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Investigating of the surface adsorption of phenol from aqueous solutions using modified chitosan

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ABSTRACT: In this study, medium molecular weight chitosan (CTS) was grafted using a mixture of monomers, itaconic acid (IA) and methacrylamide (MAm) in the presence of the radical initiator, 4, 4-azobis-4-cyanovaleric acid (ACV) and ethylene glycol dimethacrylate (EGDMA) as crosslinker. The optimal grafted product was obtained by gravimetric method (EGDMA = 2 ml, ACV = 0.01 g, IA = 0.01g, MAm = 0.09 g, t = 45min, CTS = 0.2 g). The effective parameters on the adsorption of phenol were investigated by the copolymer and the appropriate pH was determined to be 3.0 - time 45 minutes - absorbent 0.01 g - absorbate 350 mg/L, q_{max} 693 mg/g. The characterization was performed by FTIR and SEM methods.

Keywords: *Chitosan, Itaconic acid, Methacrylamide, Phenol, Surface adsorption*

INTRODUCTION

Chitosan is obtained by deacetylation of chitin with a strong base. Due to the presence of hydroxyl and amine functional groups and the flexibility of polymer chains, it can form complexes with metals such as chromium, nickel, copper, zinc, and lead. Various methods such as filtration, ion exchange, sedimentation and adsorption have been used to remove pollutants from aqueous solutions [1-6]. Chemical modification of natural polymers is a good way to produce new biomaterials with high efficiency. Various papers have been published on the graft copolymerization of acrylonitrile, dimethylaminoethyl methacrylate, acrylamide, and vinylpyrrolidone on chitosan using ceric ammonium nitrate as an initiator. In recent years, important researches have been reported on the grafting of chitosan with monomers for the removal of environmental pollutants [7-12]. Phenol is used in the production of nylon, plastic, synthetic fibers, azo dyes, bactericides, fungicides, disinfectants, cleaners, mouthwashes and its large amount causes skin burns and kidney and liver complications and for people who are in direct contact with this substance in various industries such as the production of nylon, epoxy resins and herbicides. It has shown harmful and irreparable effects. So far, no report has been published on chitosan grafting with IA-MAm monomer mixture in the presence of ACV. In this research, chitosan was grafted with IA-MAm monomer mixture in the presence of EGDMA and ACV and after identification it was used as phenol adsorbent.

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MATERIALS AND METHODS

Medium molecular weight chitosan (Sigma-Aldrich) and all chemicals such as IA and MAm as monomers, EGDMA as crosslinker, ACV as radical initiator, phenol and required solvents were purchased by (Merck. Co) and twice distilled water were used in all experiments. The structure of the synthesized copolymer was investigated by FTIR (Bruker Equinox spectrophotometer with KBr discs), SEM (Philips CM120) and the amount of adsorption was investigated by UV-spectrophotometer (Shimadzu 1208).

Synthesis of copolymer

0.2 g of chitosan was dissolved in 35 ml of 5.0 wt% acetic acid. ACV was then dissolved in 5 mL of distilled water and added to the solution. Finally, two monomers of itaconic acid (IA) and methacrylamide (MAm) and ethylene glycol dimethacrylate (EGDMA) were also added. The contents were placed in a pre-set water bath at a temperature of 90 ℃, and after the prescribed time, purification was done with Whatman filter paper, and after washing with methanol, it was dried at a temperature of 50ºC. By changing the weight percentage of monomers, initiator concentration, crosslinker concentration and time, the best conditions were determined by gravimetric method [13, 14].

Adsorption procedure

To determine the adsorption of 50 mg/L of phenol with 0.01 g of composite in a total volume of 20 ml, in an Erlenmeyer flask (250 mL) with a constant shaking speed (150 rpm) and at a constant temperature of 298 K as a function of pH, adsorbate concentration, the amount of adsorbent and time were investigated. Then the solutions were filtered and centrifuged at 3000 rpm. The concentration of the residual phenol solution was measured using a UV- spectrophotometer at λ_{max} = 275 nm and using a calibration curve. A calibration curve was drawn for phenol in the concentration range of 5 to 50 mg/l. Finally, the efficiency and effectiveness of the absorbent were calculated using the calibration curve and the following equation:

$$q = (C_0 - C_e) / m.V \quad (1)$$

In the above formula, C_0 and C_e are the initial and equilibrium concentrations of phenol (mg/L), V total volume of solution (L), m absorbent weight (g) and q is the amount of the adsorbed at the specified time (mg/g) [15].

