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Sequestration of Cu(II) ions From Aqueous Media using Natant Magnetite – Chitosan Composite

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Abstract

The present study is focused on the synthesis of Hydroxy Apatite (HAP) composite and magnetite composite using Native Chitosan (NC) as precursor by co-precipitation method,abbreviated as HAPNCC (HAP – Natant Chitosan Composite) and MHAPNCC (Magnetite –HAP - Natant Chitosan Composite) to chelate the copper ions from aqueous matrices. Quantitative efficiencies of NC, HAPNCC and MHAPNCC for sequestrating copper metal are verified through Batch Equilibration mode. Pre and post run composites are characterized using sophisticated techniques viz., FTIR, SEM and EDAX toanalyze the involvement of functional groups, changes in surface morphology and elemental composition. Impact of operating parameters viz., sorbentdosage, agitation time,Cu(II) initial concentration, pH, temperature and co-ions upon the systems Cu – NC, Cu – HAPNCC, Cu – MHAPNCC are optimized, since they play a vital role as controlling factors. A judicious comparison is made for the verified systems. It is concluded that MHAPNCC possesses excellent sorption nature with a maximum Cu(II) removal of 90%.

1. Introduction

In the world economy, water plays a significant role, owing to the increase in its requirement day by day. The main sources of water pollution include pathogens, chemicals and also elevated temperatures [1]. Water pollution is caused due to the backflow of wastewaters into the environment, in an untreated manner. Industries discharge wastewaters loaded with huge amount of toxic chemicals, along with heavy metals like nickel, copper, lead, chromium, arsenic in the form of sulphates, phosphates and silicates into the water streams [2]. In general, metals are released from their endemic spheres to different environmental sources, mainly due to the natural weathering processes. The present work aims at arriving upon the remedial measures to control the pollution caused due to copper ions. The sources of this divalent metal entry into the environment include mining industries, construction, plating and electrical equipment manufacturing units apart from natural sources [1]. Water quality deteriorates, when it contains copper concentration greater than 1.3 mg/L. Utilization of such polluted sources leads to common complaints of nausea and diarrhoea. This is because; only 50µg/L concentration of copper is permittedto be prevalent in industrial wastes as per EPA norms. Acute presence damages liver (cirrhosis in children), kidney (inhibits urine production), heart (cardiovascular defects), brain (Wilson's disease [3], Alzheimer's [4] and other neurodegenerative diseases) and even fatality [5]. Most of the copper compounds bound to water sediment. Such solubleparticles result in greatest threat to humans [6]. Coagulation [7], membrane operation, precipitation, adsorption, etc are frequently adopted methods for the removal of toxicants [8]. Adsorption is preferred for the present study amongst all the suggested methods, due to its selectivity / effectiveness to sorb even minimal concentration of organic and inorganic pollutants [9].

1.1 Objectives

Pilot studies were planned using chitosan, a linear polysaccharide i.e., deacetylated form of chitin, wherein C-2 hydroxyl groups are replaced by acetamido groups [10]. Chitosan has high reactivity, stability towards heat or radiation, sorption capacity, biocompatibility with living tissues, non-toxic and biodegradability [11]. It also exhibits bio-inert and bacteriostatic properties, good adhesion, coagulation ability and immune-stimulating activity [12]. HAP and Magnetite composites were synthesized from native chitosan, followed by planning of Batch experiments to verify their potential to sequestrate copper ions from aqueous media.

2. Methodology

Chitosan [$(C_6H_{11}O_4N)_n$], was purchased from Pelican Biotech & Chemical Labs Pvt. Ltd.,Kuthiathodu, Kerala (**Figure 1**). Raw chitosan was pulverized and used as a precursor in the synthesis of HAP (**Figure 2**) and Magnetite composites (**Figure 3**).

