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SONOCHEMICAL SYNTHESIS OF POLYACRYLICACID-NANO$CaCO_3$ NANOCOMPOSITE FOR THE ADSORPTION OF RHODAMINE-B DYE

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ABSTRACT

Synthesis of Polyacrylic acid- Nano$CaCO_3$ (PAANC) nanocomposite has been done by using Polyacrylic acid and nano$CaCO_3$ under ultrasound irradiations. The characterization of nanocomposite was done by using XRD, SEM, and FTIR analysis. The nanocomposite was used for adsorption studies of Rhodamine-B dye. The effects of various parameters such as pH, loading, initial concentration have been studied. The results were compared with the results obtained with nano$CaCO_3$ as adsorbent. It was found that PAANC nanocomposite exhibited higher percentage removal of dye (49%) than nano$CaCO_3$.The adsorption data has been correlated using Langmuir and Freundlich models. Freundlich isotherm model was found to be the best fit as compared to Langmuir isotherm model in the entire range of concentration for the adsorption data obtained on the PAANC nanocomposite.

Keywords: Adsorption, Nanocomposite, PAANC, Rhodamine-B, Sonochemical Synthesis.

I. INTRODUCTION

Chemical Industries like Textile, Printing, Cosmetic and Food are major sources of colored organic effluent [1]. The organic effluent contains high percentage of dyes. The dye from waste water brings serious threats to human health due to their toxic or mutagenic and carcinogenic nature [2]. Removal of dye is important challenge in area of waste water treatment.

Rhodamine-B is basic and xanthenes group dye [3,4]. It is widely used in processes such as, paper dyeing, production of dye laser etc., and also as a coloring agent in manufacture of textile and food stuff. Rhodamine-B is highly carcinogenic and harmful to human beings and animals. It causes irritation to the skin, eyes and respiratory track [5]. The exposure of this dye also affects the reproducibility and neurotoxicity widely [6,7,8]. Removal of dye from waste water is essential to save human health, aquatic life and the environment.

Chemical precipitation, reverse osmosis, electrochemical technique, ion exchange, membrane filtration, coagulation, extraction and adsorption are the traditional techniques used for the removal of contaminants [9]. Among these,

adsorption is the conventional, effective, economical and important separation process used for the removal of dye [10,11,12].

Polymer nanocomposites were effectively applied as adsorbent for the removal of organic pollutants from waste water using adsorption process [13]. PAA-Nanoclay, Chitosan-g-PAA/ Montomorillonite [2], Poly (AAm-co-AAc)/NaAnanocomposites [14], nanoclay filled composite hydrogel of PAA [15] were utilized for removal of various dye. PAA have carboxylic groups that have the ability to trap cationic dye [16]. $CaCO_3$ nanoparticles are insoluble in water. They are used in plastic, paint, paper, medicine and food products. These nanoparticles are easy to synthesize and comparatively cheaper than other nanoparticles [17].

As per our knowledge, the study of Rhodamine-B dye adsorption using PAANC nanocomposite was not reported in the literature. The basic objective of the study is synthesis of PAANC nanocomposite for the adsorption of Rhodamine-B dye. Equilibrium studies for adsorption and effect of various parameters such as pH, loading, concentration of dye were also verified.

II. EXPERIMENTAL

2.1 Chemicals

The chemicals used in this Experiment are AR grade and brought from reputed companies. Calcium Hydroxide and Polyacrylic acid was brought from High Purity Laboratory Chemicals Private Limited, Mumbai-400002. Rhodamine-B (> = 95% pure HPLC) was procured from Sigma Life Science. Buffer Capsules were brought from Merck Specialist Private Limited.

