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Removal of Phenol from water by using cellulose mediated hydroxyapatite and activated carbon

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Abstract

Hydroxyapatite (HAp) has been involved in different kinds of human applications ranging from ceramics and human implants (medical applications) to wastewater treatment usage. The aims and objective of this research paper is for wastewater treatment and the removal of organic impurities like phenol from wastewater. HAp along with cellulose and activated carbon was synthesized by wet precipitation method using different set precursor like calcium hydroxide and diammonium hydrogen phosphate. The characterization of synthesized powder was done by Fourier transform infra red spectroscopy (FTIR) analysis studies. Our study now investigated various materials like cellulose and activated carbon as means of making composites with hydroxyapatite in order to increase the phenol adsorption capacity of HAp alone. Composites of 2% cellulose with HAp were made which was then conjugated with activated carbon (2%) and effectiveness in phenol adsorption was studied using adsorption kinetics studies. The studies showed an increase in phenol adsorption of 22% within a time of 40 minutes when HAp+2% cellulose composites were conjugated with activates carbon.

Introduction

Recently there has been a spiked concern in the world regarding the effect of human and wildlife contact to the chemical complexes in the environment, mostly the aquatic environment. Phenolic complexes stand amongst the chemicals of foremost concern in this respect as they retain themselves in the environment for longer time duration, accumulate and exert toxicity on humans

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and animals. Some of the phenolic complexes are widely present in the environment in association with the colors of fruits and flowers. Many other complexes are synthesized for use in various aspects in the normal life. There are numerous method held for the removal of phenol from water, but each one has its own merit and demerit. [1-7]

Phenolic complexes rushed into the aquatic environment due to several natural, industrial, domestic and agricultural activities. The chemicals which reach the water bodies from industrial, natural and agricultural runoff have a tendency of undergoing changes into other moieties that are even more injurious than the basic phenolic complexes. These transformations are usually handled by different physical, chemical and biological or microbial elements in water [8], based on crystallographic and chemical studies it has been found out that synthetic HAp is similar to naturally occurring Hap. [9], investigated the effectiveness of activated charcoal for the removal of phenol from aqueous solutions and two kinds of activated charcoal were NAC1240 and NAC010. [10] investigated the elimination of phenol from aqueous solutions by red mud (activated). Latest outcomes advocated that the developments taking place in nanotechnology and Nano structured materials have enabled the modification of current adsorbents which increase the potential of these methods.

The aim of this research paper is to synthesize calcium phosphate based composite that can play an important role in reducing the phenolic organic pollutants from water by the phenomenon of adsorption. The synthesized material is hydroxyapatite with 2% cellulose along with presence of activated carbon. The developed composite material when comes in direct contact with water containing phenolic organic pollutant, it adsorbs phenol on its surface and hence can be a suitable material for the removal of toxic pollutant from water.

Methodology

Chemical synthesis of Hydroxyapatite (HAp)

The procedure for the synthesis of hydroxyapatite is shown in Figure 1. In order to prepare hydroxyapatite, calcium hydroxide (5M) and diammonium hydrogen phosphate (3M) was used. [11] Calcium hydroxide was titrated against diammonium hydrogen with continuous mixing using magnetic stirrer the beads are added to the $Ca(OH)_2$ solution and heat it at 80-90°C. Ammonia added in regular interval to increase the pH (above 10). After titration left the solution

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on a magnetic stirrer for 1 hour so it will mix properly. After stirring keep the solution without disturbing it, so that the particles settle down properly. After the sometime solution was washed in every 1 hour for 3 times. To remove the excess of Ammonia. After washing, filtration of HAp sample was performed using filter paper (cake formation). The filtrate sample was collected in Petri plates for the further drying process. The wet cake dried into the hot air oven at 80°C for 1 hour.

$$10\ Ca(OH)_2 + 6\ (NH4)_2HPO_4 \longrightarrow Ca_{10}(PO4)_6(OH)_2 + 6H_2O + 12\ NH_4OH$$

Figure 1: Laboratory set up for Preparation of Hydroxyapatite

Synthesis of cellulose-based composites using HAp and cellulose:

Hydroxyapatite-cellulose composite was synthesized by chemical precipitation method [12]. In order to synthesize hydroxyapatite-cellulose composite, diammonium hydrogen phosphate (0.6M), calcium nitrate tetrahydrate (1M) and, 2% cellulose were used. Calcium nitrate

