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Original Research Paper

Characterization and Synthesis of Chitosan-Silica Gel and Chitosan-Bentonite Composites for Adsorption of Heavy Metals

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ABSTRACT

There are several ways to curtail the cost of wastewater treatment. This desire was fuelled in the current study of different composites prepared with modified chitosan by immobilization onto bentonite and silica gel and their characterization by using different sensitive techniques such as FTIR, SEM-EDS and TGA. The assessment of synthesized composites was done for its suitability as bioadsorbent characteristics. Silica gel chitosan composite showed peaks at 1082 cm^{-1}, 1316 cm^{-1} 3420 cm^{-1} and at 3614 cm^{-1}. While, bentonite chitosan composite reveals major peak 1572 cm^{-1}, 3648 cm^{-1}, 3462 cm^{-1}, 1650 cm^{-1} and 1001cm^{-1}. SEM-EDS study showed their morphology, element composition that correlates the adsorption efficiency. However, TGA study showed their detailed study on thermal stability as more thermally stable compound which is the characteristic feature for adsorption and desorption phenomenon.

INTRODUCTION

Water is an essential, natural, inexorable, life-sustaining commodity for mankind in day to day life. But nowadays this essence is becoming inaccessible due to overwhelming water pollution as a consequence of accelerated industrial and urban growth. There are several factors influencing the water quality based on its usage. Therefore, polluted water needs a proper treatment for its recycle and reuse (Shankhwar et al. 2015a). The system overall is input intensive (Jeet et al. 2014). Heavy metal ions, including copper, cadmium, nickel, zinc, chromium, mercury and lead ions, do harm to environment and human health even at relatively low concentrations due to the fact that they can be accumulated and transferred into organisms by the food chain (Feng et al. 2005, Monier et al. 2013, Huang et al. 2008). Adsorption phenomenon is one of the promising methods for the removal of heavy metals. Hence, it is one of the most prominent clean-up technologies and described as, any system where a sorbate (e.g. an atom, molecule, and a molecular ion) interacts with a sorbent (i.e. a solid surface). It results in accumulation at the sorbate-sorbent interface (Gandhi et al. 2013).

Chitosan is immensely used as an adsorbent nowadays for the removal of organic and inorganic pollutants from wastewaters because it has excellent properties such as hydrophilicity, non-toxicity, abundance, biocompatibility and biodegradability (Gandhi et al. 2013). It can be obtained by deacetylation of chitin and widely used as an efficient adsorbent for the removal of metal ions. Chitosan has its certain limitations, when used as an adsorbent solely. Hence, it is immobilized or cross linked with other materials, such as presence of amino, acetamide and hydroxyl functional groups with chitosan act as active sites for adsorption (Futalan et al. 2011). It is the most suitable biopolymer for the removal of various heavy metals from industrial and commercial wastewater, because it possesses high amino and hydroxyl functional group content. Moreover, silica gel acts as a very good adsorbent for removal of heavy metal ions because it displays excellent chemical stability even at highly acidic conditions, although its surface contains high chemical reactivity due to the existence of silanol groups (Si-OH) (Timin et al. 2014).

Nowadays, technology involved in wastewater treatment uses innovative, efficient and advanced methods. However, these need to be economically viable, especially in the rural part of India in order to support wastewater treatment and reuses (Shankhwar et al. 2015b). In this reference, bentonite proved to be a promising immobilization material for chitosan as it is vastly available, cheap and it posses both chemical and mechanical stability. It is a very efficient immobilization material for chitosan because it has low cost as well as chemically and mechanically stable. On the other hand, modified chitosan composites exhibit very high adsorption capacity and resistance to acidic environment (Saravanan et al. 2013). In this study, both of these two different composites were formed successfully by different immobilization processes and their characterization was

done with relevant sophisticated techniques like SEM-EDS, FTIR and TGA for further study.

MATERIALS AND METHODS

Materials and methods: The chitosan flakes having a low molecular weight with 75%-85% degree of deacetylation, was obtained from molychel. Silica gel, bentonite, glacial acetic acid, glutaaldehyde was purchased from Himedia and all the chemicals which were used of analytical reagent grade. Matrex Scientific Instruments electric oven was used for drying of both the SGCs composite and bentonite chitosan composite respectively.

