

INVESTIGATIONS ON TEXTILE DYE ADSORPTION ONTO HYDROXYAPATITE-ALGINATE NANOCOMPOSITE PREPARED BY A MODIFIED METHOD

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Two major factors of concern when preparing adsorbents for textile dye removal are their cost and regeneration ability. Hydroxyapatite is an inorganic bioceramic material, which shows efficient adsorption towards various pollutants. Alginate is also an efficient biosorbent due to the presence of carboxylate functional groups along its chains. In the present study, hydroxyapatite/alginate nanocomposite adsorbent has been prepared by a cost effective method to combine the high specific surface area of nanomaterial with the stability of a polymer matrix towards dye adsorption. Adsorption experiments were conducted by the batch method; equilibrium and kinetics studies were carried out and the results are discussed.

Keywords: hydroxyapatite, alginate, adsorption

INTRODUCTION

Textile industry effluents are rich in dye components and their removal is mandatory before disposal into the environment. Adsorption has been identified as the easiest and most efficient approach to eliminate the dyes from textile effluents,¹ cost effective, regenerable and efficient adsorbents have been searched for a long time. Among the various adsorbents studied, polymeric adsorbents exhibit feasibility of regeneration under mild conditions, along with other merits such as mechanical rigidity, adjustable surface chemistry, pore size distribution etc.^{2,3} Inorganic hydroxyapatite (HA), a calcium phosphate phase with Ca/P of 1.67, is well known for its adsorption ability.⁴⁻⁶ Nanosized materials show greater adsorption affinity for soluble dyes due to their increased specific surface area, but the use of ultrafine particles for adsorption causes troubles in the stages of effective regeneration and reuse. The nanoparticles immobilized in the polymer matrix reduce the problem of size effects on regeneration.² Alginate is an efficient polymeric biosorbent due to the presence of carboxylate functional groups along its chains.

The two common procedures used for the preparation of polymer/ceramic composites are

the mechanical mixing method and the *in situ* method. In the first method, ceramic particles are prepared separately and mixed with the polymeric support, but the problem in this case is the inhomogeneous dispersion of nanoparticles in the polymer matrix. In the *in situ* method of preparation of the hydroxyapatite–alginate composite, the disadvantage is the inhibition of crystal growth of the inorganic phase HA by alginate.⁷ In the present work, a modified approach is used to prepare the ceramic (hydroxyapatite)–polymer (alginate) composite and its adsorption ability is studied.

EXPERIMENTAL

Chemicals

Calcium nitrate tetrahydrate [$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$], diammonium hydrogen phosphate [$(\text{NH}_4)_2\text{HPO}_4$] and ammonia solution [NH_4OH] were used as starting materials. All reagents used for the experiments were obtained from Merck and used without further purification. Sodium alginate was obtained from Loba Chemie, India, reactive dye was obtained from the textile industry and distilled water was used as solvent.

Synthesis

Solutions of 1 M of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and 0.6 M of $(\text{NH}_4)_2\text{HPO}_4$ were separately brought to a pH above 10, using NH_4OH solution.

The calcium solution was stirred vigorously and the phosphate solution was added into it dropwise to form a gelatinous white precipitate. After 2 h of vigorous stirring, the precipitate was mixed with 2% sodium alginate solution in different volume ratios of 1:1, 1:3 and 1:5. Then the mixture was added dropwise to 0.1 M of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ bath through a needle, using a hypodermic syringe under mild stirring and left for 24 hours for the completion of crosslinking. Of all the compositions studied, the one with the ratio 1:5 formed a stable bead, hence it was used for further investigation (HA/AL). Plain calcium alginate beads (AL) were also prepared for comparison and both types of wet beads were used as adsorbents for the removal of textile reactive dyes.

Dye adsorption studies were conducted by batch experiments with reactive blue 21 (Phthalocyanine class) textile dye as a model dye, at the initial concentration of 50 mg/L, to which the adsorbent (200, 400, 600, 800 and 1000 wet beads) was added. The rate of dye adsorption onto the plain and composite beads was studied for various time intervals at room temperature.

