolymers are investigated using a Jar test with the effluent from a paper mill located in Dhanbad, India. In this experiment, 100ml of the paper mill waste water is taken in a 250ml beaker. The synthesised graft copolymers [AP-g-PAM and AP-g-poly(AM-co-NMA)] of amylopectin along with the flocculants which are commercially available (magnafloc 1011, organopol, and hydropol OC) and PAM, taken from their respective stock solutions (0.1g of graft polysaccharide in 1000ml of water), are added individually to the beaker. The mixture is then stirred at 340rpm and a temperature of 30 °C using a magnetic stirrer. After stirring for 15 minutes, the stirring speed is lowered to 120rpm and the mixture is kept undisturbed to settle for an additional 15 minutes to form solid flocs. The clear liquid above the settled flocs, called supernatant, is collected using a syringe. The turbidity of the collected supernatant is measured using a digital nephelo turbidity meter (E1, Model 331) [60]. Figure 4 illustrates the flocculation performances of the synthesised graft copolymers AP-g-poly(AM-co-NMA), PAM, with the commercially available flocculants.

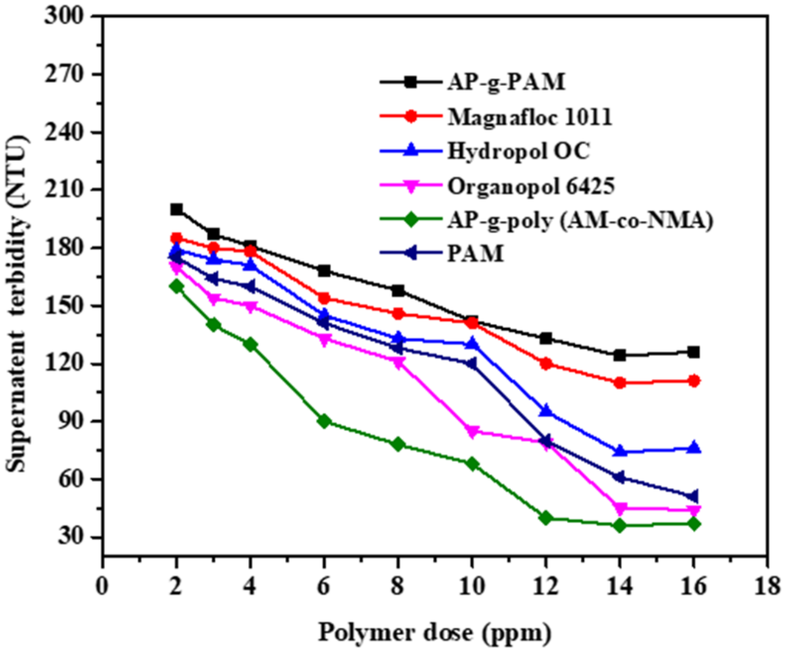


Figure 4: Comparative study of the flocculation efficiencies of the synthesised AM-g-PAM, magnafloc 1011, hydropol OC, organopol 6425, AP-g-poly (AM-co-NMA), and PAM in paper mill effluent.

Characterization of the paper mill waste water: A petri dish is used to hold 50ml of the paper mill effluent. The petri dish is then left to evaporate at a temperature of 270 °C. After a few days, the solid substance that formed in the petridish is collected for further analysis. The collected solid substance underwent measurements for zeta potential, specific gravity, average particle size, and chemical analysis, as outlined in Table 2. The procedures for these measurements are described in our previous journals [55].

Table 2: Characterizations of paper mill effluent.