2.1 Preparation of Composites (Co-precipitation Technique)

$Ca(NO_3)_2.4H_2O$ and [$(NH_4)_2HPO_4$] were dissolved as 5:1 ration in 10 mL ethanol and 3mL doubly distilled water separately. These solutions were thoroughly mixed, resulting in the formation of white residue, labeled as Hydroxy Apatite (HAP). Ferrous and ferric chloride salts were taken up in 1:2 ratio, and thoroughly dissolved in 5 mL distilled water followed by the addition of 4g NaOH pellets and ensured complete dissolution through continuous stirring. The black magnetite precipitate obtained was dried. Prepared HAP and Magnetite were mixed at 1:1 ratio to form magnetite - HAP (MHAP), later, dried in an oven at 250°C for 24 hours. 4g each of pulverized raw chitosan was transferred into two beakers labeled as 1& 2. 10 mL of 0.1N acetic acid and 5g of dried HAP and MHAP were added correspondingly to the beakers.

The contents were stirred well to obtain homogeneous mixtures, referred to as HAP - Natant Chitosan (HAPNCC) (**Figure 4**) and Magnetite - HAP- Natant Chitosan Composites (MHAPNCC). The filtered, oven dried (300°C) sorbent materials stored in air tight containers (**Figure 5**).

Figure 1. **Native Chitosan (NC)**

Figure 2. **HAP**

Figure 3. **Magnetite**

Figure 4. HAPNCC

Figure 5. MHAPNCC

2.2 Preparation of Adsorbate Solutions

A stock solution of 1000 mg/L was prepared by dissolving appropriate amount of $CuCl_2 . 2H_2O$ in double distilled water. Standard (100 mg/L) and aliquots (1 to 10 mg/L) solutionswere prepared using stock solution, respectively.

2.3 Characterization Studies

FTIR, SEM & EDAX analyses were carried out for NC and MHAPNCC to assess the peak variations pertaining to functional groups, surface texture andelemental composition correspondingly.

2.4 Batch Equilibrium Studies

Batch mode experiments were carried out to resolute the sorption capacities of the derived sorbent materials. Parameters with fixed ranges verified for Cu(II) - NC, Cu(II) - HAPNCC and Cu(II) - MHAPNCC systems include: Initial metal concentration (2– 10 mg/L: 2mg/L); material dosage (2 – 10 mg: 2 mg); contact time (2-10 minutes: 2 minutes). 50 mL of aqueous Cu(II) solutions of specified concentrations were transferred into 250 mL Erlenmeyer flasks loaded with appropriate doses of synthesized materials and agitated at 120 rpm in a mechanical shaker (KEMI model). The flasks solutions were filtered at preset time intervals, followed by analysis of Cu(II) residual concentrations along with initial concentration values using Atomic Absorption Spectrophotometer (AA 6200) at a specific wavelength (324.8 nm) and slit width (0.5 nm). Influence of variable factors like pH, temperature and co-ions were registered for MHAPNCC system under optimized data of initial concentration, dosage and contact time. pH values of the initial and final sample solutions were measured using ELICO (LI-120) pH meter.

3. Results and Discussion

Recorded values for Cu(II) – HAPNCC and Cu(II) – MHAPNCC systems reveal marked sorption nature of the latter in preference to the former. Hence, the characterization studies were restricted to magnetite-based sorbent and discussed in detail. However, the performance of the aforesaid material is compared with that of native precursor.

3.1 FTIR Analysis

Broad bands at 3410 cm^{-1} and 2818 cm^{-1} correspond to the presence of -NH and -OH groups in MHAPNCC (Figure 6). Shifts in these bands are envisaged at 1673 cm^{-1} and 858 cm^{-1} indicative of amidecarbonyl stretching and involvement of $HPO_4{}^{2-}$ (HAP). Peak stretching at 1051 cm^{-1} shows the participation of –C=C in MHAPNCC towards adsorption. The presence of aromatic ring in native precursor is evidenced by C-H bending at 661 cm^{-1}.

