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Polyacrylamide / Polyvinyl alcohol Hydrogel and its Calcium carbonate Nanocomposite as Adsorbents for Methylene Blue

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Abstract: In this work, two hydrogels were developed as cationic dye adsorbents. Polyacrylamide / Polyvinyl alcohol (PAM/PVA) composite matrix was prepared via in-situ polymerization reaction. Then, the obtained hydrogel was modified with 0.12 *wt.*% of calcium carbonate nanoparticles ($CaCO_3$), previously precipitated in a carbonate solution and modified with stearic acid, (PAM/PVA/$CaCO_3$). The prepared nano-particles were investigated with X-ray diffraction (XRD) and transmission electron microscope (TEM). Moreover, the obtained hydrogels were characterized with scanning electron microscope (SEM) and Fourier transform infrared (FTIR) compared with the incorporated carbonate nanoparticles. The results confirmed the successful preparation of PAM/PVA hydrogel and the efficient inclusion of $CaCO_3$ nanoparticles in the composite matrix. The removal of methylene blue with PAM/PVA was ~ 50 % using 2 gm after 60 min. at pH8. Meanwhile, one gram of PAM/PVA/$CaCO_3$ exhibited ~ 27 % at pH 2 and pH 12 after 30 min. which emphasized its capability to remove the dye in the acidic and the alkaline medium. No doubt, the developed hydrogels can be employed in the wastewater treatment.

keywords: Hydrogels; Calcium carbonate nanoparticles; Nanocomposites; Dye removal

1.Introduction

Dyes have a wide range of applications such as paper, painting, textiles, printing, and dyeing [1]. However, dyes are among serious water pollutants since they are toxic, nonbiodegradable, and cancer-causing compounds [2].

Several techniques have been utilized in order to remove dyes from the wastewater. For instance, precipitation, ion exchange, filtration, solvent extraction, flotation, ozonation, photocatalysis, evaporation, reverse osmosis, and electrochemical oxidation [3-7]. However, most of these techniques have many drawbacks in terms of process complexity, cost, quality of the treated water, and energy consumption [8]. So far, adsorption is one of the most promising strategies thanks to its simplicity, cost-effective, high efficiency and high capacity, and good regeneration ability [9]. Particularly, using adsorption technique, people all over the world have developed enormous adsorbents in order to remove cationic and anionic dyes from the wastewater [10-12].

Among the utilized adsorbents, hydrogels, commonly called super-adsorbents, are three 3D cross-linked polymers [13]. These compounds have high capability to decontaminate wastewater from the dissolved dyes [14]. Hydrogels enjoy good adsorption capacity, durability, less expensive, and operationality [15]. Basically, the polymeric gels can remove dyes from the wastewater via chemisorption, physisorption, ion exchange, hydrogen bonding, and complexation interactions [16]. Several hydrogels have been published in the removing of hazardous pollutants utilizing adsorption technique [15-20]. As one of the super-adsorbent hydrogels, polyacrylamide (PAM) has ionic functional groups favorable to adsorb the ionic dyes [21-23]. Moreover, polyvinyl alcohol (PVA) is a synthetic, a non-toxic, a high tensile strength, a flexible, and a biodegradable polymer [24]. PVA rich of -OH functional groups that can be chemically or physically interacted with other polymers like PAM [25, 26]. This will impart the biodegradation and enhance the properties of the composite matrix [26]. Also, the hydrogels can be improved by inclusion of fillers like metal and/or metal oxides [27-29].

Calcium carbonate is among the frequently used nanofillers for the polymers in order to obtain polymer nanocomposites [30]. This filler is relatively pure, non-hazardous, abundant, and fine powder [30]. In the field of water remediation, like most of metal and metallic oxides, $CaCO_3$ nanoparticles proved themselves in the removal of contaminants [31-33]. However, separation, reusing, and regeneration consider challenges because of its fine particles. Therefore, trapping of such fillers in the polymeric matrices represents among the possible ways to overcome their setbacks.

Accordingly, in the present work, PAM/PVA hydrogel was prepared and further modified with $CaCO_3$ nanoparticles as a filler. The obtained hydrogels along with the carbonate nanoparticles were characterized with electron microscopes (SEM/TEM) and Fourier transform infrared to confirm the successful tailoring of the proposed combinations. Finally, the prepared adsorbents were investigated in the removal of methylene blue in terms of pH, contact time, and adsorbent weight.