Sample	Chemical Analysis					Particle size (nm)	Specific gravity (gm/cc)	Zeta Potential (mv)
	Fe_2O_3 (%)	SiO_2 (%)	Al_2O_3 (%)	CaO (%)	MgO (%)			
Effluent	0.22	50.5	41.4	0.99	0.07	81.4	2.45	-3.89

Flocculation analysis of the municipal sewage waste water: The sewage waste water from the main drain of Egra municipality in East Medinipur, West Bengal, India, is collected for analysis. The efficiency of flocculation is evaluated for synthesised graft copolymers, commercially available flocculants and PMA using the method outlined in the study of paper mill effluent. Figure 5 depicts the comparison of the flocculation efficiencies of the AP-g-PAM, hydropol OC, magnafloc 1011, organopol 6425, PAM, and AP-g-poly(AM-co-NMA) in municipal sewage waste water.

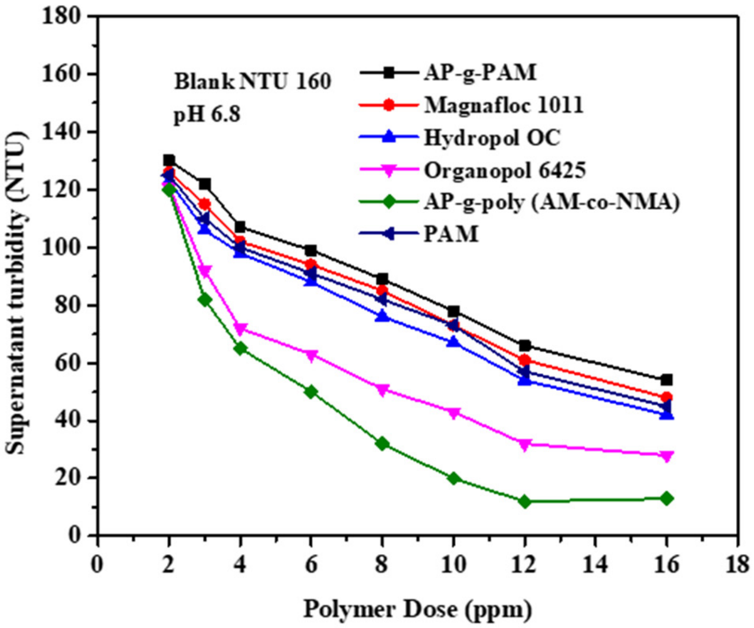


Figure 5: Comparison of the flocculation efficiencies of the AP-g-PAM, magnafloc 1011, hydropol OC, organopol 6425, AP-g-poly (AM-co-NMA), and PAM in municipal sewage waste water.

Characterizing waste water from municipal sewage systems: The gravimetric method is used to measure the levels of Total Solids (TS), Total Dissolved Solids (TDS), and Total Suspended Solids (TSS) present in the waste water of municipal sewage. To examine the Chemical Oxygen Demand (COD), the following procedure is followed [Bratby et al. 1980]. Initially, a stoppered 100ml conical flask is filled with 10ml of municipal sewage waste water and subsequently 5ml of digestion solution is added. The digestion solution consisting of concentrated sulfuric acid, potassium dichromate, mercuric sulphate, and water. Subsequently, 3ml of solution containing H_2SO_4 and $AgNO_3$ are added to the solution. Then the mixture is subjected to stir at 150 °C temperature for duration of 2.5 hours. After that, the solution is cooling at room temperature and the COD (as shown in Table 3) is measured using the HACH portable spectrophotometer (Model DR/2400).

Table 3: Flocculation efficiencies of the synthesised AP-g-PAM, Magnafloc 1011, Hydropol OC, Organopol 6425, AP-g-Poly (AM-co-NMA), and PAM on the municipal sewage wastewater.