Characterization

The X-ray diffraction (XRD) pattern was obtained using a RIGAKU MINI FLEX II diffractometer in the range $20^\circ \leq 2\theta \leq 60^\circ$ with $\text{Cu K}\alpha$ radiation. The FT-IR spectrum was recorded in the region $4000\text{--}400\text{ cm}^{-1}$ using a Perkin Elmer FT-IR spectrometer by the KBr pellet technique. The morphology of the synthesized samples was examined using a Zeiss Ultraplus scanning electron microscope. The change in the dye concentration was measured by monitoring the absorbance at λ_{max} value, using a Perkin Elmer-Lambda 35 UV-Vis spectrophotometer.

Adsorption isotherm modeling

Isotherm modeling was performed in the light of the most common Langmuir and Freundlich isotherm models in order to get insight into the adsorption mechanism, surface properties and affinity of adsorbent towards the dye molecules.

Langmuir isotherm model

This empirical model assumes monolayer adsorption with the assumption that adsorption can only occur at a finite number of definite localized sites that are identical and equivalent. Also, it assumes that there is no lateral interaction and steric hindrance between the adsorbed molecules even on adjacent sites.⁸ The non-linear form of the Langmuir model is given by:

$$q_e = \frac{q_m K_a c_e}{1 + K_a c_e}$$

The Langmuir constants q_e (mg/g) and K_a (L/mg) represent the adsorption capacity and the energy of adsorption, respectively.

Freundlich isotherm model

Freundlich isotherm model can be applied to multilayer-adsorption, with non-uniform distribution of adsorption heat and affinities over the heterogeneous surface. This model describes the non-ideal and reversible adsorption, which is not restricted to the formation of monolayer. The non-linear form of the Freundlich isotherm model is given by:

$$q_e = K_F C_e^{\frac{1}{n}}$$

where K_F (mg/g) $(\text{L/mg})^{1/n}$ is the Freundlich constant, which indicates the adsorption capacity of the adsorbent and n is a Freundlich exponent related to the intensity of adsorption.

Adsorption kinetics modeling

The rate at which the dye is removed from the aqueous solution will be an important parameter in designing an efficient treatment method based on the adsorption process. In the present study, pseudo-first-order and pseudo-second-order kinetic models have been used to investigate the kinetics involved in the present process.

Pseudo-first-order kinetic model

The pseudo-first-order model can be represented by the Lagergren's expression as:

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303} t$$

The above equation describes the adsorption rate based on adsorption capacity; q_e (mg/g) and q_t (mg/g) represent the amount of dye adsorbed at equilibrium and at various time intervals t , respectively; K_1 (min^{-1}) is the equilibrium rate constant of pseudo-first-order sorption.

Pseudo-second-order kinetic model

The adsorption kinetics may be described by the pseudo-second-order model, which is given by:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t$$

where K_2 ($\text{min}^{-1} \text{g/mg}$) is the second order rate constant of sorption, which is used to calculate the initial sorption rate. This method depends on the amount of dye adsorbed on the surface of adsorbent and the quantity adsorbed at equilibrium.

RESULTS AND DISCUSSION

XRD

The XRD pattern of plain beads indicates the amorphous nature of the polymer beads, while the diffraction peaks observed for the composite beads belong to the hexagonal phase hydroxyapatite (JCPDS File No. 09-0432) (Figure 1). The broad diffraction peaks indicate the low crystalline nature of the apatite mineral and the observed diffraction peaks can be indexed to the (002), (211), (112), (310), (222), (213), (004)

planes of hydroxyapatite. The average crystallite size of HA mineral was calculated to be 27 nm, using the Debye–Scherrer formula.