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tetrahydrate containing 2% cellulose was titrated against diammonium hydrogen phosphate with continuous mixing using magnetic stirrer beads. Ammonia added at regular interval to increase the pH greater than 10. After titration leave the solution on a magnetic stirrer for 1 hour so it will mix properly. After stirring keep the solution without disturbing it, so that the particles settle down properly. After the sometime solution was washed in every 1 hour for 3 times. To remove the excess of Ammonia. After washing filtration of HAp sample was performed using filter paper (cake formation). The filtrate sample was collected in Petri plates for the further drying process.The wet cake dried in the hot air oven at 60°C for 4 hours.

$$10Ca(NO_3)_2.4H_2O+6(NH_4)_2HPO_4+8NH_4OH \rightarrow Ca_{10}(PO4)_6(OH)_2+ 20NH_4NO_3+46H_2O$$

Synthesis of activated carbon and cellulose-based composites using Hap, Cellulose and activated carbon

Hydroxyapatite-cellulose and activated carbon composite was synthesized by chemical precipitation method. In order to synthesize hydroxyapatite-cellulose activated carbon composite, calcium nitrate tetrahydrate (1M) and diammonium hydrogen phosphate (0.6M) 2% cellulose, activated carbon (1% and 2%) were used. Calcium nitrate tetrahydrate containing 2% cellulose and activated carbon (1% and 2%) was titrated against diammonium hydrogen phosphate with continuous mixing using magnetic stirrer beads. Ammonia added at regular interval to increase the pH. PH should be more than 10. After titration leave the solution on a magnetic stirrer for 1 hour so it will mix properly. After stirring keep the solution without disturbing it, so that the particles settle down properly. After sometime solution was washed in every 1 hour for 3 times. To remove the excess of Ammonia. After washing filtration of HAp sample was performed using filter paper (cake formation). The filtrate sample was collected in Petri plates for the further drying process.The wet cake was dried in the hot air oven at 60°C for 4 hours.

FTIR spectrometers

FTIR was used for the analysis of the composite hydroxyapatite powder synthesized by the chemical precipitation method. FTIR can be used for gases, liquid and solids.

Information which FTIR provides is:

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(a) Identification of unknown materials.

(b) Determining the chemical nature of bonds in sample.

(c) Qualitative analysis of sample.

Spectrophotometer:

A spectrometer is used to measure the amount of light reflected by a sample. It deals with the interaction of electromagnetic radiations with matter. It monitors the changes in energy states of a molecule and is useful in characterization of chemical complexes in a sample on the basis of their spectral properties.

Inorganic as well as organic substances absorbs electromagnetic radiations of different frequencies. This absorption of radiation results in a transition of an atom or a molecule from its ground state to an excited state of higher energy level.

Sieving of Hydroxyapatite

The synthesized HAp was grounded in the mortar and pestle to convert it in powder form and then sieved using the sieve of size 50 micron. Sieving of Hydroxyapatite powder was done to get the uniform particle size. It was than dried in oven at 80^0C in order to remove oisture from it.

Study Adsorption Isotherms for Phenol onto various synthesized composites

The phenol stock solution was made by mixing 1gm of pure, crystalline solid phenol with distilled water to get 1% phenol stock solution. A different working concentrations of phenol were prepared from the stock solution and the tests were conducted by adding an amount of adsorbent fixed at 0.20 g to a series of 250-ml glass flasks filled with 200 ml of diluted solutions ranging from 10 to 300 mg/l.

These flasks were then kept in a shaker and rated at around 120 rpm till equilibrium was attained. Finally the liquid samples were examined using a UVspectrophotometer.

Results and Discussion

Synthesis of Hydroxyapatite powder

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Synthesis of Hydroxyapatite was done in the laboratory by the chemical precipitation method which results in the formation of precipitates. The synthesized HAp was separated with the help of filter paper and collected in Petri plates and then heated in the oven at 80^0C for one hour in order to dry the synthesized HAp. Synthesized HAp was pure, white and crystalline in nature as shown in Figure 2. Similarly cellulose mediated hydroxyapatite along with activated carbon was done successfully and the powder obtained was pure white and crystalline in nature. [11]