Synthesis of SGCs composite: Silica gel beads were heated at 110°C for half an hour to activate the surface. 20 g of silica was immersed in 30 mL of distilled water to make slurry. 4 g of chitosan dissolved in (2%v/v) acetic acid aqueous solution and stirred for 1 hour. This solution was added to the slurry and the mixture was stirred for 30 minutes. 5% glutaraldehyde aqueous solution at a 40:1 volume ratio of chitosan solution was added and stirred vigorously for 5 minutes. The mixture was stirred for 2 hours and soaked in ultra sonic bath for 30 minutes. The wet bed mixture was transferred to a refrigerator at 4°C for 24 hours to undergo complete cross linking reaction and washed to neutral pH and dried in oven at 50°C (Gandhi et al. 2012).

Preparation of chitosan immobilized on bentonite: About 5 g of chitosan was dissolved in 300 mL of 5% (v/v) HCl in a magnetic plate by stirring the solution for 2 hours at 300 rpm. Bentonite (100 g) was slowly added into the solution and was stirred for another 3 hours. The solution was added with 1N NaOH in a drop wise method until neutralization is reached. The adsorbent was washed with deionized water, dried in the oven at 65°C for 24 hours, pulverized, and sieved (Futalan et al. 2011).

Instrumental studies for characterization: FTIR spectra of the samples were recorded with BRUKER-ALPHA 200 model. The results obtained from the FTIR analysis used to depict the functional groups present in the sorbent in sorption of the metal ions. The surface morphology of the sorbent under study determined by the SEM images measured using SEM-BRUKER Model No. JEOL JSM-6610LV fitted with an EDS which allows the detection and weight percentage of elements present in adsorbent. TGA study of the two composites were done with EXSTAR TG/DTA 6300 model which showed DTA/DTG/TG characteristics of the composites respectively.

RESULTS AND DISCUSSION

FTIR Analysis

In the FTIR analysis of the Silica gel chitosan composite shown in Fig. 1 (A). The strong peaks were found between 1082 cm^{-1} and 1316 cm^{-1} due to Si-O-Si bond. Major peaks of chitosan at 3420 cm^{-1} and 3614 cm^{-1} due to OH and NH_2 . It was observed that in case of bentonite chitosan composite shown in Fig. 1(B) major peak found at 1572 cm^{-1} is assigned to the bending vibration of amine chitosan. The main bands of bentonite chitosan were 3648 cm^{-1}, attributed to the OH stretching, 3462 cm^{-1} and 1650 cm^{-1} assigned to OH deformation vibration and 1001 cm^{-1} assigned to Si-O stretching vibration (Liu et al. 2015).

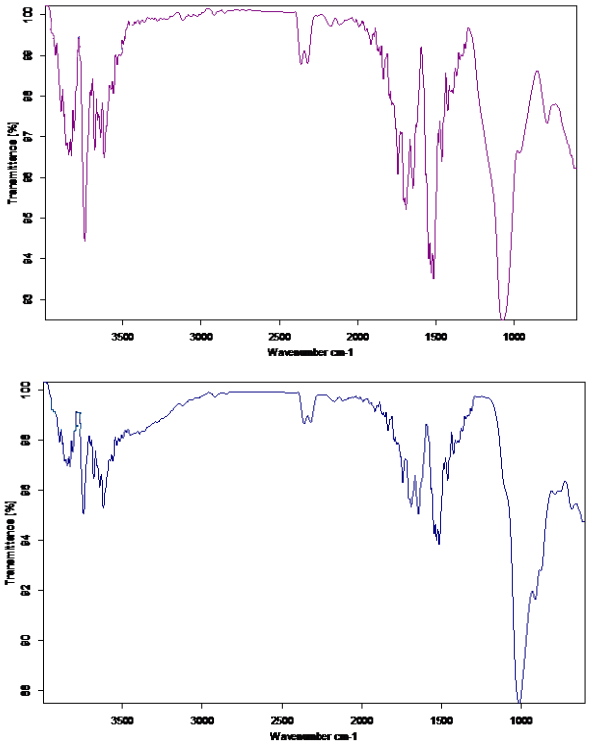

Fig. 1: FTIR spectra of (A) Silica gel chitosan, (B) Bentonite chitosan composites.

SEM-EDS Analysis

Silica gel chitosan composite: The morphology of SGC composite showed that the surface of this composite is highly rough with cracks and pores. The EDS study showed that SGC composite contain O, Si and C in the modified composite and the wt % is mentioned in Fig. 2(A).