2. Experimental

2.1. Materials

Acrylamide (AAM, 99%) was bought from ALPHA CHEMIKA, India. N, N` methylene bis acrylamide (NNMBA) was purchased from Sisco Research Laboratories Pvt. Ltd. (SRL), India. Polyvinyl alcohol and sodium nitrate were obtained from Carl Roth &CO. Kg Karlsruhe, Germany, and Sd Fine-CHEM limited, India, respectively. Potassium per sulphate, calcium nitrate tetrahydrate, sodium carbonate, and sodium hydroxide were acquired from Sigma-Aldrich, St. Louis, USA.

2.2. Techniques

The chemical structure and the morphology of the prepared hydrogel and its nanocomposite were investigated using Fourier transform infrared (FTIR, Perkin Elmer, USA) and scanning electron microscope (SEM, JEOL-SEM-USA with an acceleration voltage of 80 kV), respectively. Particularly, calcium carbonate nanoparticles were confirmed with transmission electron microscope (TEM, JEOL JEM-1400, USA) and its modification was studied with FTIR. In addition, X-ray diffraction (Bruker D 8 advance target) was used as a powerful technique and a further confirmation analysis to investigate the obtained crystal phases for the prepared $CaCO_3$ nanoparticles.

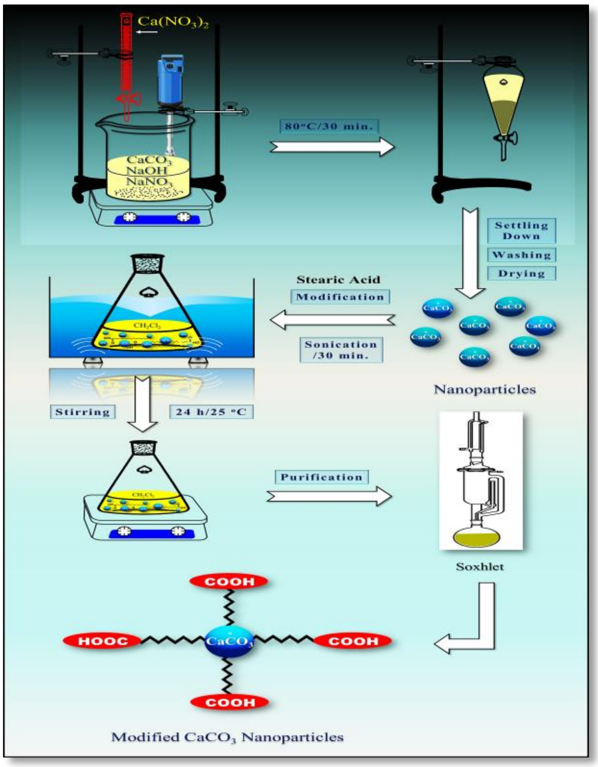
2.3. Preparation of Calcium carbonate Nanoparticles ($CaCO_3$)

In the typical method [34], an aqueous solution comprises sodium carbonate (0.1M), sodium hydroxide (0.2M), and sodium nitrate (0.18M) was prepared. The role of NaOH is to adjust pH required for the precipitation of carbonate nanoparticles. Meanwhile, $NaNO_3$ retards the dissolution of calcium nitrate via the common ion effect in the next steps. Besides, a solution of calcium nitrate (0.1 M) was formed. After that, the latter solution was added carefully drop by drop to the carbonate solution under the homogenization conditions (300 rpm), using Polytron 2100 homogenizer, for 30 min at 80 ^oC. Eventually, the mixture was left in a separatory funnel in order to settle down the formed nanoparticles. Then, the precipitate was collected, filtered out, and dried at room temperature (Scheme 1).

On the other hand, the obtained calcium carbonate nanoparticles were further modified with the long chains of stearic acid. Briefly, carbonate nanoparticles were mixed in a solution of stearic acid dissolved in a certain volume of methylene chloride. In a closed flask, the mixture was sonicated for 30 min and then kept under vigorous stirring at 25 ^oC. After 24 h, the solvent was vacuumed and collected in a vessel for a further using. For purification of the obtained modified nanoparticles, the remained powder, after getting rid of solvent, was further washed with CH_2Cl_2 in Soxhelt apparatus overnight till the stearic acid becomes un-detectable in the extract (Scheme 1). Then, the free-acid mixture was filtered out and the residue was washed several times with a mixture of ethanol / deionized water. Finally, the obtained modified calcium carbonate nanoparticles (white powder) were collected and vacuum dried overnight at 100 °C.