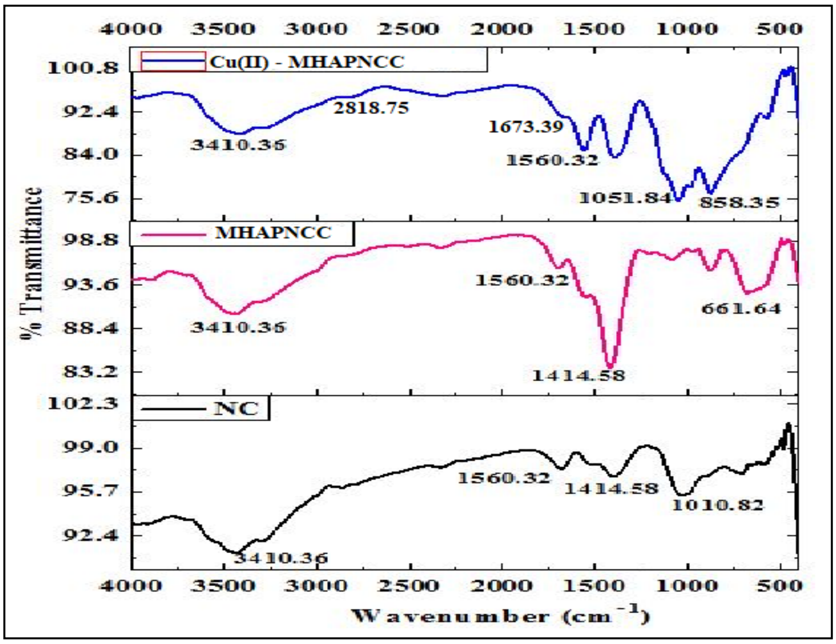

Figure 6. FT-IR Spectra - NC, MHAPNCC and Cu(II) – MHAPNCC

3.2 Scanning Electron Microscopy

SEM images (**Figures 7a, 7b**) exhibit rod shape / coarse surface texture with multiple orifices of different patterns for NC and unloaded MHAPNCC. However, a close look on Cu(II)- MHAPNCC micrograph (**Figure 7c**) reveal a smooth cubic pattern with pores being uniformly occupied by Cu(II) ions. EDAX spectra of Cu(II) - MHAPNCC (**Figure 8c**) registers a new peak (8 KeV) confirming the occurrence of Cu(II) sorption. Also, a peak at 6 KeV in **Figure 8b** shows the presence of iron in the prepared magnetite against NC (**Figure 8a**).

3.3 Effect of Adsorbent Dosage, Preset time and Initial Concentration

Dose of MHAPNCC, predetermined time and Initial Cu(II) concentrations frames play a vital role in the fixation of best sorption conditions. In this regard, the experimental run has revealed that maximum Cu(II) removal had occurred at 10 mg/L initial Cu(II) concentration; 8 mg dose with a contact time of 6 minutes for all the studied three systems (**Figures 9-13**).

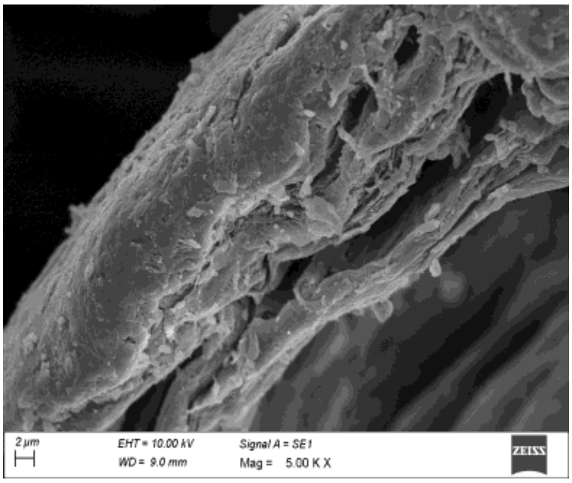

Figure 7a. SEM- Native Chitosan (NC)