Bentonite chitosan composite: The morphological image of bentonite chitosan composite was visualized using SEM. Fig. 2(B) shows highly rigid and undulated structure with compact crystals of natural bentonite. The EDS spectra of the bentonite chitosan composite depicts the presence of O, Si, Al, C, Fe, Ti, Mg and Na and the quantity of composition of elements also listed in the Fig. 2(B).

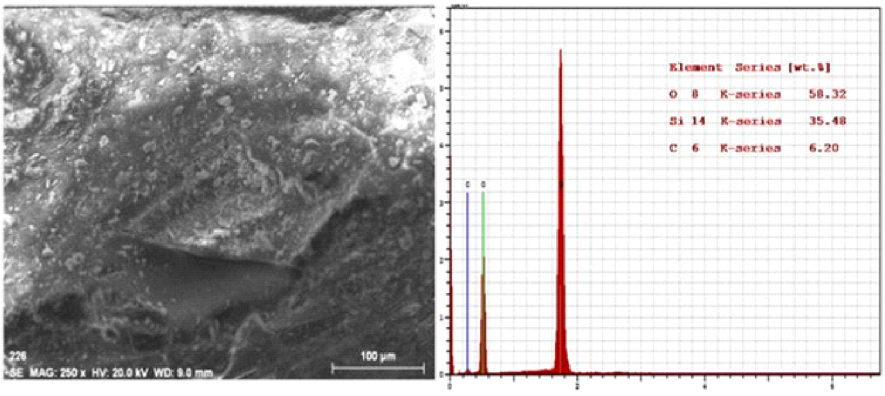

Fig. 2 (A): SEM-EDS images of Silica gel chitosan composites.

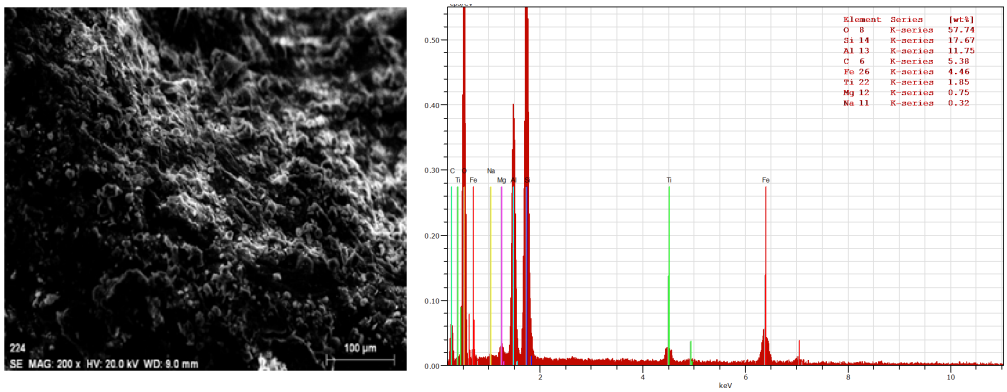

Fig.2(B): SEM-EDS images of Bentonite chitosan composites.

TGA Analysis

The thermal stability of the samples was recorded on EXSTAR TG/DTA 6300. The TGA/DTG/DTA curves of silica gel chitosan composite and bentonite chitosan composite demonstrate a similar behaviour in thermal stability (Fig. 3). Both the samples demonstrate three stages of the weight losses to be due to the evaporation of water adhered on the surfaces (dehydration), dehydroxylation (that is, release of -OH group) between the layers associated with the loss of crystal structure of the sample. In the first stage, the sample starts losing weight at ambient temperature (30°C) and sharp losses in mass goes on till 110°C associated with a loss in mass of about 10%. Then the sample remains stable up to 220°C. The second loss in mass was observed in the temperature range of 223-424°C and associated % mass loss is about 17 % w.r.t. initial wt. The third loss in mass was observed in the temperature range of 424 - 660°C and associated % mass loss is about 20% w.r.t. initial wt. Thereafter, both the samples become thermally stable showing no further loss in mass. The DTG peaks corresponding to the above changes were observed at (for first/second samples) 73/81°C, 261/277°C and 465/471°C. DTA analysis of the samples (for first/second samples) show endothermic peaks at 74/86°C, 198/207°C and 375/356°C due to the dehydration, dehydroxylation (release of OH group from octahedral sites) and loss of crystal structure. In the second sample, slight exothermic behaviour was also observed at 753°C which might occur due to recrystalization of the sample. In the second sample DTG peak has been shifted from 73 to 86 due to enhanced cross linking in comparison to first, due to the inherent nature of Glutaraldehyde and hence observed as thermally more stable.

