FUNCTIONALIZED POLYACRYLAMIDE/GRAPHITE COMPOSITES AS AN ADSORBENTS FOR THE DECOLOURISATION OF SYNTHETIC DYES AND DYEING INDUSTRY EFFLUENT FROM FABRIC PROCESSING UNITS

Abstract

In this study we have compared the decolourisation of dyeing industry effluents collected in fabric processing units and synthetic dyes like direct blue 2b, acid violet 17, reactive red M5B and methylene blue 9 from aqueous solution using functionalized polyacrylamide/graphite composites such as glucose grafted polyacrylamide/graphite, glucosamine grafted polyacrylamide/graphite and commercial activated carbon as adsorbents. The adsorption studies are performed by varying the experimental parameters like temperature, time, adsorbate concentration and adsorbent dose. The various physicochemical parameters of dyeing industry effluents such as colour, pH, conductivity, total dissolved solids, hardness, alkalinity, chloride, sulphate, dissolved oxygen, chemical oxygen demand and bio-chemical oxygen demand of the effluents are analyzed before and after adsorption by the standard methods. It is observed that the synthesized adsorbents show more efficiency towards the removal of synthetic dyes from aqueous solution than the decolourisation of dyeing industry effluent. The amount of adsorbents required and cost analysis to treat 10 M^3 of effluent is also studied and compared with commercial activated carbon.

Keywords: Textile effluent, dyes, adsorption, graphite, polyacrylamide

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I. INTRODUCTION

Applications of natural dyes such as indigo, woad or madder have been replaced by synthetic dyes in the 18th century due to the dynamic development of textile industry. Synthetic dyes have complex structures and provide variety of colours and shades, resistance to chemical factors, light and friction. Approximately 10,000 different dyes and pigments are manufactured commercially worldwide, with an annual production of 7×10^5 tons [1]. Synthetic dyes are widely used in textile, paper, food, chemical, tanning, plastics, leather, cosmetics and paint industries.

Textile industry is one of the oldest, largest and rapidly flourishing industries in India and it is a biggest consumer of different types of dyes. Dyes are non biodegradable have marked features such as high degree of chemical, photolytic and microbiological stability which affects the flora and fauna. The characteristics of wastewater produced in textile industries depend on many factors like kind of fabric used, class of dyes, dyeing process as well as apparatus. The processes require wide range of chemicals, beside dyes and auxiliaries, textile industry wastewaters contain specific contaminations such as fat, wax, oils, dextrin, leafy matter, minerals, starch, casein [2].

The textile industry wastewaters associated with huge volumes of extremely contaminated effluent and are characterized by high chemical oxygen demand (COD), biological oxygen demand (BOD), total suspended solids, total dissolved solids (TDS), extreme pH and colour, which adds odour and twist the water quality parameters [3].

Currently a wide variety of techniques such as coagulation, ion exchange process, membrane process, electrochemical treatment, advanced oxidation process and adsorption have been used for the water purification. Among them, adsorption technique has been widely used because it is inexpensive, operation is simple, shows more efficiency. Natural materials such as sand, clay, various oxides, gum, agricultural and industrial by products, carbon allotropes and synthetic polymers have been utilized as adsorbents.

This paper assesses the characteristics of dyeing industry effluents collected in fabric processing units. In addition we have compared the efficiency of synthetic copolymers such as polyacrylamide/graphite (PAM/graphite), glucose grafted polyacrylamide/graphite (Gu-g-PAM/graphite) and glucosamine grafted polyacrylamide/graphite (GA-g-PAM/graphite) composites as adsorbents for the decolourisation of synthetic dyes from aqueous solution and dyeing industry effluents. The results of adsorption of four textile dyes and dyeing industry effluent were studied and compared with commercial activated carbon (CAC). The cost analysis for preparing the synthetic copolymer adsorbents and for treating 10 M^3 of effluent are also studied and compared with CAC.