Fig 2: Synthesized Hydroxyapatite prepared by chemical precipitation technique

FTIR Analysis

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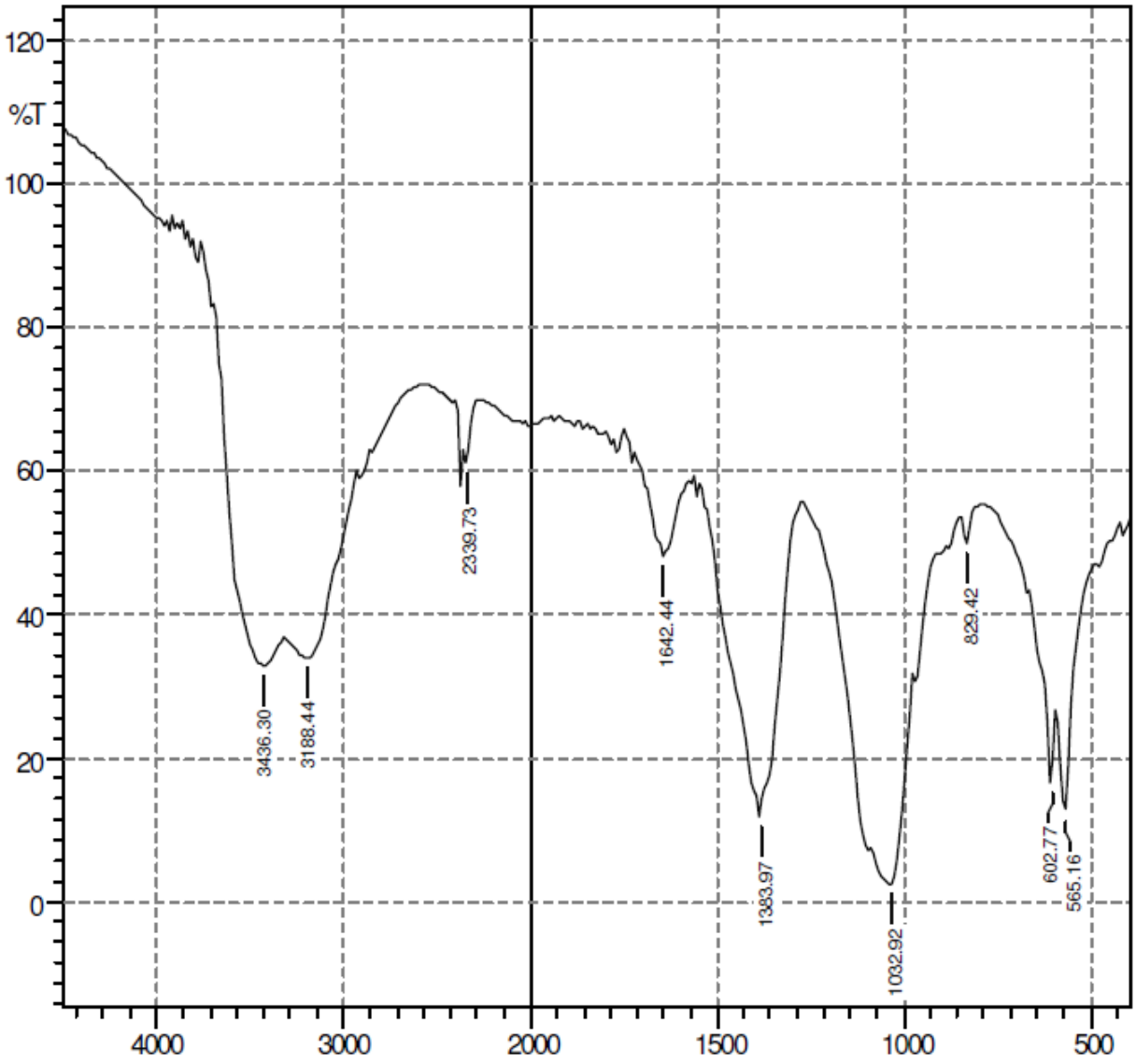

Fig:3 FTIR analysis of Hap Composites

The sample was characterized by infrared spectrum. Infrared characterization of the sample was done to analyse the spectral features which indicate the chemical bonding in the produced sample of hydroxyapatite powder Fig 3. The above spectrum obtained after the FTIR processing can be divided into four regions broadly base the range of peaks obtained. The closely positioned peaks can be classified under same range, thus the study can be done. The peaks obtained around 3400cm^{-1} is due to the presence of -OH bonds. These regions of peaks are mostly due to O-H stretching vibration in HAp. the range of 900cm^{-1} is connected with the stretching manners of the