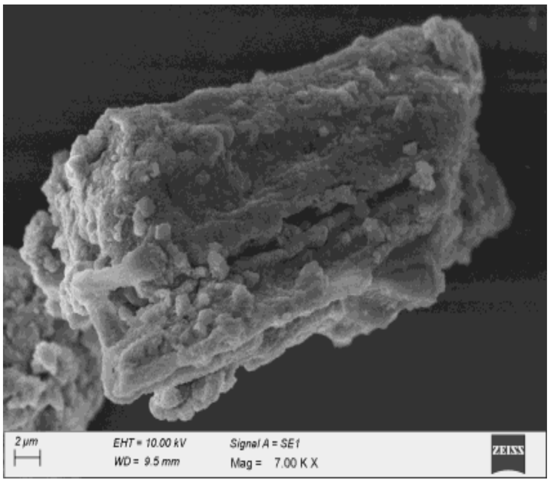

Figure 7b. SEM-Unloaded MHAPNCC

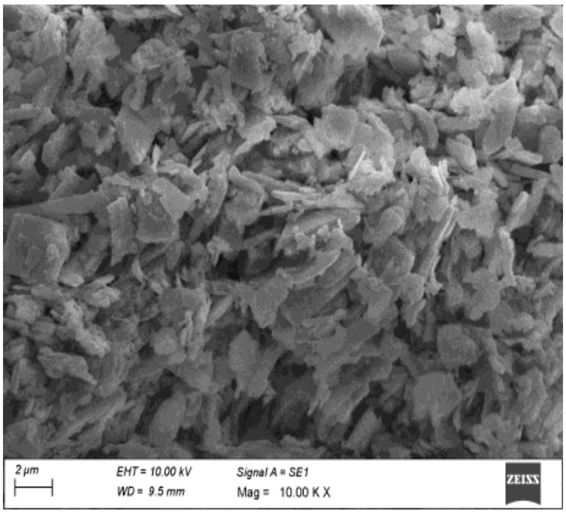

Figure 7c. SEM- Cu(II)- MHAPNCC

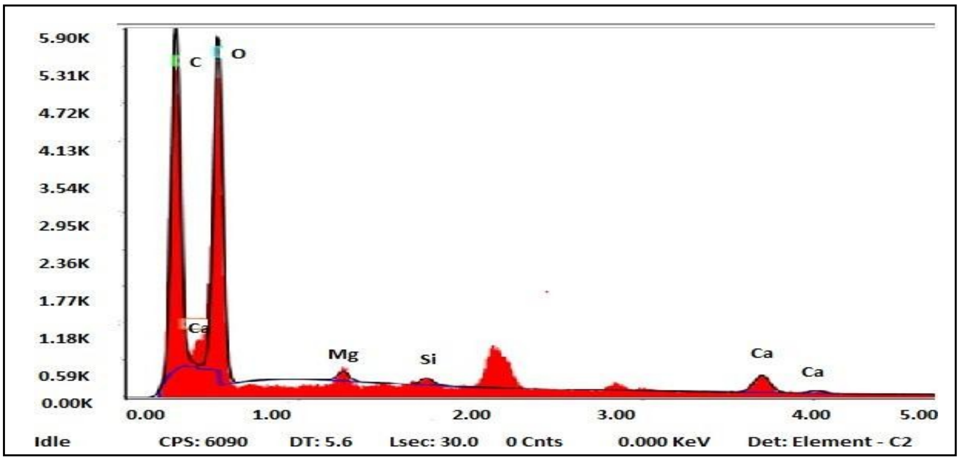

Figure 8a. EDAX – Native Chitosan (NC)