II. MATERIALS AND METHODS

Commercial dyes such as direct blue 2b, acid violet 17, reactive red M5B and methylene blue 9 were purchased from spectrum chemicals, India. CAC was purchased from merck chemicals. Molecular structures of the above mentioned dyes are presented in Figure 1. Five real dyeing industry effluents were collected from various knitted fabric processing industries in State Industries Promotion Corporation of Tamilnadu Ltd (SIPCOT), perundurai, Tamilnadu, India. The real dyeing industry effluents were diluted to 10 times for further adsorption studies.

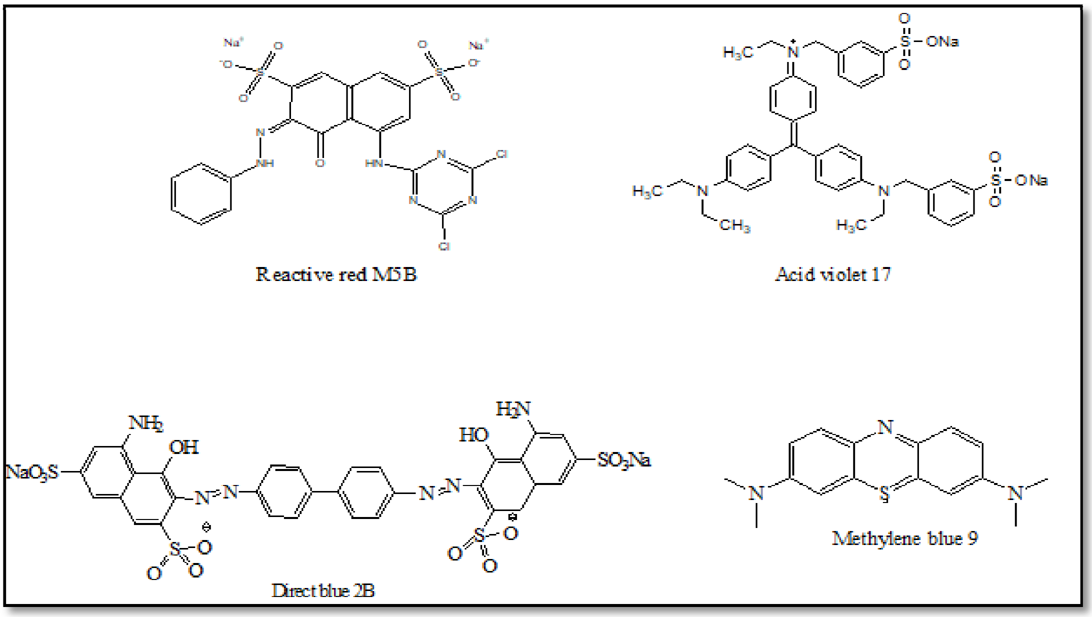

Figure 1: Chemical structure of synthetic dyes

1. **Preparation of Adsorbents:** The PAM/graphite, Gu-g-PAM/graphite and GA-g-PAM/graphite composites were prepared as reported in our earlier study [4]. To prepare Gu-g-PAM/graphite, Graphite (1.5 g) and glucose (0.02 mole) dissolved in 10 ml of distilled water was taken in a round bottom flask. Then 0.01 g of APS dissolved in 10 ml of distilled water was added to the flask at 70 °C. Thereupon 10 ml of 0.01 mole of acrylamide monomer was added slowly to the flask and the reaction was continued for 8 h. Then the reaction mixture was cooled, dispersed in acetone: ethanol mixture, dried at 60 °C for 12 h. Synthetic route for the preparation of Gu-g-PAM/graphite composite is shown in Figure 2. Similar procedure is followed for the synthesis of GA-g-PAM/graphite.