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P-O bonds of the HAp. The set of peaks around 500cm^{-1} are due to bending types of P-O bonds in phosphate groups [11,13]. Thus the presence of PO_4^{3-} group in HAp is nearly confirmed from the FTIR studies. The pH of the medium was balanced at the time of synthesis by constant addition of ammonium solution and it was removed from the suspension by repeated washing, therefore even after repeated washing using distilled water, there is a possibility for the presence of traces in the final product HAp. The FTIR analysis shows a small range of peaks around 1500cm-1, which can be characterized as the presence of NH_4^+ group [14]. The presence of peaks around 2000 cm-^{1} suggests the presence of $CaCO_3$ traces possibly present due to the conversion of $Ca(OH)_2$ to $CaCO_3$. The occurrence of cellulosic samples can be confirmed by the band from 2900 cm^{-1}, corresponding to the C–H stretching vibration [12] . The set of peaks around 2200 suggests the presence of hydroxyapatite and carbon pigment $[Ca_3[P0_4]_2$ carbon with 2200 showing medium intensity.

Adsorption Isotherms for Phenol onto various synthesized composites

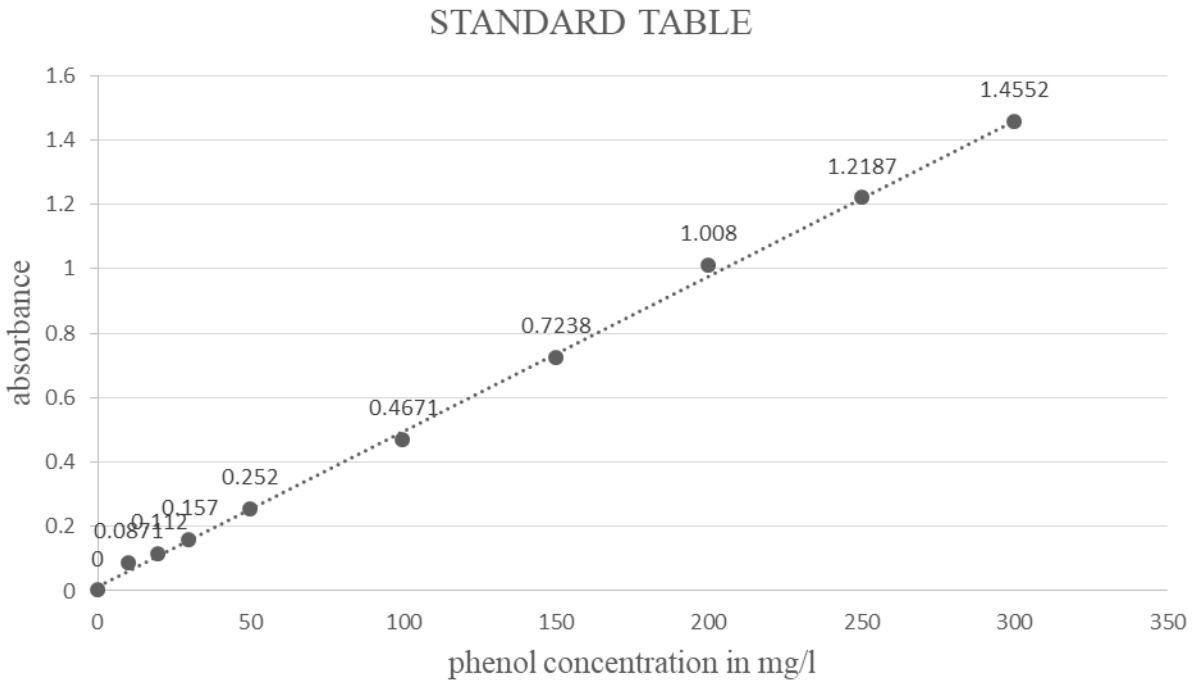

Fig. 4 Standard curve for phenol

A standard curve was plotted by taking phenol concentration (mg/l) along the x-axis and observance along the y-axis as sown in Figure 4.