2.4. Preparation of Polyacrylamide/ Polyvinyl alcohol Composite Hydrogel

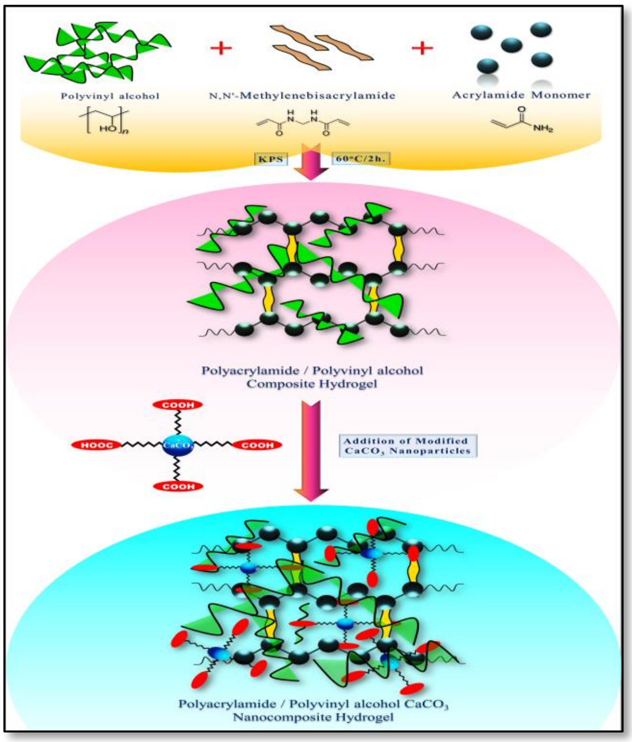
Poly acrylamide / polyvinyl alcohol hydrogel, PAM/PVA, was synthesized using free radical polymerization with N, N'-methylene bis-acrylamide as a crosslinker to create the interconnected porous structure of the hydrogel. Typically, 3 gm of PVA was dissolved in 100 ml of distilled water at 90°C for 2 h. Besides, another solution (100 mL) contains 12 gm acrylamide, 0.2 gm of NNMBA, and 0.2 gm of potassium per sulfate, as initiator, was prepared in a distilled water. Then, the two solutions were mixed and allowed to stir for 2 h till the formation of hydrogel (Scheme 2). Finally, the obtained composite PAM/PVA hydrogel was washed several times and dried at 60°C.



Scheme 1: Experimental representation for the synthesis and modification of $CaCO_3$ nanoparticles.

2.5. Preparation of Polyacrylamide / Polyvinyl alcohol / Calcium carbonate Nanocomposite Hydrogel

To synthesize PAM/PVA/$CaCO_3$ nanocomposite hydrogel, the same previous steps were tracked. However, the calcium carbonate nanoparticles (0.12 *wt.*%) were added after mixing of acrylamide and PVA solutions. Then, the mixture was well-sonicated and allowed to stir for 2 h till the formation of hydrogel (Scheme 2). Finally, the obtained nanocomposite PAM/PVA/$CaCO_3$ hydrogel was washed several times and dried at 60°C.



Scheme 2: Experimental description for the preparation of PAM/PVA and its nanocomposite hydrogel.

2.6. Adsorption Batch

A stock solution of 5 ppm methylene blue dye was prepared. In 150 mL beaker, 50 mL from the stock dye solution was mixed with a certain weight of prepared adsorbent. In each experiment, a sample was withdrawn and separated with the centrifuge at 10000 rpm for 5 min. Then, the concentration of the remained dye was determined by measuring of its intensity with UV-vis spectrophotometer (Shimadzu model spectrophotometer, UV-240IPC).

3. Results and Discussion

3.1. Morphological Study

Scanning electron microscope images were taken for the prepared PAM/PVA hydrogel, Fig.1[A]. Obviously, the structure of hydrogel is formed and no distinct differences between the two polymers can be detected. This confirms the successful incorporation of PAV in the PAM network. These findings are in agreement with the literature [35].

