# Studies on the Removal of Dye Using Filled Polymeric FIPN Hydrogel

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***Abstract*- Water-soluble Polyvinyl alcohol (PVOH) was chemically modified by in situ copolymerization of acrylic acid (AA) and acrylamide (AM) in its aqueous solution and thus producing a copolymer of polyacrylicacid-co-acrylamide designated as (PAAM) as another one soluble polymer component in PVOH solution. Finally, both the polymers PVOH and PAAM were cross-linked by glutaraldehyde (2 mass%) andN,N 0-methylenebisacrylamide (MBA) as the cross-linking agents respectively to produce a full interpenetrating network (FIPN) hydrogel. Accordingly, three different compositions of hydrogels have been synthesized varying the percentage of PAAM containing PVOH:PAAM of 1:0.25, 1:0.5 and 1:0.75 as solid polymer basis. Out of these three, hydrogel containing PVOH:PAAM of 1:0.5 designated as PAAM50 found competitive for Malachite green dye separation by adsorption compared to other two. PAAM50 was further filled with treated saw dust as low-cost filler in situ, with the mass% of 2%, 5%, 8% and 10% (of total solid polymer) thus, designated as PAAM52, PAAM55, PAAM58,and PAAM510 respectively. Unfilled PAAM50 and four filled FIPN gels along with pure saw dust were used for separation of Malachite green (Dye) from its solution of 5 ppm, 10 ppm, 25 ppm, 50 ppm, 75 ppm and 100 ppm as feed concentrations and at five different pH (4, 7, 9, 10 & 11). Percent removal of dye was calculated from the absorbance data of UV-VIS Spectrophotometer. PAAM58 gel was found most efficient compared to others with a % removal of 98.039% at the conditions of 75 ppm feed concentration and at 9 pH. Desorption study was also performed taking adsorbed PAAM58 gels at different pH.**

***Keywords*—Hydrogel, FIPN, adsorption, dye removal, sawdust.**

## I. INTRODUCTION

Textile wet processing involves the use of a verity of chemicals comprising various classes of dyes and other chemicals. The wastewater stream from the textile dyeing operation, therefore, contains unutilized dyes along with a large amount of water. This also increases the risk of pollution as about 8-20% of the total pollution load is due to incomplete exhaustion of the dye [1]. It, therefore, becomes necessary to separate the dye from the effluent stream to utilize the unused dye and also reduce the risk of pollution.

A lot of research studies have been undertaken on the treatment of wastewater especially from the textile industries using polymeric membranes [2]. Reports on successful removal of heavy metals from wastewater using Semi-Interpenetrating Polymer Network (SIPN) have been made in recent times [3].

A gel is a colloidal or polymer network with a cross-linked system which exhibits no flow when in the steady state. By weight, gels are mostly liquid but they behave like solids due to a three-dimensional cross-linked network within the liquid. It is cross-linking within the fluid that gives the gel its structure and contributes to its adhesiveness. Gels can be classified into many types depending upon the dispersing medium, composition, and method of preparation. Hydrogels are one such category of gel [4]. Hydrogels are currently considered as water-insoluble, crosslinked, three-dimensional networks of polymer chains plus water that fills the voids between polymer chains. Crosslinking facilitates insolubility in water and provides required mechanical strength and physical integrity. The ability of the hydrogel to absorb water arises from hydrophilic functional groups attached to the polymer backbone while their resistance to dissolution arises from cross-links between network chains. Water inside the hydrogel allows free diffusion of some solute molecule while polymer serves as a matrix to hold water together. Hydrogels may exhibit drastic volume changes in response to specific external stimuli, such as the temperature, solvent quality, pH, electric field, etc. [4].