Polymer	Turbidity (NTU)	TS (ppm)	TDS (ppm)	TSS (ppm)	COD
With out polymer	160	855	530	325	650
AP-g-PAM	53	340	300	221	193
Magnafloc 1011	48	210	210	167	175
Hydropol OC	45	180	120	123	160
Organopol 6425	29	160	110	80	155
AP-g-poly (AM-co-NMA)	13	110	80	35	140
PAM	54	350	310	230	230

Textile dye removal studies

The textile industrial effluent from Srivari Exims Pvt. Ltd., located in Kolkata, India, is collected and analysed in the following manner. Evaporating the effluent in a Petridis at 60 °C to eliminate the liquid component of the effluent, leaving behind the solid residue. The solid residue is collected and dissolved in water. Then it is subjected for the spectral analysis using UV-VIS spectrophotometer. Comparing the UV-VIS spectra of pure MG (Malachite Green) solution, MB (Methylene Blue) solution, and the UV-VIS spectrum of the textile industrial dye can provide insights into the similarities in their absorption characteristics and the results are illustrated in Figure 6. The synthesized nanocomposite, graft copolymers and hydrogels are then used as adsorbent to separate dyes from the textile industrial effluent by batch experiment. A simple experimental process is as follows; 20mg of synthesized nanocomposite is added into 60mL of textile industrial dye effluent taken in a beaker. The dye mixture is stirred by magnetic stirrer for 40min at 40 °C, pH 7.5 with 300rpm speed. After equilibrium is reached, 3-4mL of effluent solution is removed from the medium and centrifuged. The concentration of residual dye in centrifugate is estimated by using UV-VIS spectrophotometer. Equation 1 employed to compute the dye adsorption capacity.

$$\textit{Dye removal capacity } q = \frac{C_0 - C_e}{m} \times V \qquad \text{Equation 1}$$

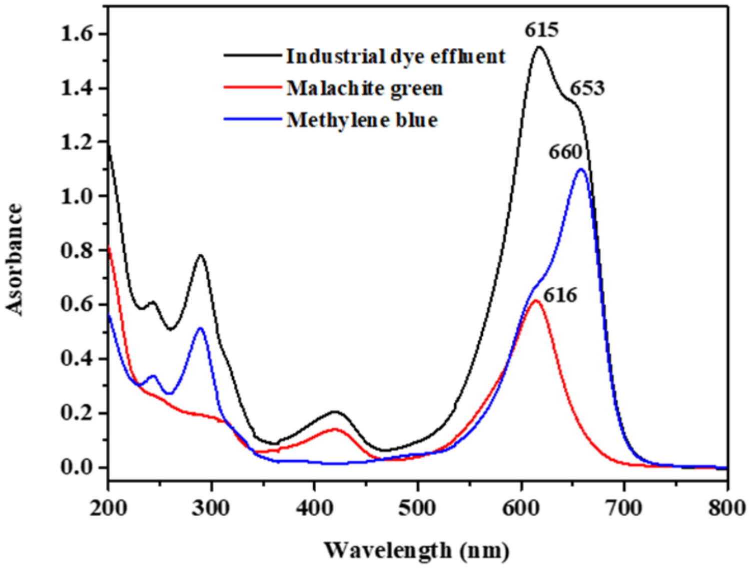


Figure 6: UV-VIS spectra of the industrial effluent, methylene blue and malachite green solution.

Where, q refers to the dye removal capacity (mg g^{-1}), C_0 and C_e refer to the initial and final concentrations of dye solution mg/l, V refers to the volume of dye solution in litre and m refers to the mass of the graft copolymer in gram.

Result and Discussion

Determination of the specific surface area and pore size distribution analysis by Brunauer-emmett-teller (BET) method

Figures 1-4 depict the N_2 adsorption-desorption isotherms and pore size distributions of AP, AP-g-PAM, AP-g-PDMA, AP-g-poly(AM-co-NMA), sulphated products (Sulfated AP, Sulfated AP-g-PAM, Sulfated AP-g-PDMA), KG-cl-poly (AM-co-NMA), KG-cl-poly (AA-co-NVI) and h-dext-g-PMA/SiO_2. The isotherms demonstrate a characteristic type-IV curve with a type-H4 hysteresis loop in the relative pressure (P/P_0) range of 0.1 to 1.0. This hysteresis loop signifies the presence of a mesoporous structure of AP, KG, Dextrin, synthesised graft copolymers, sulphated products, hydrogels, and silica composites. Table 1 show the BET surface areas and pore size distribution values. From the values, all the synthesised graft copolymers have larger specific surface area compared to corresponding virgin polysaccharides. This confirms the grafting of monomers onto the polysaccharide's backbone.

