Cresol and its derivative Organic pollutant removal from waste water by adsorption the magneto chitosan nanoparticle

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Abstract
Cresol and its derivatives organic pollutants are harmful to human health. Natural chitosan adsorbent, due to its considerable properties such as the presence of functional groups of –NH2 and –OH, non-toxicity, low cost, and biocompatible, has gained much attention in organic pollutant cresol removal. Therefore, in the present study, adsorption of cresol and its derivative ions was conducted in a adsorption isotherm system using magnetic chitosan nano composites. Most of these compounds are toxic and refractory organics pollutants they are resistant to microbial degradation, The impure water is toxic and carcinogenic for human and animals and treatment of waste water with mangneto-chitosan Nano composites (MCNCs) can result in good water adsorption technique. A simple and an effective approach was used for preparing magneto nano composites (NC's) on the surface of chitin. The MCNCs were characterized using analytical and spectroscopic techniques including, SEM, TEM, TEM EDAX of MCNCs etc. The MCNCs were optimized for removal of organic pollutants (o-cresol, m-cresol, p-cresol and it derivative), varying different amount of absorbent, initial concentration of organic pollutants, pH etc. In optimum conditions MCNCs could recover organic pollutants, Cresols and derivatives removed (49%) by adsorption process from aqueous solution using man neto chitosan nano composites (MCNCs) Cresol and its derivative. The efficiency for removal of toxic cresol and its derivatives in magnetic field magneto chitosan nanoparticles chitosan composites were studied to remove cresol and its derivatives organic pollutants from waste water. The MCNPs have high capacity as an adsorbent which could explore a new bio-compatible and eco-friendly strategy for organic pollutants removal, and appears to be the new promising material in water treatment application.

Key words: Magnetite, Adsorption, Chitosan, cresol and its derivatives

1. Introduction
Chitosan is an amino polysaccharide and cationic polymer produced by the N-deacetylation of chitin. It is one of the most naturally biopolymers. It is a nontoxic, biodegradable biocompatible hydrophilic, and biodegradable material with the ability to form compounds with organic pollutants. The content of amino groups also made possible many chemical changes on the polymer with the purpose of improving its adsorption features, such as adsorption and selectivity capacity its adsorption performance can be further improved by cross-linking with reagents such as epichlorohydrin glutaraldehyde, ethylene glycol. Tri polyphosphate salts, or diglycidyl ether, which can stabilize chitosan in acid solutions and increase its chemical properties The organic pollutants cresol presence in drinking water is extremely detrimental to human health. Many countries are implementing the maximum permissible limit of cresol in drinking water of 0.002 μg/L recommended by the World Health Organization. Chitosan derivatives, obtained through chemical and physical modifications, cross-linking, modifying its physical structure, immobilizing it on insoluble supports, or impregnating it with metals, are preferred. Chitosan and chitosan derivatives, as kinds of cresol-removing agents, were receiving more and more attention. Nano chitosan zerovalent iron encapsulated chitosan, mixed metal oxide impregnated chitosan nanocomposites (MCNCs) o-Cresol, m-cresol, p-cresol, and mixed cresols have been identified in at least 210, 22, 310, and 72 of the 1,578 hazardous waste sites that have been proposed for inclusion on the EPA National Priorities List (NPL), respectively (Haz Dat 2016)(08).

2. Materials: Standard reference sodium hydroxide and chitin and chitosan with a deacetylation degree of 80–95% were used without any further purification.
All the other chemicals used were of analytical grade including 28% (m/v) ammonia, 0.5% (v/v) acetic acid, 0.5 g of chitosan in 200 mL of 0.5% (v/v) acetic acid solution, 4.7 g of FeCl₃⋅6H₂O and 2.4 g of FeSO₄⋅7H₂O, 6 mL of Epichlorohydrin and cresol and its derivatives liquid chemical (atul products ltd.)