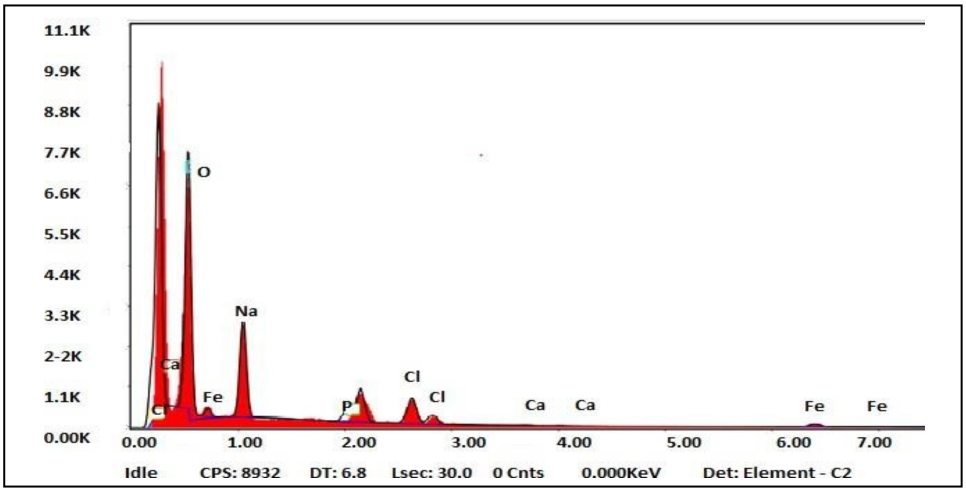

Figure 8b. EDAX-Unloaded MHAPNCC

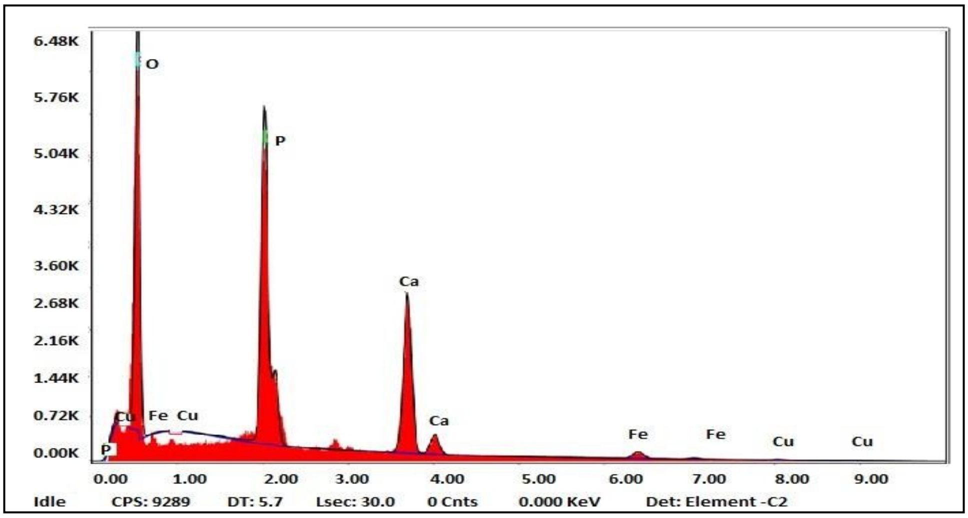

Figure 8c. EDAX-Cu(II)-MHAPNCC

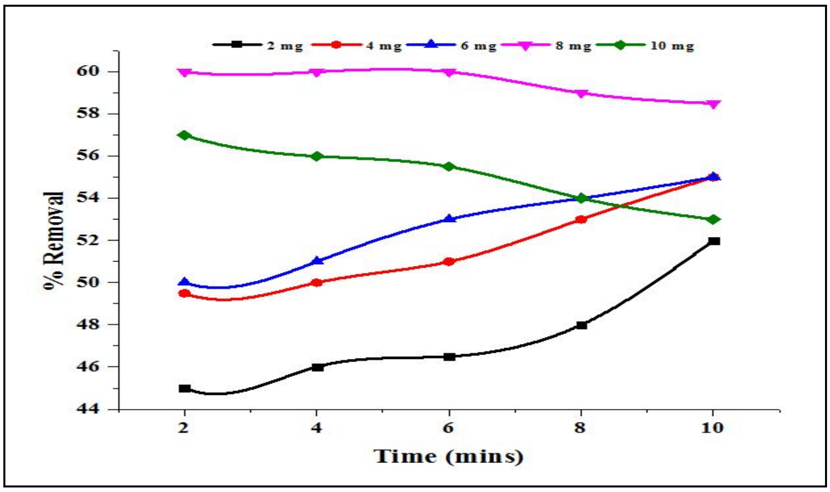

Figure 9. Effect of NC Dosage and Contact Time

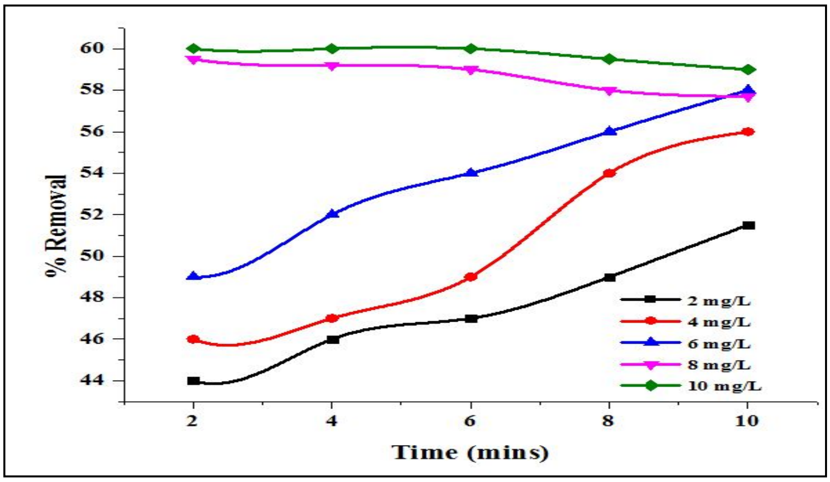

Figure 10. Effect of Initial Cu (II) Concentration onto NC

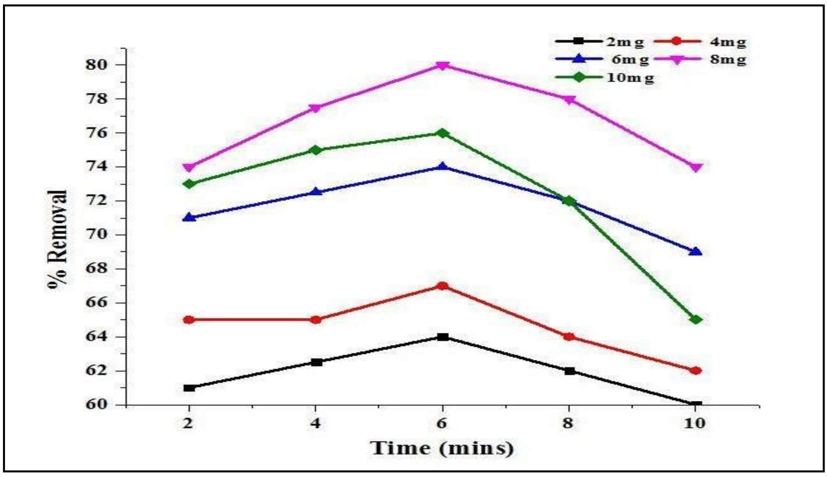

Figure 11. Effect of HAPNCC Dosage and Contact Time

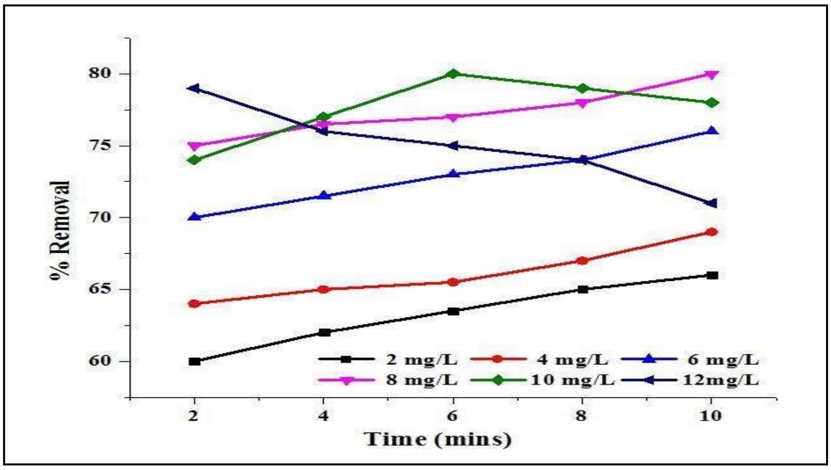

Figure 12. Effect of Initial Cu (II) Concentration onto HAPNCC

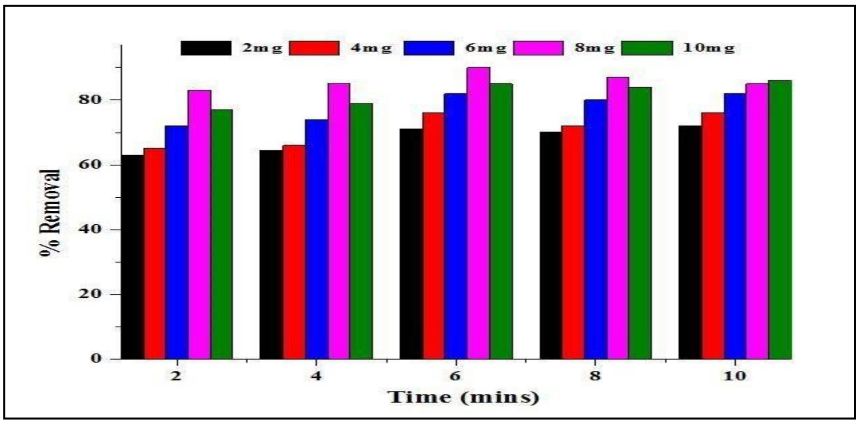

Figure 13. Effect of MHAPNCC Dosage and Contact Time

3.4 Comparison