2.2 Sonochemical Synthesis of PAA-Nano$CaCO_3$ Nanocomposite

Synthesis of nan$CaCO_3$ was carried out using Calcium Hydroxide and CO_2 gas under ultrasound [18].The PAANC nanocomposite was synthesized under ultrasound using nano$CaCO_3$ particles as per following procedure. 5 grams of nano$CaCO_3$ nanoparticles were dispersed in 100 ml of distilled water and sonicated for 10 minutes at 25-30 ^{0}C temperature. Buffer solution of pH = 4 was also added to the same flask with 100 grams of PAA (40% aqueous) and sonicated continuously for 30 minutes at 4^{0}C. The resulting sticky mass was centrifuged and dried at 60 ^{0}C. The dried PAANC was then used for adsorption study. The procedure for synthesis of nanocomposites is represented as follows:

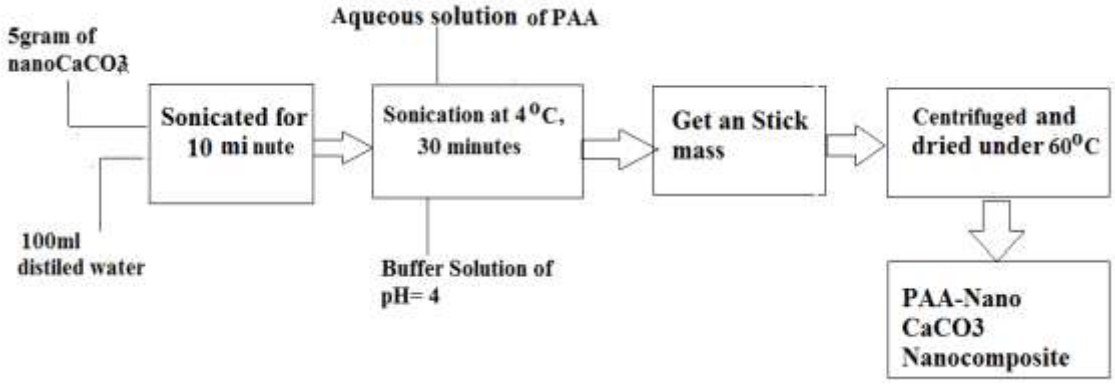


Fig. 1: Representation of Sonochemical Synthesis of PAANC Nanocomposite.

2.3 Characterization of NanoCaCO$_3$ and the PAA-NanoCaCO$_3$ Nanocomposite

XRD diffraction patterns for nanoCaCO$_3$ and PAANC was determined by X-ray diffractometer (Aolong Y-200C). FTIR spectra were recorded on Perkin Elmer FTIR Spectrometer (RAYLEIGH WQF-520A) in the range 3500–500 cm^{-1}. The surface morphology of the PAANC was determined by scanning electron microscope (JEOL, Tokyo, Japan). The concentration of Rhodamine-B was determined by UV-Spectrophotometer (Lab India Analytical UV-3000$^+$ model). Distilled water was used as reference in the UV-Spectrophotometer. The maximum wavelength for the absorbance of Rhodamine –B dye was found to be 552 nm. The pH meter was used to study the effect of pH on adsorption.

2.4 Adsorption Study

Batch study for the adsorption of dye was carried out in 200 ml beaker. A 100 ml aqueous solution of desired concentration of dye was taken in 200 ml flask. The reaction was carried out on the magnetic stirrer with 250 rpm and 303 K temperature with 0.5 gram of PAANC. The reaction time was 80 minutes to get the desired adsorption equilibrium. Each experiment was repeated to overcome the experimental error, and it was found lower than 2 %.

The adsorption study was carried out at different concentration of PAANC ranging from 0.5-2grams at constant temperature and pH value of 8. The effect of initial dye concentration on adsorption was studied by varying the initial dye concentration from 100-500 mg/l. The effect of change in the pH value on adsorption of dye was also studied. The percentage removal of dye was calculated by the following formula:

Percentage Removal= $(C_0 - C)/(C_0) * 100$ (1)

Where, C_0 = Initial Concentration of dye solution (100mg/l)

C = Final Concentration of dye Solution

The amount of dye adsorbed per mg of adsorbent is given as follows,

$q = (C_0 - C_e) * V/M$ (2)

Where, q= Amount of dye adsorbed per mg of adsorbent (mg/g)

C_0 = Initial Concentration (mg/l)

C_e= Equilibrium concentration of solution (mg/l)