2.1 Method of cresol and its derivatives removal from waste water

2.1.1 Adsorption studies

Impure Water samples originating from a local chemical plant were spiked with known amounts of cresol ranging from 15 to 50 mg/L and adsorption studies were carried out batch wise in order to obtain and equilibrium data and kinetic rates. The Closed flasks containing a known amount of adsorbent were agitated by shaking (160 rpm) for a period of 24 h at a particular pH and all experiments were conducted at room temperature (20±2 °C). pH changes during the course of the measurements were not observed. The effects of the dosage of adsorbent (2.4 x 10⁻³ to 2.4 x 10⁻² g/mL) and of pH (2 to 10) were studied. Kinetics and isotherms were determined using 0.2 g adsorbent and 20 mL cresol solution (15 to 50 mg/L) at equilibrium. After filtration (0.40 mm membrane porosity), the residual cresol concentration was determined by HPLC. The adsorption capacity was obtained using Equation where: qₑ is the adsorption capacity concentrations (mg/L), respectively, of weight (g) of the adsorbent Cross-linked Chitosan magneto with Epichlorohydrin A solution of 0.02M Epichlorohydrin containing 0.06M NaOH was prepared using 250 ml standard flask. Freshly prepared wet chitosan-magneto was added to this Epichlorohydrin solution to obtain a ratio of 1:1. Chitosan magneto in Epichlorohydrin solution were heated to a temperature between 45 to 510 °C for 2 hours and stirred continuously. Decant off Epichlorohydrin solution, washed intensively with distilled water to remove the traces of un reacted Epichlorohydrin and dried in air. The newly formed chitosan- Epichlorohydrin s was ground to a constant size, ~<250mm the chitosan- Epichlorohydin magneto were confirmed System Spectrometer (*there use the Removal of Chromium (VI) ions from Aqueous solution onto Chitosan and Cross-linked Chitosan Beads the PS JASSAL*, VP RAUT and NEELAM ANAND (2010)(09)

2.1.2 Cresol and its derivative Chitosan for Adsorption

Cresol and its derivative chitosan composite cresol-chitosan were the adsorbents used for removal of cresol and its derivative from aqueous solutions. For the synthesis of cresol-CH, chitosan was dissolved in acetic acid in order to be mixed and then an amount of cresol and its derivative was added and stirred for 24 hr. The resulted mixture was dropped to NaOH solution in order to form magneto. The adsorption isotherm curves were added to the Langmuir, Freundlich and \( q_m = 260 \text{mg/g at 280 °C} \). In the present study, the abbreviation of \( q_m \) corresponds to the maximum theoretical adsorption capacity calculated after added to the Langmuir (Freundlich or Langmuir- in kind cases) (10) equation.

2.1.3 Preparation of magnetic chitosan Nano-composites (MCNCs).

The MCNCs was synthesized as the methods described in our former study [11], with the main steps as follows. Chitosan solution was prepared by dissolving 0.5 g of chitosan in 200 mL of 0.5% (v/v) acetic acid solution with continuous stirring. 4.7 g of FeCl₃·6H₂O and 2.4 g of FeSO₄·7H₂O, which were dissolved in 22 mL of distilled water, respectively, were added to the chitosan solution by stirring at 1000 rpm for 20 min in a water bath at 40 °C. After that, 40 mL of 28% (m/v) ammonia was added drop wise into the reaction system. After 20 min, the temperature of the reaction system was adjusted to 60 °C and then 6 mL of Epichlorohydrin was added to the system with continuous stirring at 1000 rpm for 3 h. The resulting MCNP was separated by a magnet field. Finally, the obtained MCNP was washed by 0.5% (v/v) acetic acid,
distilled water, and alcohol for three times, respectively and dried in an oven at 60 °C till reaching constant weight. The total amount of amine groups, or the degree of deactivation (DDA%) of MCNP can be determined with the carbon-to-nitrogen the highest cresol and its derivative removal was in the range of 4–6 (more protons were available to proton amino groups to form NH$_3^+$ because the pka of chitosan is 6.5–7.5). The qm after (Freundlich Langmuir equations) was estimated to be 2.70 g/g (28 °C). Describes the preparation of a based on chitosan and Glutaraldehyde the chemical modification was chemically achieved using NH$_4$OH for producing which was then cross-linked with Epichlorohydrin. A study of Elwakeel et al this reaction taken between hydroxyl groups of chitosan molecules. The resultant cresol chitosan compounds was further modified with cresol-chitosan compounds to synthesize the cresol chitosan was prepared for binding/removing a cationic cresol-chitosan from aqueous media

2.1.4 Characterizations of MCNCs
Characterization by transmission electron microscopy (TEM) materials, ceramic matrix nano composites (MCNCs), in particular. For the case of MCNCs, structural and morphological characterizations of Chitosan and nanostructure phases were carried out, and for the case of MCNCs, distribution and dispersion of Nano composites as well as inter particle distances between them were investigated. Scanning electron microscopy is a great way to obtain information about a sample's surface topography and composition in industries such as microelectronics, medical devices, general manufacturing semiconductor and litigation support and food processing. Digital image resolution as low as 16 nanometers Magnification for all imaging is calibrated to a traceable standard. Image analysis for coating thick nesses, grain size determinations and particle sizing can be applied to the saved Qualitative images. Elemental analysis, quantitative analysis, x-ray line scans and mapping can be performed on both of the SEM systems. Chemically nano composites have been prepared by a gel-sol ways. Analysis by TEM-EDAX confirmed that the, magneto chitosan had been incorporated into the product. Each sample displayed variability in the level of do pant incorporation in different particles within the same analysis. Particle sizes were ≤ 110 nm for samples modified by magneto-chitosan adding with dimensions with particle morphology ~ 200nm × 60 nm
3. Result & Discussion
3.1 Adsorption isotherms