Polymeric hydrogel networks may be formed by various techniques, the most common synthetic route being the free radical cross-linking copolymerization of a hydrophilic non-ionic monomer such as acrylamide (AA) with a small amount of a cross-linker, e.g., N, N methylene-bis-acrylamide (MBA). In order to increase their swelling capacity, an ionic comonomer is also included in the reaction mixture. Since the monomers for hydrogel preparation are usually solid at the usual polymerization temperature, it is necessary to carry out the polymerization reactions in an aqueous solution [5]. Hydrogel structure and, thus, the hydrogel properties are closely related to the conditions under which the hydrogels are formed, i.e., the cross-linker concentration, the initial degree of dilution of the monomers and the chemistry of the units building the network structure. The understanding of the formation mechanism of hydrogels under various experimental conditions is of great interest to predict their physical properties [6].

This interest has led to research in the absorption properties of hydrogels made from poly-(acrylic acid-co-itaconic acid) [6] and gelatin-based hydrogels [7]. Previous studies show the removal of dyes like methylene blue from aqueous media using superabsorbent hydrogel [8] and Polymer Inclusion

Membranes or PIMs [9]. Removal of cobalt and copper ions by employing hydrogels have also been in popular research [10, 11].

The adsorption properties of the polymer gel can be enhanced by the addition of adsorbent filler into the polymer matrix. There have been recent studies on the use of agricultural waste material for adsorption of heavy metal ions from aqueous solutions [12]. Apart from such wastes, low-cost adsorbents have also been incorporated in the removal of metals like Cr (VI) [13].

Sawdust which is an example of a low-cost adsorbent has found a major role in the separation of metals ions from the wastewater [14, 15, 16]. Previous research also gives reports of successful separation of Malachite Green dye by using treated sawdust [17].

The current study employs experimental optimization of the polymer gel and filler (sawdust) composition to obtain the best results of the separation of the Malachite Green dye used. It also compares the results obtained for varying concentrations and pH of the Malachite Green dye solution and optimizes the pH for maximum utility of the gel. Also, desorption studies of the best performing gels were done to measure the extent of desorption of the gel as it is one of the major factors of the gel synthesis.

## II. EXPERIMENTAL

### *A. Materials:*

The monomers and cross-linker i.e. acrylic acid(AA), acrylamide (AM), N methylene-bis-acrylamide (NMBA) and glutaraldehyde, all synthesis grades were procured from S.D. fine chemicals, Mumbai and used as obtained. Ammonium persulfate and sodium meta-bisulfite were used as redox initiator pair for the copolymerization reaction. Polyvinyl alcohol (PVOH) of number average molecular mass 125,000 and hydrolysis of 98-99% was obtained from S.D. fine chemicals, Mumbai and used as obtained. The cross-linker Methylene-bis-acrylamide (MBA) for Poly (Acrylic acid –co-Acrylamide) was obtained from S.D. fine chemicals, Mumbai and used as obtained.Sawdust collected from local sawmill was used as the low-cost adsorbent. Before using it as filler, it was treated with Formalin solution for 72 hours to eliminate the lignin portion and to enhance its adsorption characteristics.

### *B. Preparation*:

*1) Gel Synthesis:* The PVOH solution was prepared by adding 13.75 gm of PVOH in 250 ml of water, confining the temperature of mixing in the range of 60-70$^0$C. Taking Acrylic acid and acrylamide in the mole ratio of 1:10, the mixture was added to 40 ml of the PVOH solution and considering it as the basis, three different weight ratios of PVOH: Poly-Acrylic acid–co-Acryl amide i.e. 1:0.25, 1:0.50, 1:0.75 were taken as shown in Table 1. After adding the redox initiators at 0.5 weight percent of total monomer and stirring at 60˚C for one hour, 0.88ml of Sulfuric acid, 0.6 ml of acetic acid & 0.2 ml of methanol were added [18]. Stabilizing the pH of the solution at 3.5 for better cross-linking, MBA solution equivalent to 2 weight percent of acrylamide and 0.4 ml of glutaraldehyde was added in the mixture and stirred till gel formation was complete [19]. The gel was cut into small pieces and kept in the oven for drying at 60˚C.