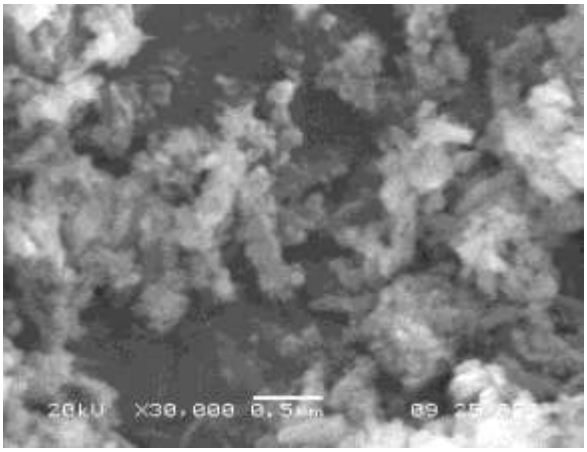
V = Volume of dye solution (L)

M = Mass of adsorbent used. (g)

III. RESULTS AND DISCUSSION

3.1 Characterization of Nanoparticles and Nanocomposite

Fig. 2 shows the SEM image for nanoCaCO$_3$ and PAANC. It gives the surface morphology for the nanoparticles. According to SEM results, the nanoparticles are cubic in shape [19]. Fig. 2 (b) gives the SEM image for the PAANC which shows that the nanocomposite particle is spherical in shape.



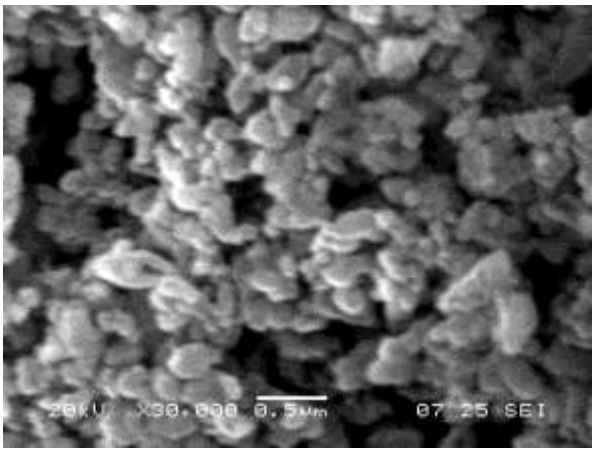
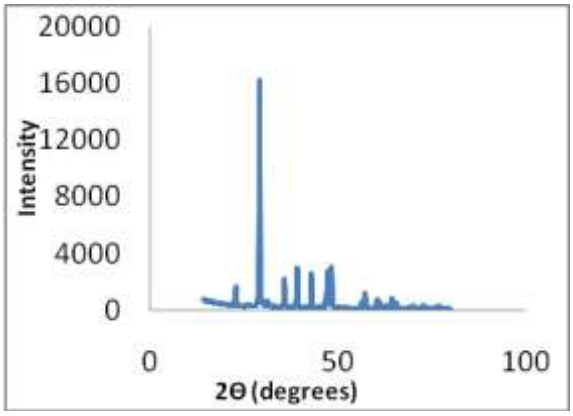


Fig. 2: (a) SEM Image for nano$CaCO_3$ Nanoparticles (b) SEM Image for PAANC Nanocomposite

The X-Ray diffraction for nanoparticles and nanocomposite is given in Fig. 3. This pattern gave the phase present and composition in the nanoparticles and nanocomposites. The Bragg Reflection peak gave the presence of calcite and small amount of aragonite in nanoparticles in Fig. 3(a). The particle size of nanoparticles is around 8 nm calculated by Scherrer's formula [20]. Fig. 3(b) shows the peak for the presence of PAANC nanocomposite.