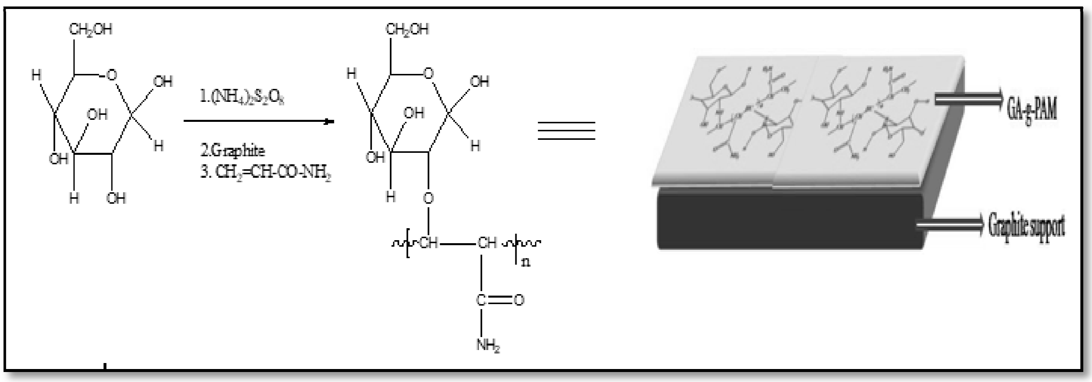

Figure 2: Preparation of glucose-g-PAM/graphite composite.

2. **Batch Adsorption Studies:** The adsorption studies of the synthesized polymer composites were performed for the removal synthetic dyes from aqueous solution by varying the experimental parameters like temperature, time, adsorbate concentration and adsorbent dose. The effect of temperature change was performed at temperatures: 303 K, 313 K and 323 K. For kinetic studies the samples were withdrawn at the predetermined time. The concentration of adsorbate dye varied from 10 mg/L to 100 mg/L. The dose of adsorbent was varied from 0.01 g to 0.120 mg. The optimized conditions investigated for the removal of synthetic dyes from aqueous solution are: Time 90 min; temperature 303 K; adsorbent dose 0.05 g/50 ml; dye concentration 50 mg/L and pH = solution pH.

3. **Adsorption of Dyeing Industry Effluents:** The color, pH, conductivity, Total Dissolved Solids (TDS), hardness, alkalinity, chloride, sulphate, Dissolve Oxygen (DO), Chemical Oxygen Demand (COD) and Bio chemical Oxygen Demand (BOD) of the effluents were estimated by the standard methods [5]. The colour of the effluents were analyzed using DR3900 spectrophotometer. The pH of the effluent was analyzed using Elico LI 120 pH meter. The TDS of effluents are measured using Hanna HI-98301 pocked sized meter. The electrical conductivity of the effluents was measured using Elico CM 180 conductivity meter. Sulphate content is estimated by gravimetric analysis using barium chloride solution. Chloride content of effluent is determined volumetrically by Mohr's method. Total hardness caused due to the presence of calcium and magnesium salt is estimated by EDTA titrimetric method. The **a**lkalinity was caused due to the presence of carbonates, bicarbonates and hydroxides of metal ions and is estimated by titrimetric method. Dissolved Oxygen (DO) is estimated by Winkler's method. Chemical Oxygen demand (COD) is the amount of oxygen consumed to chemically oxidize organic water contaminants to inorganic end products. It is determined by open reflux method using potassium dichromate a strong oxidizing agent under acidic conditions. Biological oxygen demand (BOD) is the amount of oxygen consumed by bacteria and other microorganisms to break down organic matter under aerobic (oxygen is present) conditions at a specified temperature. It is estimated by keeping an effluent containing a known amount of O_2 over a 5-day period at 20^{o}C. Then O_2 content is measured again and BOD is calculated.

   After that, decolourisation of effluents was carried out using the adsorbents PAM/Graphite, Gu-g-PAM/graphite, GA-g-PAM/graphite and CAC under the conditions optimized for the removal of synthetic dyes from aqueous solution such as: Time 100 min; temperature 303 K; adsorbent dose 0.05 g/50 ml; and pH = effluent pH. Then the above said water quality parameters of treated effluents were determined by the standard methods [5]. The obtained results before and after adsorption is listed in Table 1 for PAM/graphite, Table 2 for Gu-g-PAM/graphite and Table 3 for GA-g-PAM/graphite. The results were also compared with BIS standards and MoEF's Environment Protection Rules, 1986.

Table 1: Physico - Chemical Characteristics of effluents before and After Adsorption onto PAM/graphite.