TEM image of $CaCO_3$ nanoparticles was inserted in Fig.1[A]. As shown, the nanoparticles have a semi spherical shape with different particle sizes which confirmed the successful synthesis of $CaCO_3$ nanoparticles [35]. Fig.1[B] shows SEM scenery of the obtained $CaCO_3$ nanoparticles after the incorporation in the PAM/PVA matrix. As depicted, the nanoparticles are well distributed (yellow arrows). However, some aggregations can be seen which might be attributed to the gel grains since these pictures were taken for the oven dried samples. Moreover, the result confirms that the structure of hydrogel was not changed even after the modification step.

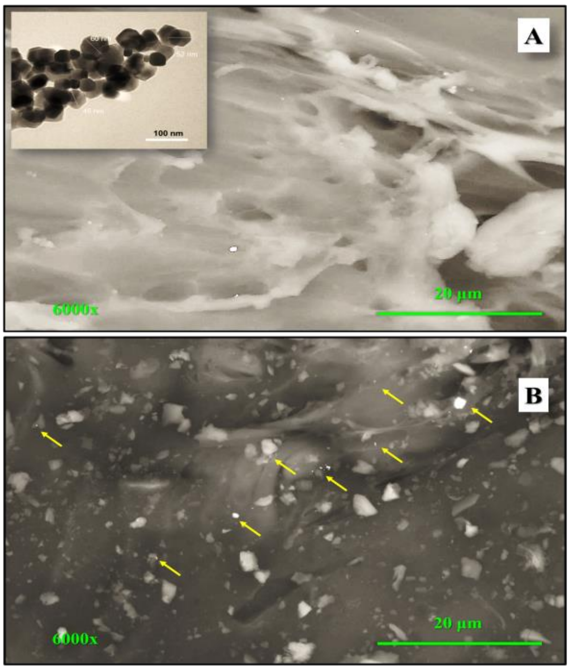


Figure 1: SEM of [A] PAM/PVA composite hydrogel, the inset image is the TEM micrograph of $CaCO_3$ nanoparticles, and [B] PAM/PVA/$CaCO_3$ nano composite hydrogel.

3.2. FTIR

Fig.2 displays FTIR spectra of calcium carbonate nanoparticles, PAM/PVA hydrogel, and their nanocomposite. The spectral analysis of $CaCO_3$ nanoparticles revealed absorption peaks at 713 and 878 cm^{-1} which correspond to the asymmetrical stretching vibration peaks of O-C-O. The adsorption bands at ~ 2929 and 3400 cm^{-1}, that correlate to the vibration mode of stearic acid C-H and -COOH functional groups, respectively [36].

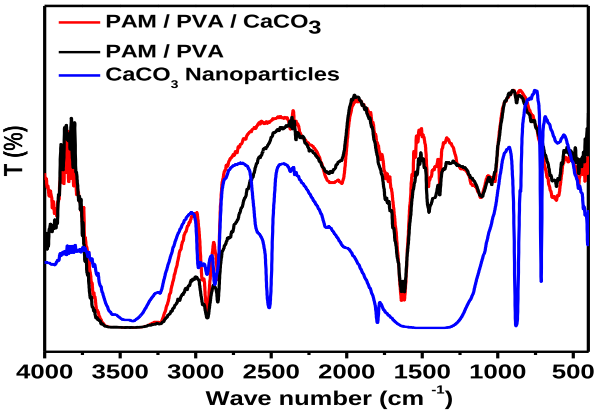


Figure 2: FTIR spectra of PAM/PVA, $CaCO_3$ nanoparticles, and their nanocomposite hydrogel**.**

Moreover, the PVA was added during the synthesis of PAM; therefore, most of their characteristic bands are overlapped. However, the pronounced absorption bands at 3447, 2921 and 2852, 1626, and 1109 cm^{-1} corresponding to NH- groups embedded under OH broad band, aliphatic CH, C=O, and C-N, respectively [35, 37]. However, it could be claimed that PAM and PVA are combined in an interpenetrating network via hydrogen bonding [38].