FT-IR

The FT-IR spectra of AL and AL/HA are given in Figure 2, and their spectral assignments are given in Table 1. Composite beads show the characteristic PO_4^{3-} (ν_4) vibrational bands at 563 cm^{-1} and 603 cm^{-1} , along with (ν_3) bending mode around 1032 cm^{-1} . The bands at 873 cm^{-1} and 1425 cm^{-1} indicate the formation of carbonated apatite. For both plain and composite beads, the peak at 818 cm^{-1} indicates the combination of three possible vibrational modes ($\tau\text{CO} + \delta\text{CCO} + \delta\text{CCH}$) of calcium alginate and the peaks at 1425 cm^{-1} and 1608 cm^{-1} are ascribed to the symmetric and asymmetric stretching vibrations of the COO^-

group of alginate.⁷ The broad band extending from 2500 cm^{-1} to 3600 cm^{-1} indicates the O-H stretching vibration of H_2O molecule. The absence of ν_1 and ν_2 stretching vibrational modes and the broad nature of the ν_3 mode of PO_4^{3-} in the case of composite beads indicate the interaction of the polymer matrix with the apatite mineral.

SEM

Figure 3 shows the SEM images of AL and HA/AL samples. An interconnected network like morphology is observed in the case of plain alginate beads, whereas in the composite beads the surface morphology indicates blending of the nanocrystalline apatite mineral with the polymer matrix.

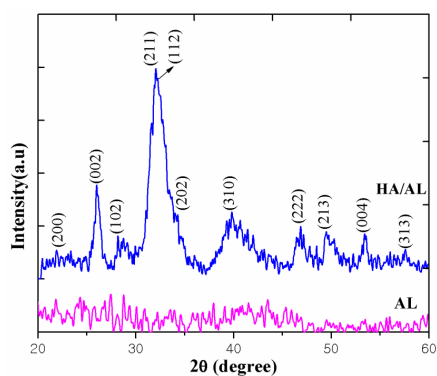


Figure 1: XRD pattern of AL and HA/AL

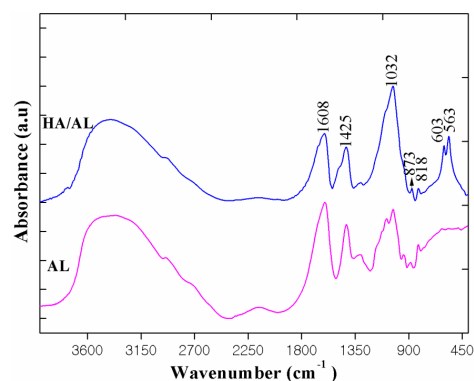


Figure 2: FT-IR spectra of AL and HA/AL

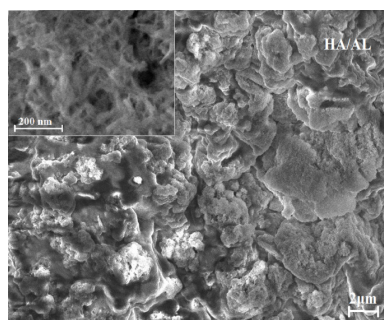
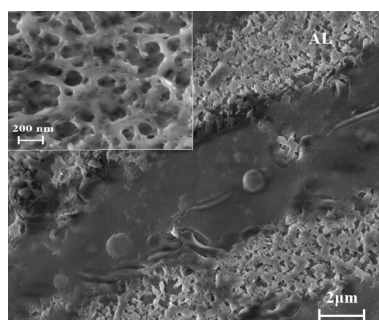


Figure 3: SEM images of AL and HA/AL

Table 1
FT-IR spectral assignments for samples AL and AL/HA

| Sample | Vibrational modes (cm^{-1}) | | | | |
|--------|--|--------------------|-----------|---|--------------------|
| | PO_4^{3-} | CO_3^{2-} | H-O-H | ($\tau\text{CO} + \delta\text{CCO} + \delta\text{CCH}$) | (COO^-) |
| AL | - | - | 2500-3600 | 818 | 1425, 1608 |
| HA/AL | 1032, 563 and 603 | 873, 1425 | 2500-3600 | 818 | 1425, 1608 |