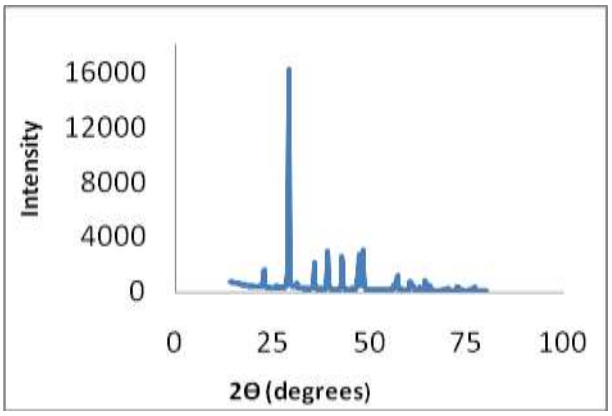


Fig. 3: (a) XRD for Nano$CaCO_3$ (b) XRD for Nanocomposite

FTIR for nanoparticles and nanocomposite are given in the Fig. 4. The FTIR for nanoparticles show spectrum around the wavelength of 3500-500 Cm^{-1}. The spectrum shows the absorbance peak around 872 cm^{-1} which indicates the presence of calcite. The presence of aragonite is shown by 702 cm^{-1} peak [15]. Fig. 4(b) shows the FTIR spectrum for nanocomposites. The presence of PAA in films was confirmed by the presence of C-O-H bending belonging to pendant group (COOH) of PAA at 1412 cm^{-1}[21].

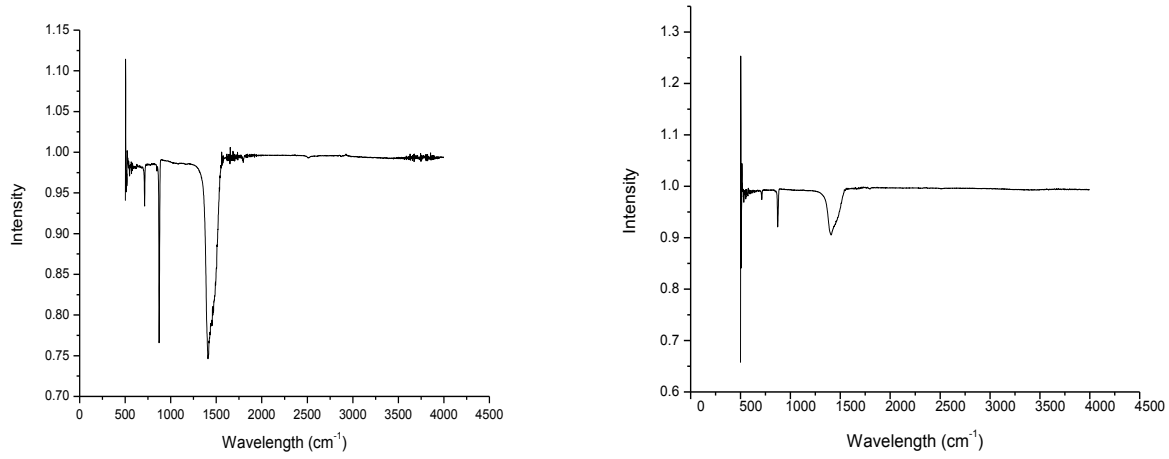


Fig. 4: (a) FTIR for Nanoparticles **(b) FTIR for Nanocomposite**

3.2 Effect of pH on the Adsorption of Dye

PAANC nanocomposite contains different functional groups like carbonyl and carboxyl. These groups present in nanocomposite affect the pH of the solution. It also affects the Rhodamine-B dye solution. Hence, the study of the effect of pH is important for the adsorption of dye. The experiment was carried out at different pH values ranging from 6 to 10 at constant temperature 303 K. The percentage removal of Rhodamine-B dye at different pH values is shown in the Fig. 5.The results show that at pH value of 6, the percentage removal was about 40% and this percentage reduced at the pH value of 7. At neutral pH, there was lower percentage removal as compared to other pH values. Percentage removal was increased at pH 8 and 9, and was found in the range of 45-48%. The optimum value of pH at which maximum removal of dye took place was 8.