On the other hand, after the inclusion of $CaCO_3$ nanoparticles in the PAM/PVA matrix, the FTIR was performed in order to confirm the nature of interaction within the obtained nanocomposite, Fig2. However, comparing with the spectrum of PAM/PVA, one can observe a slight shift in the characteristic peaks of the pristine matrix with a changing in their intensities which might confirm the physical interaction in terms of hydrogen bonding between the polymers composing matrix and the incorporated nanoparticles (Scheme 3)

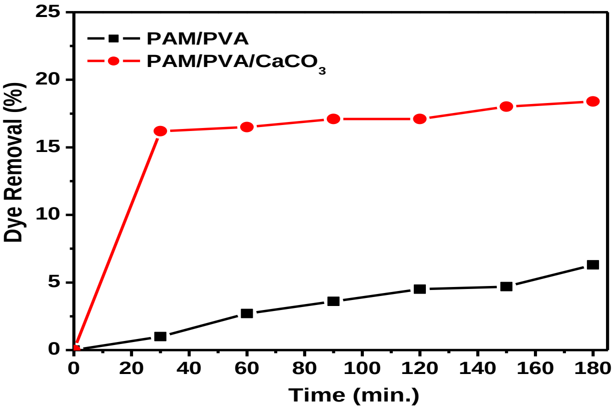
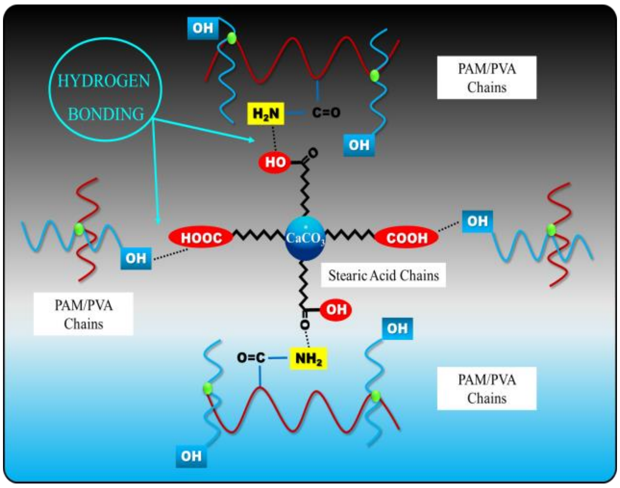


Figure 3: XRD spectrum of $CaCO_3$ nanoparticles.



Scheme 3: Illustration for the proposed interaction between PAM/PVA and $CaCO_3$ nanoparticles.

3.3. XRD

X-ray diffraction pattern of nano $CaCO_3$ is depicted in Fig. 3. The spectrum revealed the main diffraction peaks of the prepared particles. Particularly, the presented lines are totally matched with the standard diffraction patterns of calcite $CaCO_3$ (JCPDS card no. 47-1743) which emphasized the high crystallinity and the high purity of the obtained nanoparticles.

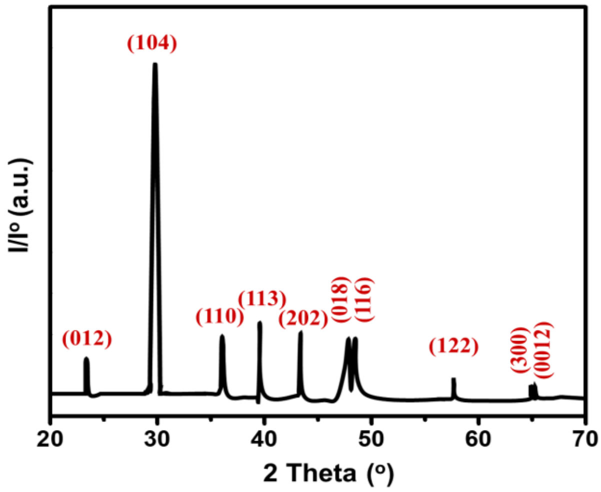


Figure 4: Effect of time on the removal of methylene blue dye over PAM/PVA and its nanocomposite hydrogel using 1 gm of adsorbent in 50 mL of 5 ppm dye concentration at normal pH and ambient temperature.

3.4. Methylene Blue Adsorption

The prepared PVA/PAM and its $CaCO_3$ nanocomposite hydrogel were investigated as adsorbents in the removal of methylene blue. The effect of the contact time, pH, and the catalyst weight were studied for the both adsorbents.