**TABLE I:** SYNTHESIS OF HYDROGEL WITH THREE DIFFERENT COMPOSITIONS

| *Poly (Ac. A –co-Ac.Am) as % of PVOH* | *Acrylic Acid + Acryl Amide (gm)* | *Acryl Amide (gm)* | *Acrylic Acid (gm)* | *MBA (2 weight % of Acrylamide) (gm)* | *Produced polymeric Gel* |
|---|---|---|---|---|---|
| 25% | 0.55 | 0.05 | 0.5 | 0.001 | (PAAM25) |
| 50% | 1.1 | 0.1 | 1.0 | 0.002 | (PAAM50) |
| 75% | 1.65 | 0.15 | 1.5 | 0.003 | (PAAM75) |

Basis: 2.2 gm PVOH / 40 ml PVOH solution

*2) Malachite green dye solution preparation:* Considering basis as 1gm in 1000ml equal to 1000ppm, a 50ppm solution of Malachite green was prepared by adding 0.0125 gm of Malachite Green in 200ml of water and 50ml of make-up water was added to form 250ml of the total solution thus maintaining pH at 7.

### *C. Selection of optimum gel composition*

*1) Optimization of the percentage composition of the prepared hydrogel:* Initial absorbance of feed solution was measured in U.V-VIS spectrophotometer (Shimadzu Analytical India Pvt. Ltd. Make) with pure water basis and the value at 614 nm = 2.308 A was taken as the standard. Four samples of 15ml each were taken adding equal amounts 1 gm of gel in each sample and allowed to equilibrate for 72 hrs. and from the absorbance values shown in Table 2, PAAM50 was found optimum as the best performing gel composition among the gel samples for further studies.

*2) Modification of the optimum hydrogel by sawdust filler:* From the U.V. absorbance studies, PAAM50 showed the highest separation efficiency and was selected for further research. Since sawdust filler can alter the surface property, the porosity of hydrogel and adsorption capacity [17], the selected sample was infused with four quantities of sawdust i.e. 2%, 5%, 8%, 10% for experimentation. These are named as PAAM52, PAAM54, PAAM58 & PAAM510 respectively. PAAM50 & pure filler were also taken for further studies along with these modified samples.

*3) Optimization of the filler composition:* Dye solutions of 10 ppm, 25 ppm, 50 ppm, 100 ppm were prepared and buffers were added to each solution to obtain the five pH values which are 4, 7, 9, 10 and 11. Pipetting out 10 ml of each of these solutions in test tubes, 1 gm. of each of these 5 gel samples were added into it separately. The absorbance values were reported after 72 hours.

**TABLE 2:** ABSORBANCE OF THE DYE SOLUTION AFTER ADSORPTION BY DIFFERENT COMPOSITION OF HYDROGELS

| *Gel composition* | *Gel amount (in gm)* | *Time for gel adsorption (hours)* | *Absorbance in U.V. Spectro-photometer* |
|---|---|---|---|
| **PURE PVOH** | 1.021 | 72 | 1.338 |
| **PAAM25** | 1.021 | 72 | 0.203 |
| **PAAM50** | 1.021 | 72 | **0.144** |
| **PAAM75** | 1.021 | 72 | 1.876 |