Properties	Dyeing Effluent										BIS standards
	E-1		E-2		E-3		E-4		E-5		
	BA	AA	BA	AA	BA	AA	BA	AA	BA	AA	
Color, Hazen	Violet	Light blue	Grey	Colorless	Blue	Colorless	Black	Colorless	Reddish Orange	Pale yellow	25
pH	11.3	10.4	10.4	9.7	9.2	8.7	11.0	10.1	12.7	10.6	5.5-9
Conductivity, ms	9.57	8.33	7.68	5.82	9.86	8.09	7.13	4.53	11.87	9.52	-
TDS, mg/L	14500	8970	7630	5380	9600	6280	6742	3940	14950	10090	2100
Hardness, mg/L	162	139	135	108	97	72	83	67	187	159	500
Alkalinity, mg/L	120	91	90	65	105	82	77.5	51	132.5	106	200-600
Chloride, mg/L	829	387	669	232	717	429	413	233	1476	672	600
Sulphate, mg/L	391	165	232	141	206	144	218	161	370	307	1000
COD, mg/L	1180	773	867	597	935	678	769	523	1045	671	250

* BA-before adsorption; AA-after adsorption

Table 2: Physico-Chemical Characteristics of Effluents Before And After Adsorption Onto Gu-G-PAM/Graphite.

Properties	Dyeing Effluent										BIS standards
	E-1		E-2		E-3		E-4		E-5		
	BA	AA	BA	AA	BA	AA	BA	AA	BA	AA	
Color, Hazen	Violet	Light blue	Grey	Colorless	Blue	Colorless	Black	Colorless	Reddish Orange	Pale yellow	25
pH	11.3	9.5	10.4	8.7	9.2	7.9	11	8.7	12.7	9.9	5.5-9
Conductivity, ms	9.57	6.63	7.68	3.17	9.86	5.18	7.13	2.74	11.87	7.52	-
TDS, mg/L	14500	6736	7630	4660	9600	5867	6742	3043	14950	8069	2100
Hardness, mg/L	162	122	135	94	97	63	83	61	187	137	500
Alkalinity, mg/L	120	74	90	53	105	69	77.5	32	132.5	89	200-600
Chloride, mg/L	829	387	669	232	717	429	413	233	1476	672	600
Sulphate, mg/L	391	137	232	111	206	108	218	137	370	281	1000
COD, mg/L	1180	572	867	379	935	476	769	384	1045	467	250

* BA-before adsorption; AA-after adsorption

Table 3: Physico - chemical characteristics of effluents before and after adsorption onto GA-g-PAM/graphite.

Properties	Dyeing Effluent										BIS standards
	E-1		E-2		E-3		E-4		E-5		
	BA	AA	BA	AA	BA	AA	BA	AA	BA	AA	
Color, Hazen	Violet	Light blue	Grey	Colorless	Blue	Colorless	Black	Colorless	Reddish Orange	Pale yellow	25
pH	11.3	9.1	10.4	8.6	9.2	7.4	11	8.7	12.7	9.8	5.5-9
Conductivity, ms	9.57	5.89	7.68	3.06	9.86	4.63	7.13	2.59	11.87	6.17	-
TDS, mg/L	14500	6582	7630	4387	9600	5729	6742	2147	14950	7876	2100
Hardness, mg/L	135	95	162	120	97	62	83	61	187	138	500
Alkalinity, mg/L	120	63	90	49	105	61	77.5	26	132.5	88	200-600
Chloride, mg/L	829	387	669	232	717	429	413	233	1476	672	600
Sulphate, mg/L	391	119	232	102	206	101	218	98	370	253	1000
COD, mg/L	1180	557	867	364	935	461	769	372	1045	455	250

* BA-before adsorption; AA-after adsorption

III. RESULTS AND DISCUSSION

The synthesized polymer composites were used for the removal of dyes namely MB-9, Av-17, RR-2 and DB-2b from aqueous solution. The adsorption capacity of polymer composites is directly proportional to temperature and initial dye concentration. But the percentage of dye removal indirectly proportional to initial dye concentration. Due to pK_a of dyes and zero point charge of adsorbents the amount of dye adsorption increased for MB with increase of pH from 2 to 11. On the other hand adsorption capacity of anionic dyes (Av-17, RR-2 and Db-2B) decreases with pH change from 2 to 11.