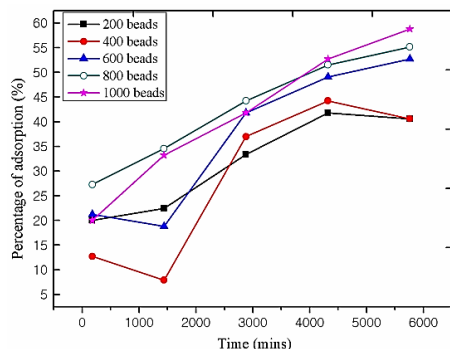


Figure 4: Percentage of adsorption as a function of time for different adsorbent dosages of composite beads

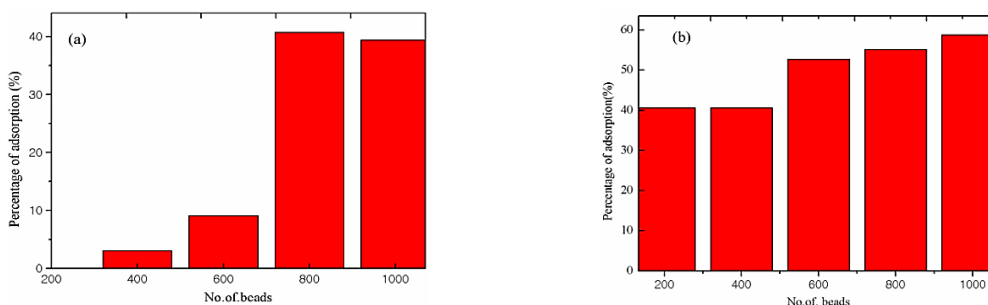


Figure 5: Percentage of adsorption vs adsorbent dosage for (a) AL and (b) HA/AL

Adsorption studies

The amount of dye adsorbed on the adsorbents q_e (mg/g) was calculated using the mass balance equation:

$$q_e = \frac{(C_0 - C_e)V}{W}$$

where C_0 and C_e are the initial and equilibrium concentration (mg/L), V is the volume of solution (L), and W is the weight of the adsorbent (g). The dye removal efficiency of the adsorbent was calculated by the equation:

$$\text{Percentage removal (\%)} = 100 \times (C_0 - C_e) / C_0$$

Figure 4 shows the process of adsorption with contact time for different adsorbent dosages. The adsorption of dye increased with the increase in adsorbent dosage and the maximum dosage percentages of dye removed at equilibrium by

plain and composite beads were 40 and 60, respectively (Figure 5).

Equilibrium analysis for the dye adsorption process was carried out using the non-linear form of Langmuir and Freundlich isotherm models, in which the Langmuir model showed a better fit to the experimental data, suggesting monolayer adsorption of dye on adsorbents. The kinetic studies carried out using the pseudo-first and -second-order models revealed that the pseudo-second-order model exhibited the best fit to the experimental data with a higher correlation coefficient value. The isotherm and kinetic model constants and correlation coefficients are given in Table 2.

Table 2
Isotherm and kinetic model constants and correlation coefficient

| Adsorbent | Langmuir isotherm | | | Pseudo-second-order kinetics | | | |
|-----------|-------------------|--------------|-------|------------------------------|--------------------|---------|-------|
| | q_m (mg/g) | k_a (L/mg) | R^2 | q_e (mg/g) (cal) | q_e (mg/g) (exp) | k_2 | R^2 |
| AL | 0.0173 | 8.945E-5 | 0.271 | 0.1390 | 0.1378 | 47.192 | 0.998 |
| HA/AL | 0.1672 | 0.0281 | 0.894 | 0.3276 | 0.2598 | 2013.04 | 0.987 |

In order to achieve enhanced adsorption of dye, composites with 1:2 and 2:5 ratios were analysed qualitatively. Complete dye removal was observed in 24 hours, but the beads were not intact in that case.

CONCLUSION

Reactive blue dye adsorption studies were carried out using plain and composite beads. The results of the study revealed that the composite beads had a better dye adsorption capacity.

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