### *D. Gel Characterization*

#### *1) Gel Characterization by SEM:*

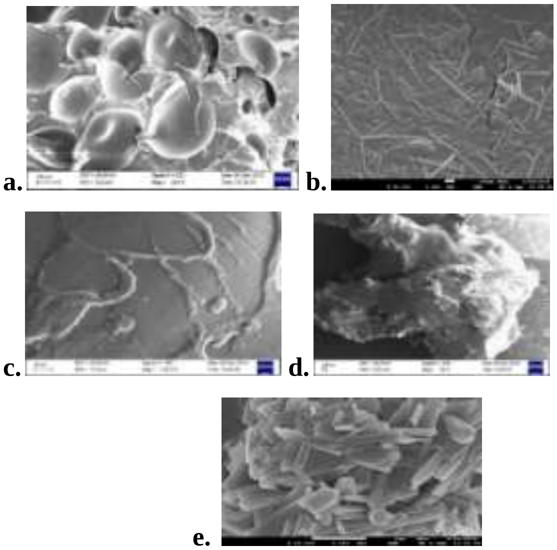


Figure 1: SEM of hydrogels: a) PAAM50 b) PAAM52

c) PAAM55 d) PAAM58 e) PAAM510

SEM studies of the unfilled PAAM50-Gel (50% Polymer-II) and the four filled FIPN-Gel i.e. PAAM52, PAAM55 PAAM58 and PAAM510 are shown in Fig. 1. a, b, c, d, and e, respectively. PAAM52, PAAM55, PAAM58, and PAAM510 are reinforced with the incorporation of 2%, 5%, 8%, and 10% concentrations of "Saw-Dust" respectively. The SEM image of a pure polymer like PVOH always gives a dense feature. IPN is different from a blend due to the interpenetration of the constituent polymers in the former hence making the extent of compatibility very high in an IPN [18]. Thus, much higher magnification is required (higher than those used for a conventional blend) for getting morphology of an IPN through SEM. Hence, SEM of the PAAM50 Gel was carried out at 14 KV in 5micron scale to get morphology of the constituent polymers. In an IPN the size and shape of the polymer II domains (i.e. Poly acrylic acid-co-acrylamide copolymer) are controlled by the cross-link density of polymer I (PVOH) and the relative proportions of the two polymers. The SEM of the filled IPN is shown at lower magnification (50 microns) to understand the distribution of fillers physically dispersed in the IPN matrix. The distribution of filler in the polymer matrix is understood from SEM of the filled polymeric gels. From Fig.1. b, c, d, and e, it is clear that with increasing filler loading distribution becomes more uniform and fig.1c i.e. SEM of PAAM55 gives a well-distributed morphology. However, as the PAAM58 & PAAM510 are loaded with more filler, filler-polymer compatibility becomes poorer and the morphology becomes coarser as seen in SEM of PAAM58 & PAAM510 containing 8% and 10 mass% filler in fig.1 d and e.

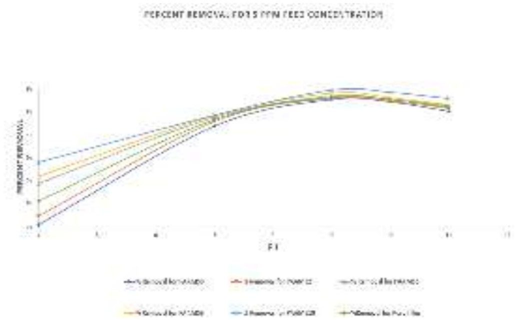
#### *2) Adsorption Experiment*

All of these five gels along with pure treated sawdust were also studied for batch adsorption experiment in 20 ml test tube taking 1 gm of each sample. Studies of adsorption were carried out with six different feed concentration of Malachite green dye solutions, i.e. 5 ppm, 10 ppm, 25 ppm, 50 ppm, 75 ppm and 100 ppm at five different pH, i.e. 4, 7, 9, 10 and 11 for each of the feed concentrations. Every experiment was repeated three times and the results were averaged to minimize error. The results for each adsorption experiment were reproducible and the errors inherent in the UV-absorbance were less than 3%.

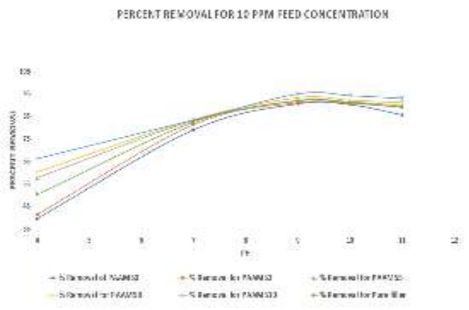
## III. RESULTS AND DISCUSSIONS

The plots of percentage removal of dyes from individual feed concentration at five different pH for all five gels and pure filler are shown below.