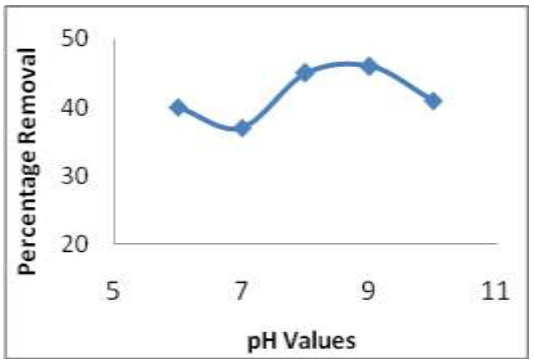
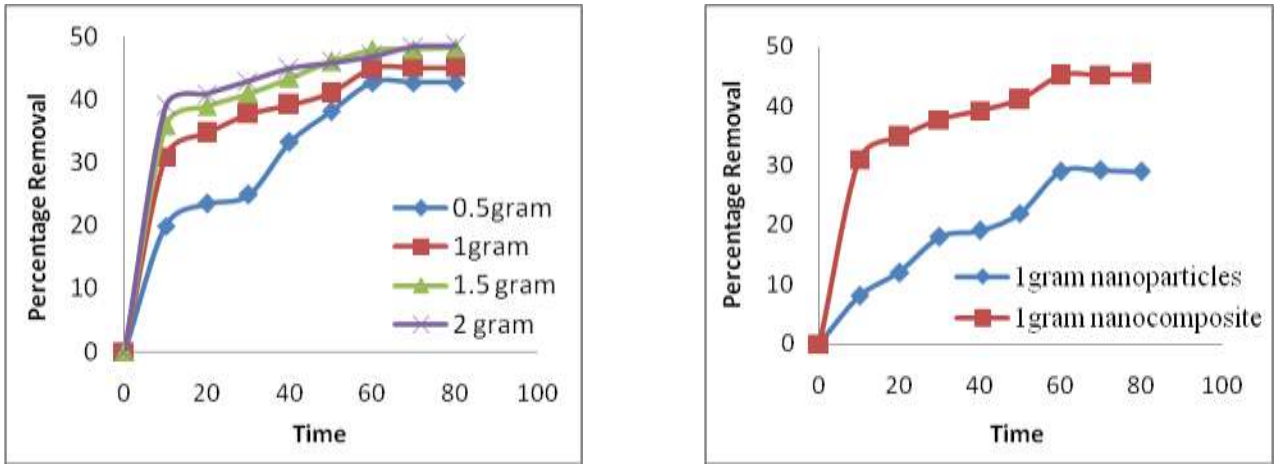


Fig. 5: Effect of pH on the Equilibrium Adsorption of Rhodamine-B on Nanocomposite

3.3 Effect of Different Loading of PAA-Nano$CaCO_3$ Nanocomposite

The effect of different concentration of PAA-Nano$CaCO_3$ on the adsorption of Rhodamine-B dye was studied. The result for percentage removal of dye V/S time was shown in the Fig. 6 (a). The result shows that adsorption increases with time and with nanocomposites loading. The experiment was done for 80 minutes and the adsorption equilibrium

was attained in 60-70 minutes. For this condition the nanoparticles gave adsorption (29%) lesser than that of nanocomposites (49%), which is shown in Fig. 6 (b).



(a) **(b)**

Fig. 6: (a) Effect of Concentration of PAANC at 30^{0}C and pH=8 with an initial concentration of dye solution C_o = 100mg/l. (b) Comparative study of nanoparticles and PAANC nanocomposite as adsorbent.

3.4 Effect of Initial Concentration of Dye

Fig. 7 shows the effect of initial concentration of dye solution on adsorption process. The experiment was performed with 1 gram nanocomposites at different initial concentration of dye solution, in the range of 100-500 mg/l. The duration of batch cycle was kept as 80 minutes, and pH was maintained at 8. The result show that concentration decreases with time for first 50 minutes, then equilibrium is attained in 60-80 minutes. The percentage removal of dye decreases with increase in initial dye concentration.

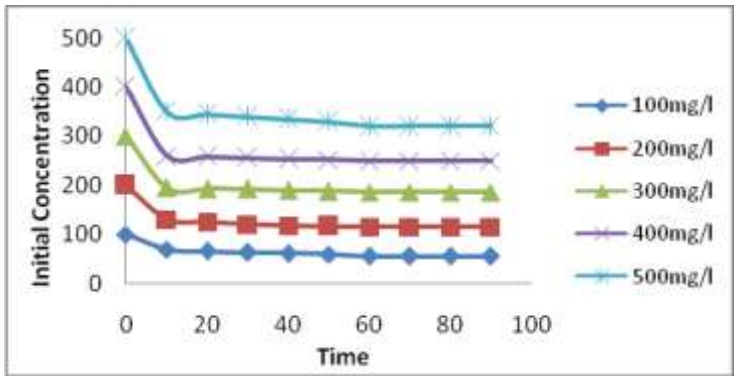


Fig. 7: The effect of Initial Concentration of Rhodamine-B on Equilibrium Adsorption (pH=8, Weight of Nanocomposite= 1gram, Temperature=30 ^{O}C)