RESULTS AND DISCUSSION

Synthesis and Characterization

By changing the variables affecting the graft product, the best conditions were recorded (EGDMA = 2 ml, ACV = 0.01 g, IA = 0.01g, MAm = 0.09 g, t = 45 min, CTS = 0.2 g). The recorded FTIR spectral changes are as follows: The main characteristic peaks of pure chitosan are at 3436 cm^{-1} (O-H stretch), 2879 cm^{-1} (C-H stretch), 1605 cm^{-1} (N-H bond), 1379 cm^{-1} (C-N stretch), 1089 cm^{-1} (C-O stretch) and 1155 cm^{-1} (bridge O stretch). In addition to chitosan peaks, 2 new peaks at 3106 cm^{-1} (N-H stretch of amide) and 1725 cm^{-1} (C=O stretch of acid) confirm the correlation of two monomers IA, MAm to chitosan (Figs. 1, 2). SEM

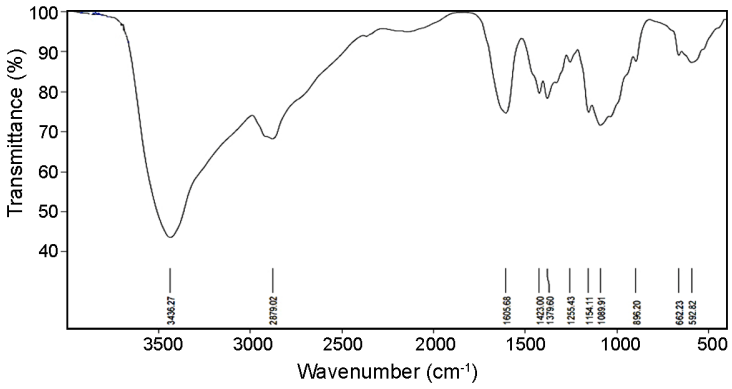

Fig. 1. FTIR spectrum of chitosan

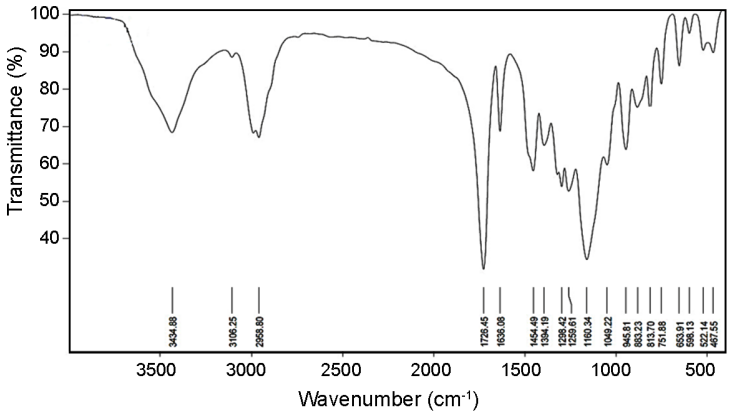

Fig. 2. FTIR spectrum of IA/MAm grafted onto chitosan

Fig. 3. SEM micrograph of chitosan

images show that the surface of chitosan is smooth and dense. But the surface of chitosan grafted with IA-MAm is rough and porous. This image is a confirmation of grafting (Figs. 3, 4).

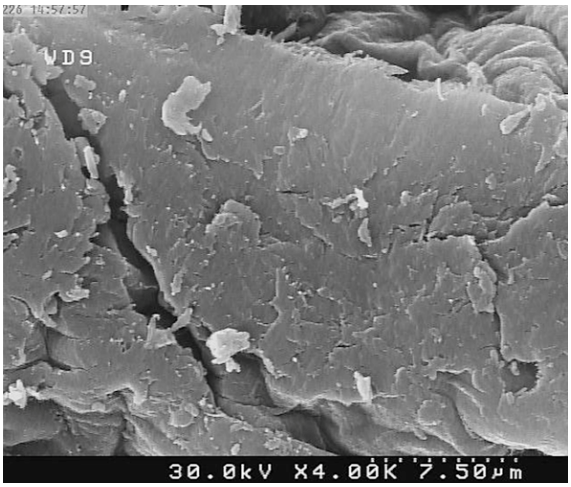

Fig. 4. SEM micrograph of IA/MAm mixture grafted onto chitosan

Effect of pH

pH was varied from 2.0-10.0 under constant conditions, adsorption time (60 minutes), adsorbent (0.01 g), shaker speed (150 rpm), adsorbent concentration (50 mg/L), total volume (20 mL), temperature 298K. The best adsorption was recorded at pH, 3.0 (Fig. 5). Due to the presence of functional groups in chitosan and monomers grafted to it, high adsorption was ob-