The adsorption isotherms (relationship between adsorption efficiency and cresol concentrations at equilibrium) are given equation the equilibrium adsorption data of cresol are well described by Langmuir and Freundlich models:

\[
\log q = \log K_F + \left(\frac{1}{n}\right) \log C_e
\]

This is equation freundlich

\[
\frac{1}{q} = \frac{1}{q_{\text{max}}} + \frac{1}{K_L q_{\text{max}} C_e}
\]

3.2 This is equation of Langmuir

Where: \( q \) is the amount adsorbed (mg/g), \( C_e \) is the equilibrium concentration of o-cresol, m-cresol, p-cresol and (mg/L), \( q_{\text{max}} \) and \( K_L \) are the Langmuir constants related to maximum adsorption efficiency (mg/g) and energy of adsorption, respectively, and \( K_F \) and \( n \) are Freundlich constants related to adsorption capacity and adsorption intensity, respectively.

The Langmuir and Freundlich constants calculated from the linear plots of \( 1/C_e \)versus\( 1/q \) and \( \log C_e \)versus \( \log q \) together with the correlation coefficients (r2) are given in Table. The theoretical data using Langmuir and Freundlich parameters from Table to assess the validation of the model from the experimental data indicating that the adsorption equilibrium data for cresol followed the Langmuir and Freundlich isotherms for the adsorbents.

A better criterion to test the correctness of the fits of the data is the normalized percent deviation,

\[
P = \left( \frac{100}{N} \right) \sum 1 \left\{ \frac{q_{\text{ex}} - q_{\text{pred}}}{q_{\text{ex}}} \right\}
\]

Where: \( q_{\text{ex}} \) is the experimental adsorption capacity, \( q_{\text{pred}} \) is the predicted adsorption capacity, and \( N \) is the number of observations.

The lower the value of the percent deviation \( P \) is, the better the fit is (for values less than 6). The calculated \( P \) values suggest that the adsorption process for both adsorbents follows a Langmuir model w was found to be 1.97 and 1.27 mg/g for chitin and chitosan, respectively.

The favorable nature of adsorption can be expressed in terms of the separation factor RL,

\[
R_L = \frac{1}{1 + K_L C_0}
\]

Where: \( K_L \) is the Langmuir constant and \( C_0 \) is the initial cresol concentration adsorbents reported in other papers. It can be seen that activated carbon, fly ash, and chitin are efficient for removal of cresol and its derivatives. Also, chitin and chitosan have efficiencies comparable to other low-cost adsorbents like Cooke breeze rice husk, and grain Rusk. New method to increase the adsorption capacity of chitosan has been developed through chemical modification including cross-linking of chitosan and chitin substitution.

### Table: Parameters for Langmuir and Freundlich models

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<th>Langmuir</th>
<th>Freundlich</th>
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<tr>
<td></td>
<td>( q_{\text{max}} ) (mg/g)</td>
<td>( K_L )</td>
</tr>
<tr>
<td>Chitin</td>
<td>1.27</td>
<td>0.04</td>
</tr>
<tr>
<td>Chitosan</td>
<td>1.97</td>
<td>0.12</td>
</tr>
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</table>

\( c_e \) gm/L Grape; adsorbent of chitosan and chitin

4. Conclusion
Magneto chitosan Nanocomposites were prepared using cresol and its derivatives organic pollutants cresol and its
derivatives which is a simple method and used as adsorbent for the removal of organic pollutants cresol from aqueous solutions. In adsorption studies, the effects of adsorbent dosage, contact time, initial organic pollutants concentration, pH and temperature on the adsorption capacities of magneto chitosan Nano composites were investigated, and the following results were obtained: The adsorption capacity of MCNCs increased with the increase of organic pollutants concentration and the decrease of adsorbent dosage and temperature. The adsorption capacity of cresol MCNCs maximum value at pH 6.5. The Langmuir equation gave the best fit to the equilibrium data of MCNCs.

5. Reference


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