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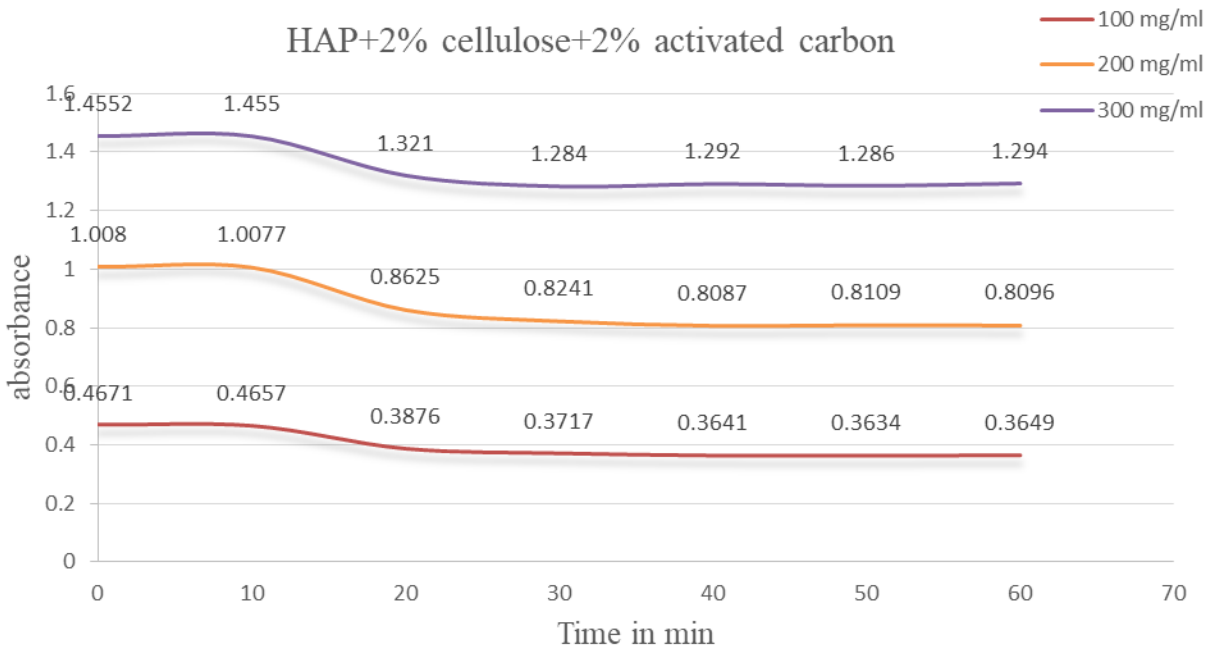

Fig. 5 Change in absorbance value with an increase in time

Changes in absorbance vs time plots were plotted which in turn shows the changes in the concentration of phenol over time Fig 5. The above graph plot validates that the absorbance of phenol at three different concentrations in presence of adsorbent HAp+2% cellulose+2% activated carbon. The readings can be interpreted as a steady decrease of phenol concentration over time and then come to a more stable concentration which means that there is no notable change in concentration [15]. Concentration-time profile of three different samples carbon shows a steady decline at three different concentrations with almost 20 to 25% decrease in concentration in the first 30 to 40 minutes. It can be therefore concluded from above analysis that the maximum absorbance of phenol takes place during the first 40 minutes and than there is a substantial decline in absorbance value beyond 40 minutes. However, since the activated carbon used is of only one type further study with different types of activated carbon may show more astounding results.

Conclusion:

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Hydroxypatite was prepared by using different precursors like activated carbon, cellulose, calcium nitrate, di-ammonium hydrogen phosphate. During the synthesis of Hap excess of ammonium hydroxide was added to the solution in order to maintain pH greater than 10 which favors the formation of Hap crystals. The synthesized Hap was white and crystalline in nature. We made various composites of HAp, like cellulose based HAp composite and activate Carbone-cellulose based HAp composite. The characterization of synthesized Hap composites were done by using FTIR analysis. From FTIR analysis it was observed that the synthesized material was HAp. In order to study absorption kinetics of phenol in the water by various HAp composites U-V spectrophotometer analysis was done at 270 nm. The adsorption isotherms explain adsorption of phenol on the surface of HAp composites. As time increases the concentration of phenol decreases and absorbance value also decreases as both are directly related.

We calculated the percentage of phenol removal by studying various isotherms and observed 2% carbon have maximum phenol absorbance then by 0% carbon composite. In future, such composites can be a suitable material to remove organic pollutant like phenol from water.

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