### A. *Percentage Removal with variable feed concentration at constant pH:*



a.



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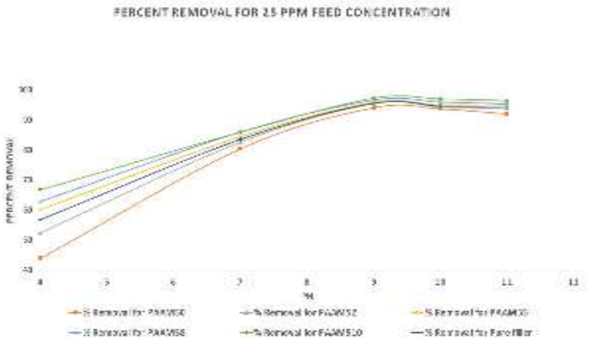

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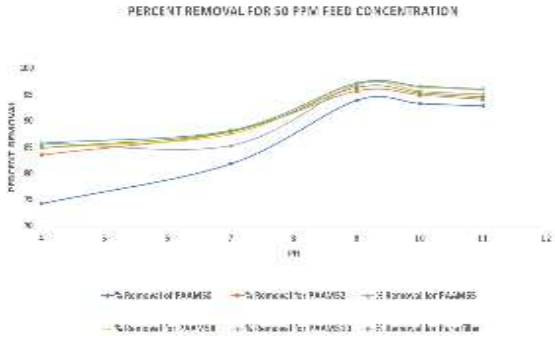
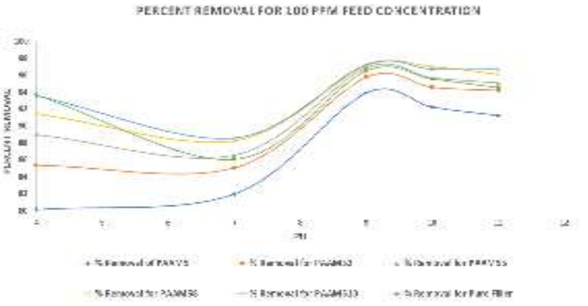
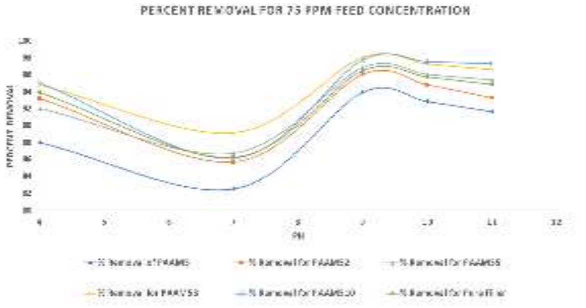


d.



e.

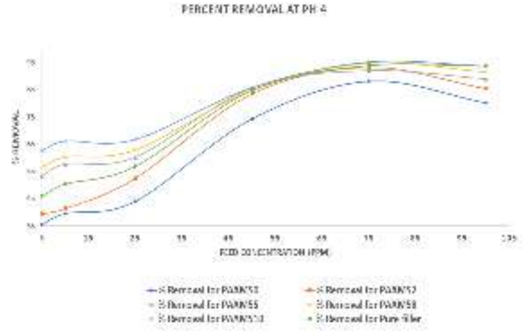


f.