A judicious comparison made among the studied systems viz., NC, HAPNCC, MHAPNCC reveal that MHAPNCC system exhibits better sorption characteristics against HAPNCC & NC (**Figure 14**). The reason may be the contribution of unpaired electrons in Fe atom to exhibit magnetic moment, which attract the sorbate cations [13]. Thence, MHAPNCC possess better surface ability to aggregate Cu(II) ions than HAPNCC:

Order of preferential: **MHAPNCC** > HAPNCC > NC

Percentage removal: **90%** > 80% > 60%

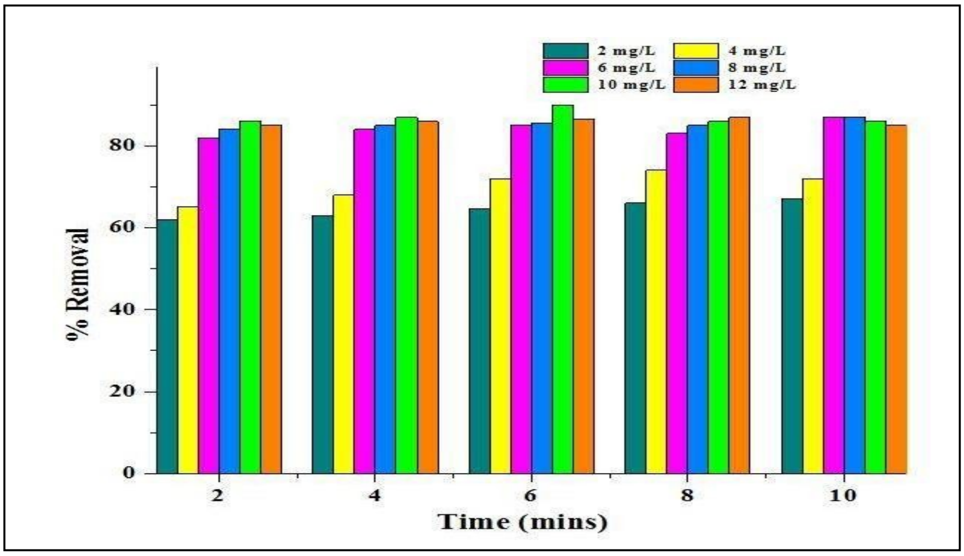

Figure 14. Effect of Initial Cu (II) Concentration onto MHAPNCC

3.5 Effect of pH

Influence of pH environment on Cu(II) - MHAPNCC revealed that maximum trapping ofsorbate species had occurred at pH 7. This is evident from the inverted parabola as depicted in **Figure 15**. Competency of H^+ ions against Cu^{2+} ions is greater due to the smaller ionic radii of the former in acidic pH. Also, the sorbate species tend to form complexes with OH^- ions preferentially, thus minimizing their availability to get sorbed on MHAPNCC surface.

3.6 Effect of Temperature

The influence of temperature holds to be an important role in the sorption process. The bar graph (**Figure 16**) implies an inverse relation between the experimented temperatures and removal of the divalent ion. The reason for the above statement shall be due to the rapid mobility of the sorbate ions at higher temperatures leading to diminishing removal.