Size exclusion chromatography (SEC)

Molecular weight and molecular weight distribution using size exclusion chromatography (SEC): Molecular weight and molecular weight distribution of the synthesised graft copolymers are determined using the size exclusion chromatography. It is obvious from the Figures 1-3 that the molecular weight of the all-synthesised graft copolymers, hydrogels and nanocomposites are higher compared to the amylopectin, katira gum and dextrin respectively. This increase in molecular weight can be explained by considering the presence of PAM, PMA, PDMA, PAM-co-PNMA, PAM-co-PAA, and PAM-co-PDMA, grafted chains onto the amylopectin backbone. Table 1 shows that the AP-g-poly(AM-co-NMA) exhibit higher molecular weight compared to the AP-g-PAM. This enhancement of the molecular weight can be explained due to the presence of extra PNMA chains in the amylopectin backbone. Again, sulfation of AP, AP-g-PAM and AP-g-PDMA results the increase in molecular weight from their respective parent molecules due to incorporation of -SO_3H groups at the -OH functionalities of amylopectin backbone (Table 1).

Flocculation study of a paper mill effluent

According to the Table 3, the major components of the paper mill effluent are SiO_2 and Al_2O_3, which are present in the kaolin clay also [Bratby et al 1980]. Figure 4 illustrates the flocculation performances of the synthesised graft copolymers AP-g-poly(AM-co-NMA), PAM, and commercially available flocculants. From the Figure 4 it is evident that, AP-g-poly(AM-co-NMA) shows superior performance in flocculation. This better performance can be attributed to the following reason. The polymeric chains of AP-g-poly(AM-co-NMA)contain both $-CONH_2$ and -CONH(Me) groups, which facilitate strong interactions with the aluminium silicate (as major component of the effluent) through hydrogen bonding or electrostatic attraction. These interactions enhance the bridging capacity of the grafted AP-g-poly(AM-co-NMA) polymeric chains. As a result of which AP-g-poly(AM-co-NMA) shows better flocculation performance.

Flocculation study of municipal waste water

Figure 5 shows the comparison of the flocculation efficiencies of the AP-g-PAM, magnafloc 1011, hydropol OC, organopol 6425, AP-g-poly(AM-co-NMA), and PAM in municipal sewage waste water. Table 3 shows the minimum NTU value for AP-g-poly(AM-co-NMA). Most of the municipal sewage waste water contains the suspended particles as major amount. The suspended particles are coagulated by the strong interaction with AP-g-poly(AM-co-NMA) than the other flocculants. The reason of the higher flocculation efficiency of the AP-g-poly(AM-co-NMA) is described in the previous context of flocculation of solid suspension.

Colour removal analysis of the effluents of a textile industry

The Figure 6 shows that methylene blue and malachite green are the two dyes present in the dye effluent obtained from the textile dye industry. The higher intensity of the methylene blue in the UV plot indicates that the dye effluent contains methylene blue as major dye component over the malachite green. The cationic dyes (MB and MG) removal efficiencies of the Sulfated products are shown in Figure 7(a). This effective dye removal capacities of the Sulfated products (Sulfated AP, Sulfated AP-g-PAM, and Sulfated AP-g-PDMA) can be explained by considering the presence of $-SO_3H$ groups on the amylopectin backbone, which can dissociate into $-SO_3^-$ groups. These anionic sulfonate groups can interact with the cationic dyes through electrostatic interactions. The higher surface area of the Sulfated products is also an additional reason for their effective dye removal efficiencies.