3.4.1 Effect of Contact Time

One gram of each prepared hydrogels was mixed separately in 50 mL of 5 ppm dye solution over 3 h at normal pH, Fig. 4. As shown, PAM/PVA has a quite limited adsorption of dye during the reaction time as the concentration of dye decreased hardly up only ~ 6 % after 180 min. On the other hand, the adsorption amounts of dye increased over the modified PAM/PVA matrix up to ~ 17 % after only 30 min., thanks to the presence of $CaCO_3$ nanoparticles. Moreover, the rate was very high at the beginning of the reaction compared with unmodified matrix. The same observations were recorded by Jahani et al., as they found in their research that the inclusion of calcium carbonate nanoparticles improved the adsorption capacity of the PVA hydrogel [39]. However, it is expected that the removal percentage would be increased by increasing the nanoparticles content. Particul- arly, by elapsing the time over 30 min., the removal increased hardly until reached ~ 18 % at the end of adsorption process.

Accordingly, it could be claimed that the adsorption over PAM/PVA/$CaCO_3$ nanocomposite hydrogel reached equilibrium after 30 min. and no further adsorption was observed which might be attributed to the un-availability of the active sites [40]. Thus, for the next experiments, 60 min. and 30 min. were chosen for PAM/PVA and PAM/PVA/$CaCO_3$ as an optimized contact time for each adsorbent, respectively.

3.4.2 Effect of Adsorbent Weight

The effect of adsorbent weight was investigated under the optimized time and the normal conditions as depicted in Fig. 5. Obviously, the weight of solid materials has an effect on the adsorption process. For unmodified PAM/PVA matrix, one gram was not enough to remove MB, the weight should be increased up to 3 gm to eliminate ~ 37 %. Meanwhile, one gram of PAM/PVA/$CaCO_3$ nanocomposite was sufficient to remove ~ 20 % and the removal percentage was further improved up to 27 % by increasing the weight due to increasing of the available active sites. These results are in accordance with the state of art [41-43].

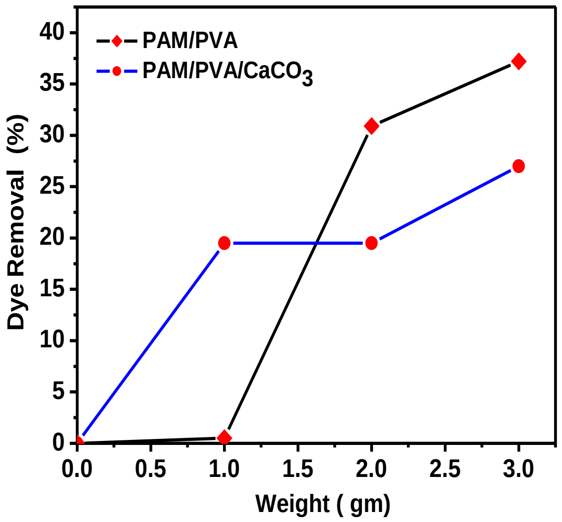


Figure 5: Effect of adsorbent catalyst weight in 50 mL of 5 ppm dye concentration at normal pH and ambient temperature over 60 min. and 30 min. for PAM/PVA and PAM/PVA/CaCO$_3$, respectively.

Particularly, it is observed that, at 2 gm and 3 gm of adsorbent weight, the pristine matrix showed a higher removal than the nanocomposite hydrogel which might be referred to the splitting effect of flux or the concentration gradient between the dye molecules and the adsorbent [44, 45]. However, the removal % did not show a drastic increase while using 2 gm or 3 gm of adsorbents. Therefore, based on the obtained results, 1 gm and 2 gm were selected as the optimized adsorbent weights for PAM/PVA/CaCO$_3$ and PAM/PVA, respectively.

3.4.3 Effect of pH

One of the most effective parameters of the dye adsorption process is the impact of pH. The initial pH values recorded for the adsorption systems contain PAM/PVA and PAM/PVA /CaCO$_3$ were 6 and 4, respectively.

As shown in Fig. 6, the removal of dye increases from the acidic to the alkaline medium containing PAM/PVA. The highest removal percentage (54 %) was recorded at pH 12. However, pH 8 was selected as the optimum pH for PAM/PVA adsorbent since the removal of dye at this pH (51 %) is close to that recorded at pH 12.