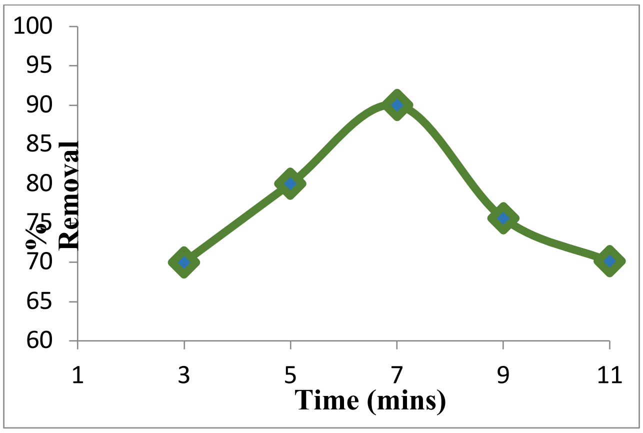

Figure 15. **Effect of pH in MHAPNCC**

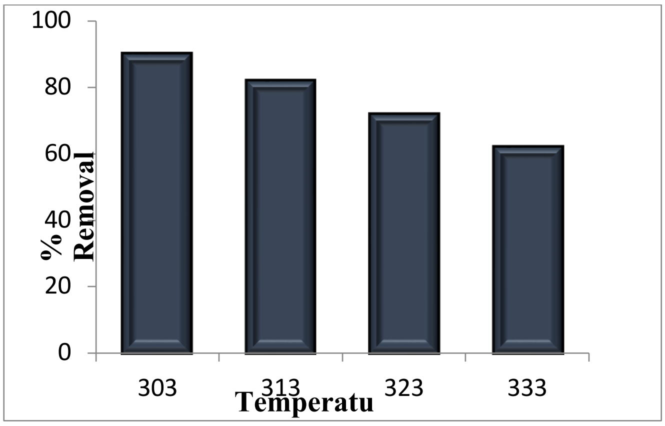

Figure 16. **Effect of Temperature in MHAPNCC**

3.7 Effect of Co-ions

The prime idea of studying the impact of cations / anions / co-ions is due to their presence inthe effluent discharges, thereby assessing the sorption efficiency of MHAPNCC under their influence. **Figure 17** shows a notable reduction in Cu(II) sorption due to inhibition caused by Mg^{2+}, Na^{2+}, K^{+}, NO_3^{2-}, Cl^{-} ions on the studied system. Mg^{2+} & Cl^{-} ions registered pronounced hindrance upon Cu(II) sorption by MHAPNCC, due to their lower ionic radii which facilitating preferential sorption against the other verified cations and anions, whose ionic radii values are marginally higher. As far as, co-ionic study is concerned, the metalbinding property of MHAPNCC is little affected, as evident from the minimal inhibition exhibited by Ni (II)ions in the bar chart.

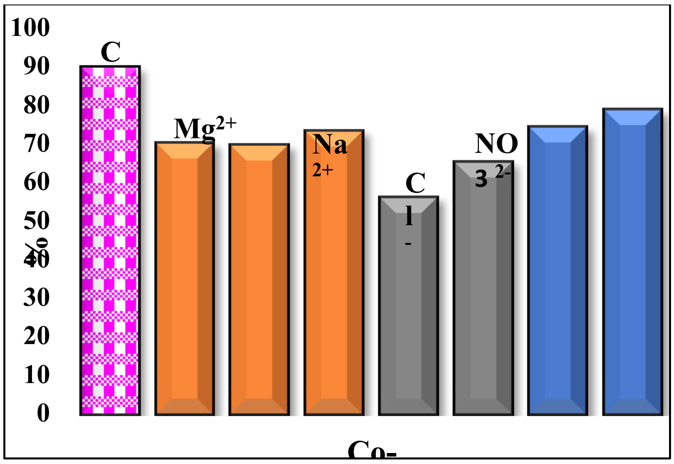

Figure 17. Effect of Co-ions

Conclusion

Batch experiments were conducted for three systems involving Cu(II) chelation by NC, HAPNCC and MHAPNCC to determine the enhanced sorption efficiencies of the functionalized materials against their native precursor. The experimental results reveal that MHAPNCC exhibited maximum Cu(II) removal (90%) from aqueous solutions. Under optimized factors viz., 10 mg/L initial metal concentration, 8 mg dosage, 6 mins agitation time; pH 7 and temperature 303 K, MHAPNCC is found to be a potential eco-friendly sorbent against other prepared samples in sequestering toxic copper ions, since magnetite has large specific surface area,reversible adsorption behavior and high reactivity, chitosan is used as a precursor which also manifest good sequestering property against Cu(II) ions.

Conflict of Interest: The authors declare that there are no conflicts of interest.

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