The adsorption kinetics was fast and attained equilibrium within 40, 50 and 60 min for MB-9, Av-17 and Db-2B. RR-2 attained equilibrium within 80 min. The kinetic data of all dyes were in good agreement with pseudo-second order model. The equilibrium data were fitted well with Freundlich isotherm for Db-2B and Langmuir isotherm for MB-9, Av-17 and RR-2. The thermodynamic parameters ΔG, ΔH and ΔS showed that the adsorption process was spontaneous ($\Delta G < 0$), endothermic ($\Delta H > 0$) and has decreased entropy ($\Delta S>0$). The activation energy values E_a reveals that all dye molecules are adsorbed physically onto the surface of polymer composites. Regeneration studies reveal that composites could be effectively regenerated by inexpensive reagent 0.1M HCl for MB-9 and 0.1 M NaOH for Av-17, Db-2B and RR-2. All the adsorbents retained considerable adsorption capacity after five adsorptions-desorption cycles. The FT-IR characterization results of GA-g-PAM/graphite before and after adsorption with dye reveals that H-bonding, electrostatic attraction, n-π and π-π interactions are involved in adsorption process [6]. The adsorption capacity of polymer composites are in the following order GA-g-PAM/graphite > Gu-g-PAM/graphite > PAM/graphite for all the dyes. Grafted polymers show higher adsorption capacity than PAM/graphite due to more adsorption sites. Among grafted polymers GA-g-PAM/graphite showed higher adsorption capacity than Gu-g-PAM/graphite due to -NH group.

Polymer composites were also used for the treatment of five real dyeing industry effluents. The various physico-chemical parameters of effluents before and after adsorption were evaluated. The Table 4 shows the percentage of colour removal of dyeing industry effluents and synthetic dyes under the optimized conditions by PAM/graphite, Gu-g-PAM/graphite, GA-g-PAM/graphite and CAC. Though the effluent samples are highly coloured, polymer composites decolourized the effluent samples significantly. Conductivity measurements and TDS values states that effluents have more ionic strength and dissolved solids which reduces adsorption efficiency of polymer composites [7]. pH results signifies that all the effluents are alkaline in nature but after treating with polymer composites pH of effluents reduced significantly. It is observed that hardness of effluents before and after adsorption is within the permissible level. The chloride and sulphate content of effluents are reduced almost 50 % after treating with adsorbents. The various physico – chemical parameters result of effluents before and after adsorption indicates that the polymer composites reduced all the parameters of effluents within the permissible limit recommended by BIS standards except TDS and COD.

It was noticed that the percentage of colour removal by GA-g-PAM/graphite composite was more compared to PAM/graphite and Gu-g-PAM/graphite. This might be due to its functional groups such as $–NH_2$, -OH and $–CONH_2$ groups. The percentage of colour removal of synthetic dyes by the composites was more than the real dyeing industry effluents. This is because synthetic dyes are free from dissolved solids, sulphate, chloride and other chemicals.

The efficiency of CAC was higher than the synthesized composites for the treatment of synthetic dyes and dyeing industry effluents. This behaviour may be justified as follows. (1) The adsorption capacity of CAC is insignificantly affected by the solution pH and ionic strength [8,9]. (2) CAC is a porous material with high surface area enhances adsorption capacity whereas the surface area of synthesized PAM/graphite composites where found to be in the range of 3 - 5.79 $m^2\ g^{-1}$ [7]. The literature studies reveals that surface area and pore volume play a vital role in adsorption of dyes and adsorption follows pore filling mechanism [10]. (3) CAC contain more active functional groups such as carboxylic acids, phenols, alcohols, acetylens, ethylene and –C-O [11] than the synthesized PAM/graphite composites. The more functional groups interacts with the functional groups of dyes through H-bonding, electrostatic attraction, n-π interaction and π-π interaction. All the aforementioned factors of CAC support the high adsorption capacity and colour removal of dyes than synthesized PAM/graphite composites.