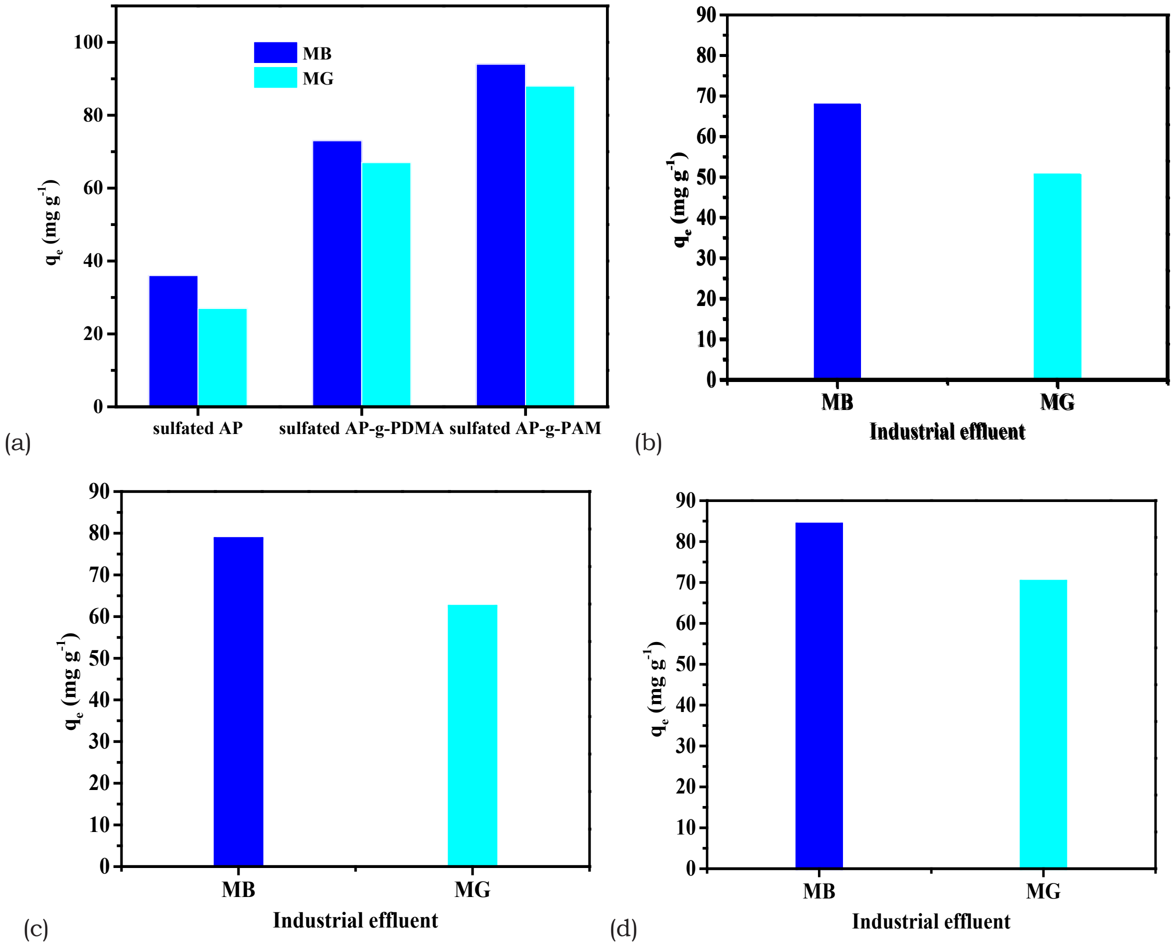


Figure 7: Color removal efficiencies in industrial textile dye effluent by (a) sulfated AP, sulfated AP-g-PAM, and sulfated AP-g-PDMA, (b) KG-cl-poly(AM-co-NMA) hydrogel, (c) KG-cl-poly(AA-co-NVI) hydrogel, (d) h-Dext-g-PMA/SiO_2 nanocomposite.