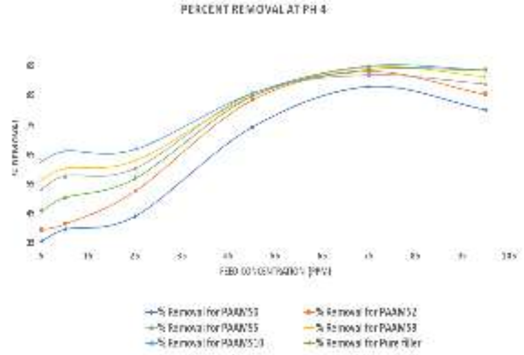
Figure 2: Percentage Removal variation a) At 5 PPMb) At 10 PPMc) At 25 PPM d) At 50 PPM e) At 75 PPM f) At 100 PPM

From the above curves, it has been seen that for lower feed concentration of the dye, the trend is similar and the % removal of dye increases with increasing pH. But in case of higher concentrations, a dip in the % removal is seen at neutral pH followed by an increase. This may be due to the fact that maximum adsorption was reached at this point and any disintegration caused would directly affect the surface area and hence the dye removal capacity of the gel. It has also been referred that with the concentration increase of the feed, adsorption increases which is consistent with the change in equilibrium as more cations are attracted towards the surface of the gel [20]. Also, almost all the curves have flattened after reaching a peak of Percent Removal which indicates saturation point of the IPN. This saturation is sensitive to pH as seen from the above graphs. The %Removal shown by the IPN is dependent not only on the pH of the dye and its feed concentration but also on the composition of the polymer itself. Reinforcing the IPN with a low-cost adsorbent like Sawdust gives better removal of the dye than what is achieved by the polymer or the filler alone. Effective separation comes after 2% inculcation of sawdust in the optimized synthetic hydrogel. This enhanced property due to reinforcement is known as coupling effect. The coupling effect is also pH sensitive.

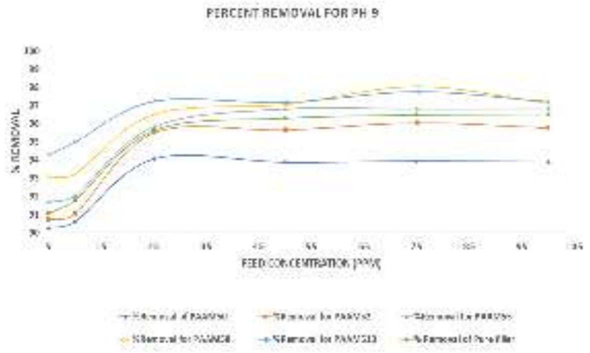
### *B. Percentage Removal with variable pH at constant feed concentration:*



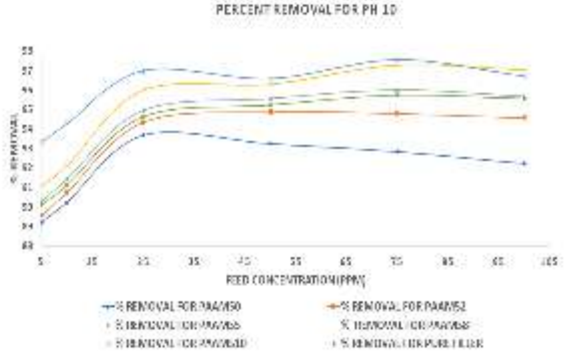
a.



b.



c.



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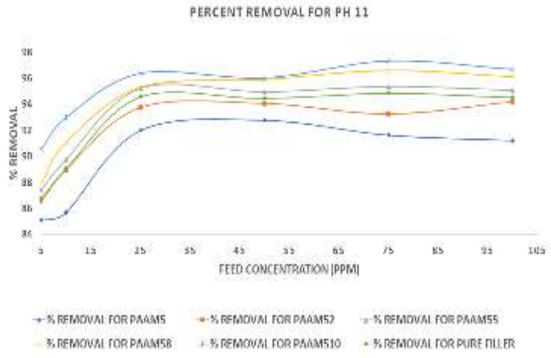
d.



e.