3.5 Adsorption Isotherm

Adsorption isotherms are used to study the adsorption properties and the equilibrium data, which provide the empirical equations. These equations give the interaction between adsorbate and adsorbent surfaces. Generally two models,

namely, Langmuir and Freundlich are used to study the adsorption isotherm. The empirical equations for these models are given in equation (3) and (4) respectively.

Langmuir Equation

$$\frac{Ce}{q} = \frac{1}{qo} * K_l + \frac{Ce}{qo} \quad (3)$$

Freundlich Equation

$$lnq = K_f + \frac{1}{n} * lnCe \quad (4)$$

The values of slope and intercept were calculated by plotting the graph C_e v/s C_e/q, as shown in Fig. 8 and the graph between ln C_e and ln q shown in Fig. 9 for Langmuir and Freundlich isotherm model respectively. The values for the same are shown in Table 1. Freundlich isotherm fits the data very well as compared to the Langmuir isotherm. This was decided from the value of "$R^{2"}$, which is close to 1 for Freundlich isotherm model.

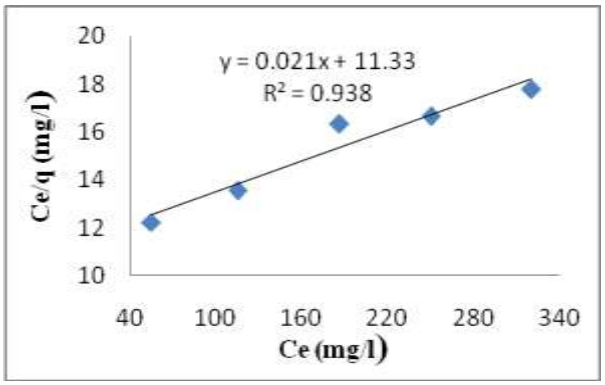


Fig. 8: Langmuir Adsorption Isotherm

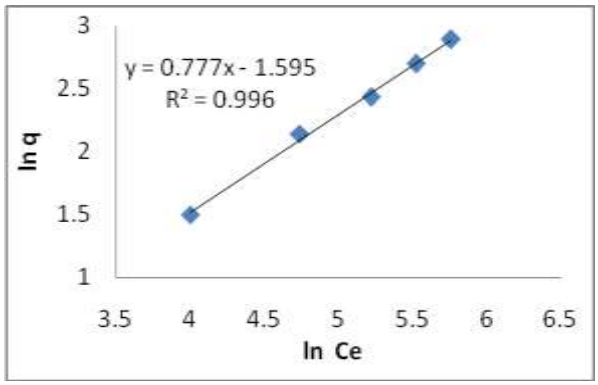


Fig. 9: Freundlich Adsorption Isotherm

Table 1: Parameters of Langmuir and Freundlich Isotherm Model

Model	Intercept	Slope	Correlation Coefficient
Langmuir Isotherm	1/qo* K_l = 11.33	1/qo = 0.021	R^2= 0.938
Freundlich Isotherm	K_f = 1.595	1/n = 0.777	R^2= 0.996

IV. CONCLUSION

Using a combination of Polyacrylic acid and nano$CaCO_3$, a new polymer nanocomposite was synthesized via ultrasound route. The formation of nanocomposite was confirmed by FTIR and XRD. The comparative study was done using PAA-nano$CaCO_3$ and nano$CaCO_3$ for the effective adsorption of Rhodamine-B dye. The PAANC is effective nanocomposite for the removal of dye as compare to nano$CaCO_3$.The result show that the percentage removal of dye was higher by using PAANC nanocomposite than nano$CaCO_3$.The percentage removal increases with the increase in time, catalyst loading and pH. The equilibrium of adsorption was attained near to the 60minute.Freundlichisotherm fits the equilibrium data very well as compare to Langmuir adsorption Isotherm.

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