Table 4: Comparison of percentage of colour removal of synthetic dyes and dyeing industry effluent by PAM/graphite, Gu-g-PAM/graphite, GA-g-PAM/graphite and CAC.

Samples	Adsorption Parameters	Percentage of color removal			
		PAM/ graphite	Gu-g-PAM /graphite	GA-g-PAM /graphite	CAC
Direct blue 2b	Dye concentration = 50 mg/l Adsorbent dose = 50 mg Contact time = 100 min Temperature = 30 °C pH = dye pH	59.01	72.72	86.36	94.23
Acid violet 17		52.38	71.42	90.47	98.47
Reactive red m5b		50.00	63.15	72.36	92.61
Methylene blue		72.83	83	7.4	100
Effluent 1	Adsorbent dose = 50 mg Contact time = 100 min Temperature = 30 °C pH = effluent pH	66.66	70.66	77.81	78.89
Effluent 2		76.13	82.13	88.13	89.47
Effluent 3		74.41	79.81	85.81	86.36
Effluent 4		83.16	87.16	91.16	92.34
Effluent 5		70.27	72.27	79.27	80.19

1. **Cost Analysis of the Textile Effluent Treatment:** In an economical view the cost analysis for the preparation of polymer composites and the amount of adsorbent required to treat 10 M^3 of effluent is compared with CAC. Though CAC shows better efficiency then the synthesized composites, higher amount of CAC is required for the complete decolourisation of effluent [12,13] than the synthesized composites. CAC shows slow adsorption kinetics to attain adsorption equilibrium whereas PAM/graphite composites reach equilibrium within 30 min. We have compared the cost analysis for the preparation composites with CAC. The cost comparison includes raw material cost, solvents cost and electricity consumption. Table 5 compares the amount of adsorbents required for treating 10 M^3 of dyeing industry effluent and the cost of preparing the adsorbents. It can be seen from Table 5, the unit cost of PAM/graphite, Gu-g-PAM/graphite and CAC were lower than GA-g-PAM/graphite but the amount required for the complete decolourisation of effluents is less for GA-g-PAM/graphite.

   The quantity of polymer composites required and the cost for preparing composites were compared with commercial activated carbon also. The analysis states that dyeing effluent treatment with PAM/graphite and Gu-g-PAM/graphite is more economical than GA-g-PAM/graphite and CAC. Though the preparation cost of GA-g-PAM/graphite is little higher than PAM/graphite and Gu-g-PAM/graphite, the quantity required for the treatment of effluent is less. The preparation cost of GA-g-PAM/graphite (1Kg - 4.93 $) is comparable with that of CAC (1Kg - 4.29 $).

Table 5: The amount of adsorbents required for treating 10 M^3 of dyeing industry effluent and the cost of preparing the adsorbents.

Effluent	Amount of adsorbent required to treat 10 M^3 of effluent ($Kg/10M^3$)				Treatment cost in dollars ($)			
	PAM /graphite	Gu-g-PAM /graphite	GA-g-PAM /graphite	CAC	PAM /graphite	Gu-g-PAM /graphite	GA-g-PAM /graphite	CAC
E-1	15.00	14.15	12.85	13.91	157	156	351	160
E-2	13.14	12.18	11.35	11.84	138	134	309	141
E-3	13.44	12.53	11.65	12.29	141	138	318	146
E-4	12.03	11.47	10.97	11.19	126	127	299	137
E-5	14.23	13.84	12.62	13.30	149	153	344	157

IV. CONCLUSION

The functionalized polyacrylamide/graphite composites and CAC were utilized as adsorbents for the decolourisation of dyeing industry effluent collected from the fabric processing unit and synthetic dyes. Based on the batch adsorption results such as effect of contact time, initial concentration of solution, pH, temperature, kinetics, isotherms, thermodynamics, reusability, dyeing effluent treatment and cost analysis, it was concluded that GA-g-PAM/graphite could be used as an alternative adsorbent for the removal of organic dyes from aqueous medium than PAM/graphite, Gu-g-PAM/graphite and CAC.

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