CONCLUSION

In nutshell, the characterization via different techniques of both the different immobilized composites revealed the strong peaks between 1082 cm^{-1} and 1316 cm^{-1} due to Si-O-Si bond. Moreover, the major peaks of chitosan at 3420 cm^{-1} and 3614 cm^{-1}. In case of bentonite chitosan composite, major peaks were obtained at 1572 cm^{-1}, main bands of bentonite chitosan at 3648 cm^{-1}, 3462 cm^{-1}, 1650 cm^{-1} and 1001 cm^{-1} respectively. Hence, SEM-EDS study showed that SGC composite is highly rough with cracks and pores, the morphology of bentonite appeared to be highly rigid and undu-

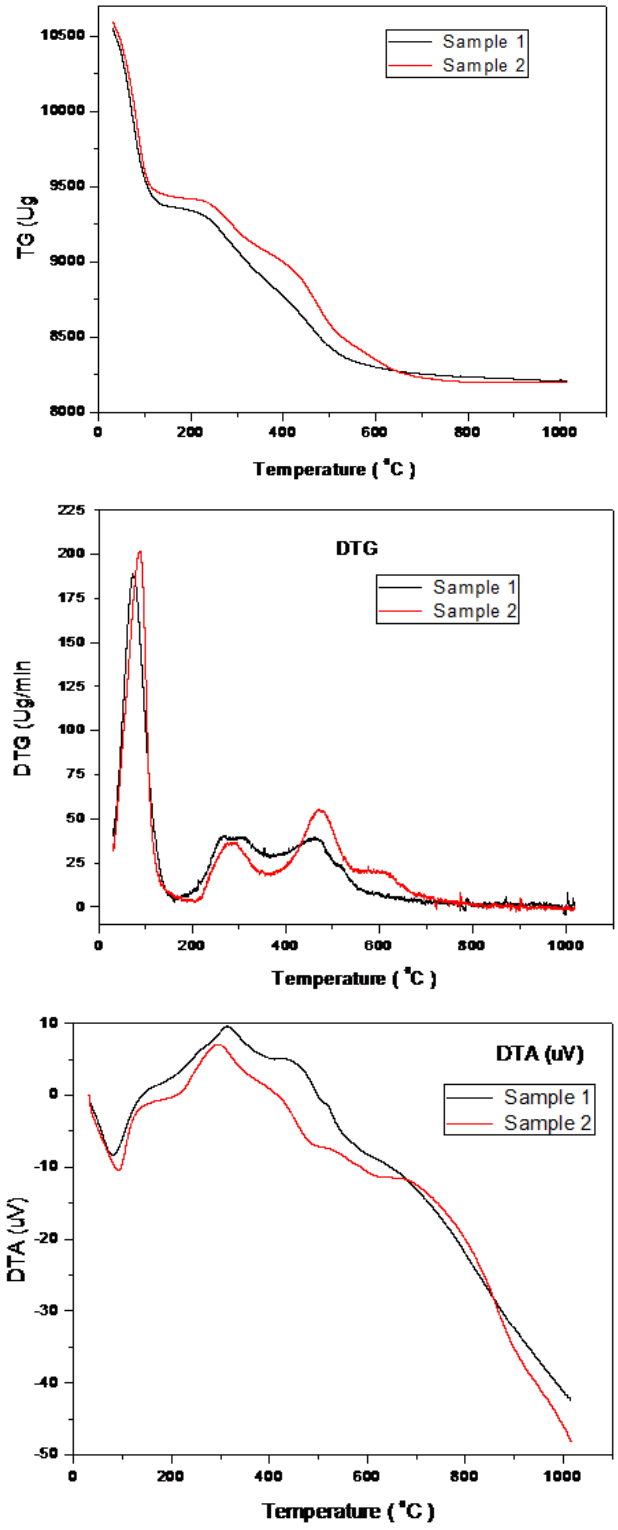

Fig. 3: Thermo gravimetric (TG), differential thermal gravimetric (DTG) and differential thermal analysis (DTA) curves of silica gel chitosan (Sample 1) bentonite chitosan (Sample 2) composites.

lated, a specific desired characteristics for excellent adsorbent. TGA/DTG/DTA studies showed the three stage weight loss due to the evaporation of water adhere to the surface, due to dehydration and dehydroxylation.

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