Furthermore, Figure 7(a) shows a higher dye removal efficiency for Sulfated AP-g-PAM compared to Sulfated AP and Sulfated AP-g-PDMA. This observation can be explained by considering the Amide Group (-$CONH_2$) in Sulfated AP-g-PAM. The 'H' atom present on the 'N' atom can interact with MB and MG through intermolecular H-bonding, which is absent in the other two Sulfated products. Again, the polar group [-$CON(CH_3)_2$] present in Sulfated AP-g-PDMA can interact with methylene blue through effective polar interactions, which is responsible for the higher dye removal efficiency of Sulfated AP-g-PDMA compared to Sulfated AP. The dye removal capacities of Sulfated AP, Sulfated AP-g-PAM, and Sulfated AP-g-PDMA for MB are 93.87, 72.85, 35.88 and for MG are 87.59, 66.57, 26.72 respectively.

Figure 7(b) shows the removal efficiency of industrial effluent using KG-cl-poly(AM-co-NMA) hydrogel. This effective dye removal efficiency of KG-cl-poly(AM-co-NMA) hydrogel is explained in the following way: Both the dyes are cationic and bear a positive charge at the nitrogen (N) centre. At the pH 7.5, the hydrogel's surface carries negative charges because of the partial hydrolysis of amide functionalities. These anionic functionalities can interact with the cationic dyes (MB and MG) molecule through electrostatic interactions resulting in an increase in colour removal efficiency of the industrial effluent. Figure 7(c) shows higher dye removal efficiency for KG-cl-poly(AA-co-NVI)hydrogel compared to KG-cl-poly(AM-co-NMA). This observation is explained by considering the presence of imidazole groups in NVI contributes to the higher dye removal efficiency of KG-cl-poly(AA-co-NVI) hydrogel. Imidazole groups can form coordinate bonds with cationic dyes like methylene blue, malachite green facilitating their removal from the solution. Again, the presence of carboxylic acid groups (from AA) in KG-cl-poly(AA-co-NVI) hydrogel can provide additional ionizable sites, which can facilitate electrostatic interactions with cationic dyes. This can enhance the dye adsorption and removal efficiency of industrial effluent. On the other hand, the presence of only amide groups (from AM and NMA) in KG-cl-poly(AM-co-NMA) hydrogel may have a weaker affinity for cationic dyes, resulting in lower dye removal efficiency. The dye removal efficiencies of KG-cl-poly(AM-co-NMA) are 68.12 % for MB and 51.31 % for MG. Again, the industrial dye removal efficiencies of KG-cl-poly(AA-co-NVI) are 79.13 % for MB and 62.54% for MG

Figure 7(d) showed the percentage removal efficiency of industrial effluent using h-Dext-g-PMA/SiO_2 nanocomposite under the optimum conditions obtained from the experiments. Hence, both the cationic dyes adsorbed well by the synthesized silica nanocomposite. Although, the percentage of removal efficiency is more for MB (84.26%) than MG (70.29%), possibly due to compact structure of MB.

Conclusion

In conclusion, this study successfully demonstrates the efficiencies of synthesized graft copolymers over commercially available flocculants and PAM in treating wastewater from municipal sewage and paper mills. The flocculation performance of AP-g-poly (AM-co-NMA) is important for its greater efficiency compared to some commercially available flocculants in both paper mill and municipal sewage effluents. Moreover, this investigation is also extended to the removal of textile dyes, revealing the effective adsorbing properties of sulphated products, hydrogels, and nanocomposite for cationic dyes (MB and MG) which are the major constituents of an effluent of a textile dye industry through electrostatic interactions and other molecular mechanisms. The cationic dye removal capacities of the Sulfated products, hydrogels, and nanocomposite follow the order: Sulfated AP-g-PAM>h-Dext-g-PMA/SiO_2>KG-cl-poly(AM-co-NMA)>Sulfated AP-g-PDMA> KG-cl-poly(AA-co-NVI)>Sulfated AP. These findings provide a valuable insight into the sustainable and environmentally responsible solutions for wastewater treatment.

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