Figure 3: Percentage Removal variation a) At 4 pH b) At 7pH c) At 9 pH d) At 10 pH e) At 11pH

From the above curves, it has been observed that for acidic pH, there is an initial dip in the %removal before a gradual increase towards a peak. This may be due to the disintegration of the IPN in acidic medium. As the gel was prepared under acidic pH, exposing the same IPN under acidic conditions during adsorption makes inter-linking of bonds a susceptible phenomenon and the bonds that were activated during the gel formation, get activated again due to the pH conditions and take part in the degradation of the polymeric cross-linking.

It is observed that at low feed concentration, the % removal is least which is due to the fact that the adsorption was done in a batch process with no stirring and agitation. As a result, only a fraction of the volume of the dye is available for adsorption and hence only the dye in the vicinity of the gel is adsorbed. As mention earlier, the fact of equilibrium is also applicable here[19].

*C.*

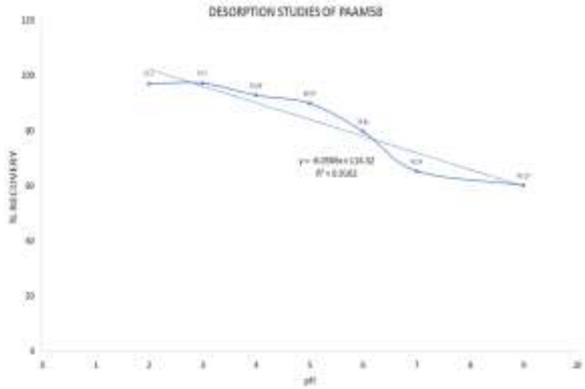


Figure 4: Percentage Recovery variation at different pH.

### *C. Optimum Gel:*

From Figures 2 and 3, it can be affirmed that the best results were shown by the PAAM50 gel sample at a feed concentration of 75 PPM with a filler concentration of 8 percent under pH 9 with 98.039 % removal of the dye.

### *D. Recovery Studies:*

For the sake of future research purposes and to ascertain the practicality of the experiment conducted, the studies on recovery of the dye from the gel is of high importance. The recovery studies give an insight on further developments required for large-scale applications. In this study, the best performing adsorbed gel from its best conditions was taken as the test sample. 8% filled adsorbed gel (PAAM58) from 75% feed solution at pH of 9 has been taken and allowed to put into demineralized water of different pH from 2 to 9. After allowing its equilibrium, the absorbance of the solutions was studied from UV- Spectrophotometer. The result reveals that percent recovery from the adsorbed gel was quite higher at acidic pH compared to basic pH. The highest recovery shown is 97.3 percent at pH 3. The nature of the graph of recovery is gradually decreasing from lower pH to higher pH more or less linearly and the regressed value of the graph is found quite satisfactory (R2 = 0.9162).

## IV. CONCLUSION

PVOH hydrogel was chemically modified by allowing copolymerization of acrylic acid and acrylamide with 10:1 comonomer ratio in the matrix of PVOH with mass ratios of

1:0.25:1:0.5, and 1:0.75 followed by crosslinking of copolymer with N,N-methylene bis acrylamide and crosslinking of PVOH with glutaraldehyde. These chemically modified full inter penetrating network (FIPN) type polymers designated as PAAM25, PAAM50 and PAAM75. Out of these three compositions, PAAM50 had shown best performance in dye removal from 50 ppm malachite green solution. It was then physically modified further by incorporating 2, 5, 8 and 10 mass% treated saw dust filler to produce four filled FIPN membranes designated as PAAM52, PAAM55, PAAM58 and PAAM510, FIPN505, and FIPN510. All the filled membranes showed higher percent of dye removal compared to unfilled gel and pure filler by adsorption. Among those FIPN gels, PAAM58 was found to show highest separation efficiency of 98.0.39% dye removal from 75 ppm malachite green solution at the pH of 9. The study of dye recovery from the highest adsorbed PAAM58 gel was performed by desorption at demineralized water of different pH and 97.3% dye recovery was observed at the condition of an acidic pH of 3, which was quite encouraging for its reuse and hence support economic feasibility too. This gel may be tried for the separation of other dyes as well as in the drug delivery system also.

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