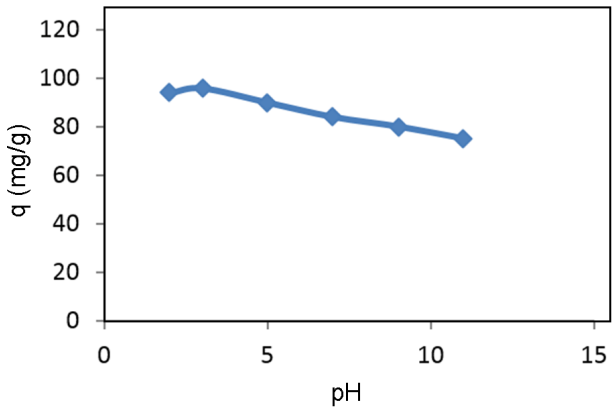

Fig. 5. Effect of pH on the adsorption of phenol

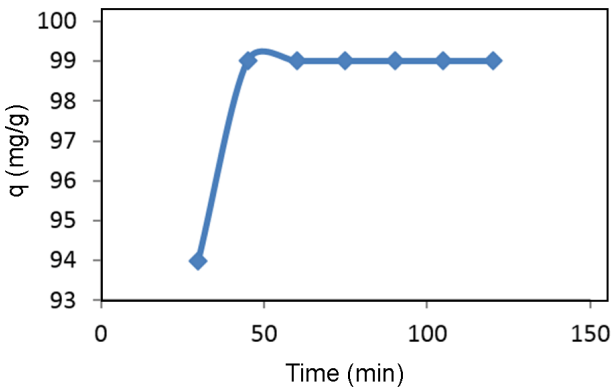

Fig. 6. Effect of contact time on the adsorption of phenol

served at different pH. On the other hand, in alkaline pH, phenol is formed as phenolate, but in acidic pH, there is a possibility of bonding, especially with the amide group.

Effect of Time

The effect of contact time on adsorption from 30 to 120 minutes in constant conditions of other variables (pH= 3.0, volume of solution, 20 mL, temperature 298K, absorbent, 0.01 g, phenol concentration,50 mg/L and shaker speed, 150 rpm). As shown in Fig. 6, the best adsorption time for phenol was recorded at 45 minutes.

Effect of Adsorbate Concentration and Adsorbent Amount

By changing the concentration of phenol, from 50 to 450 mg/L, in optimal conditions, absorption tests were performed. Maximum adsorption was observed at a concentration of 350 mg/L. With increasing amount of adsorbent, the highest adsorption was recorded with 0.01 g. In the mentioned amount, the removal percentage reached 99% (Figs. 7, 8). The value of q_{max} was 693 mg/g. Due to the grafting of monomers and the presence of functional groups, the adsorption capacity has increased significantly.

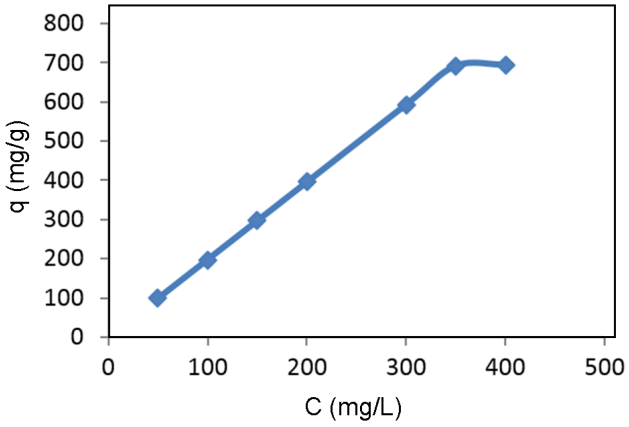

Fig. 7. Effect of phenol concentration (mg/L)

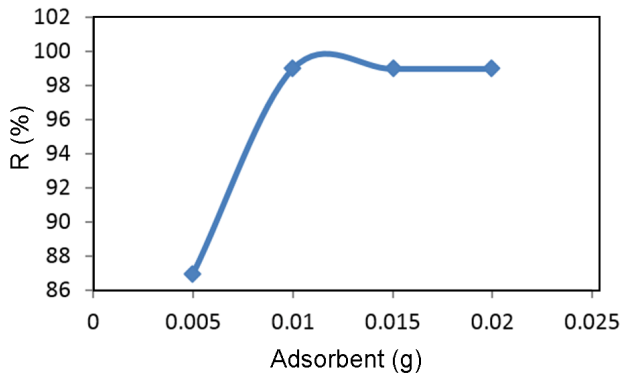

Fig. 8. Effect of adsorbent amount on the adsorption

Desorption and Regeneration Study

Adsorption and desorption were carried out by 0.1 M nitric acid, and after 5 times, the adsorbent efficiency reached about 92% [14].

CONCLUSIONS

In this study, a new adsorbent based on chitosan grafted with a mixture of IA-MAm monomers was synthesized and characterized. Its efficiency in adsorbing phenol was evaluated according to the batch technique and parameters affecting adsorption were optimized. In acidic pH, high adsorption efficiency was obtained. On the other hand, the results of adsorption-desorption experiments showed that the adsorbent has good efficiency and reproducibility.

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