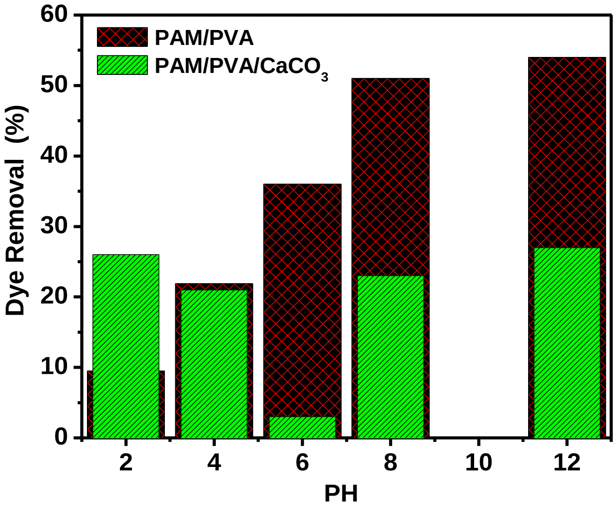


Figure 6: Effect of pH at the optimized adsorbents weight and contact time in 50 mL of 5 ppm dye concentration at the room temperature.

Moreover, the lowest removal was observed at the lower pH. Indeed, the surface oxygenated functional groups and the amide groups in PAM/PVA composite matrix are protonated in the strong acidic medium causing a repulsion with the cationic dye molecules and hence decreasing the dye adsorption [42]. On contrast, in the strong basic medium, the surface functional groups carry negative charges facilitating the adsorption of dye via the electrostatic interaction and hence the removal percentage increased [46].

On the other hand, in the presence of CaCO$_3$ nanoparticles, the behavior was significantly changed. The dye removal increased in highly acidic and highly alkaline solutions with a limited adsorption at almost neutral conditions. This might be attributed to the pH sensitivity of calcium carbonate nanoparticles; as it has a strong applicability in the drug delivery [47]. Also, it is worth to mention that, pH of the mixture was adjusted with hydrochloric acid and sodium hydroxide. Particularly, calcium carbonate can react with these reagents to produce calcium chloride and calcium hydroxide, respectively. Calcium chloride might cause cross-linking for PVA polymer chains [48] in the PAM/PVA composite matrix and hence the functional groups occupied in the hydrogen bonding, between the two polymers, became free (c.f. section 3.2). This might lead to improve the adsorption of dye. Oppositely, in the alkaline medium, calcium hydroxide is formed and the dye molecules can be adsorbed electrostatically on its surface thanks to the plenty of negative charges [49].

4. Conclusion

PAM/PVA composite hydrogel was prepared via in-situ polymerization of acrylamide monomer in the presence of NNMBA as a cross-linker and potassium per sulphate as an initiator. The morphology of the obtained hydrogel was confirmed with SEM. Also, the chemical structure analysis using FTIR showed the effective combination of the two polymers in the interpenetrating network via hydrogen bonding. Calcium carbonate nanoparticles was precipitated in a carbonate solution and further modified with stearic acid. TEM displayed the prepared nanoparticles have a semi-spherical shape and FTIR depicted the successful stearic acid treatment. The obtained nanoparticles were well-dispersed in PAM /PVA matrix due to a strong physical interaction as emphasized with SEM and FTIR in order to eventually produce PAM/PVA /$CaCO_3$ nanocomposite hydrogel. Upon investigating in the methylene blue removal, the results exhibited that PAM/PVA has a limited adsorption of dye at a little weight and in a short time as well as in the acidic medium. Therefore, the optimum conditions for PAM/PVA were found 60 min. contact time, 2 gm adsorbent weight, and pH 8 to achieve ~ 51 % removal of dye. On the other hand, PAM/PVA/$CaCO_3$ showed a good performance in the both acidic and alkaline media in a short contact time consuming a little amount. Thus, the operating conditions were recorded as 30 min. contact time, 1 gm adsorbent weight, and pH 2 or pH 12. Under these conditions, PAM/PVA/$CaCO_3$ displayed ~ 27 % removal of dye thanks to the presence of $CaCO_3$ nanoparticles. Indeed, it is expected that, by increasing the nanoparticles content, the removal percentage of dye would be improved which would be taken in the account in the future studies. Finally, it could be claimed that, the obtained hydrogels deem promising and effective adsorbents for water decolorization applications.

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