THE PREPARATION OF COMPOSITE MATERIALS BASED ON MAGNETITE NANOPARTICLES AND SODIUM ALGINATE FOR WASTE WATER PURIFICATION

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Abstract: The use of synthetic chemical dyes in various industries, including plastics, paper manufacturing, cloth dyeing, printing and leather treatment, has increased considerably over the last years, resulting in the release of dye-containing effluents into the aquatic and soil ecosystems. There are many techniques to remove the waste after dying process (coagulation, chemical precipitation, reverse osmosis, extraction, filtration, biological treatment and adsorption). The releasing of dyes from many industrial plants is environmentally hazardous. The most important goal for the waste water purification is to find the low-cost adsorbents with high selectivity and long life. In our study, an effort has been made to prepare efficient composite materials for dyes removal from aqueous solution based on medium molecular weights deacetylated chitin i.e. poly(D-glucosamine) and a biodegradable nontoxic anionic polysaccharide sodium alginate filled with magnetite nanoparticles. Alginate composite beads coated with poly(D-glucosamine) were prepared using layer-by-layer (LbL) deposition method. During the adsorption process the concentrations of dyes in solution waste were determined according to the general spectrophotometer method.

Keywords: waste water, adsorption, nanotechnology, polymer composites.

1. INTRODUCTION

Over the last few decades, society has become increasingly sensitive towards the protection of the environment. Wastewater containing dyes is very difficult to treat, since the dyes are recalcitrant molecules and resistant to aerobic digestion. There are more than 100,000 commercially available dye [1]. Many of the industrial dyes are toxic, mutagenic, teratogenic, and carcinogenic. A synthetic dye cannot be efficiently decolorized by traditional methods. All technologies for colour removal (biological, chemical and physical) have advantages and drawbacks. Chemical methods include coagulation or flocculation combined with flotation and filtration, conventional oxidation methods by oxidizing agents, precipitation-flocculation with $Fe(II)/Ca(OH)_2$, electroflotation, irradiation or electrochemical processes. These chemical techniques are expensive, and although the dyes are removed, there are problems with accumulation of concentrated sludge. Biodegradation methods such as fungal decolourization, microbial

degradation, adsorption by microbial biomass and bioremediation systems are commonly used for industrial effluents treatmant because many microorganisms such as bacteria, yeasts, alges and fungi are able to accumulate and degrade different pollutants. The physical method adsorption does not result in the formation of harmful substances and is superior to other methods in terms of initial cost, flexibility and simplicity of design, ease of operation and insensitivity to toxic pollutants. Decolourisation is a result of two mechanisms: adsorption and ion exchange and is influenced by many physio-chemical factors, such as, dye/sorbent interaction, sorbent surface area, particle size, temperature, pH, and contact time. The first step to the efficient adsorption process is to search for the low-cost adsorbent materials with long life, with high capacity and high selectivity to reduce the procedure cost. Synthetic dyes are considered the most difficult to treat because they contain complex aromatic structures, which make them more stable and more difficult to be biodegraded. The adsorbent should possess few basic qualities such as porous in structure

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(resulting in high surface area), smaller in size and time taken for adsorption equilibrium should be as depressed as possible with the purpose that it can be used to remove dye wastes in a short period [2,3]. The emergence of tailored nanoparticles with magnetic properties and high adsorption competence for an extended mixture of compounds, offer a novel tool to deal with waste water purification [4]. Magnetic adsorbents can be efficiently used for the separation of various dyes both from solutions and suspensions. The magnetic adsorbents could be separated based on their nanostructures because the ease of direction of magnetization would vary depending on the ordering of atoms in the magnetic structure. In general, adsorbent used are smaller in size since smaller size adsorbents have increased surface area leading to highest adsorption capacity. External magnetic field applied to materials determines the property of magnetic particles. Descriptions of orientations of the magnetic moments in a material aid to identify different forms of magnetism observed in nature. Five basic types of magnetism can be described: diamagnetism, paramagnetism, ferromagnetism, antiferromagnetism and ferrimagnetism. Diamagnetism is a central attribute of all atoms, and the magnetization is very small and opposed to the applied magnetic field direction. As it is rewieved in bibliography, [5] many materials exhibit paramagnetism, where a magnetization develops parallel to the applied magnetic field as the orbit is increased from zero, however, the effectiveness of the magnetization is small. Ferromagnetism is the property of those materials that are inherently magnetically ordered and which develop spontaneous magnetization without the need to utilize a field. A disparity on ferromagnetism is ferrimagnetism, where different atoms possess different moment strengths, but at that state is still an ordered state below a certain critical temperature. The magnetic material can be sorted based on their susceptibility, i.e., diamagnet ($\chi < 0$), paramagnet ($\chi > 0$), ferromagnet ($\chi \gg 0$). It has been proven that many of the unique magnetic properties of nanoparticles can be atributed to the high surface-to-volume ratio. The substantial characteristic of an adsorbent is the quantity of adsorbate accumulated on adsorbent, which is generally estimated from the adsorption isotherms.

2. EXPERIMENTAL PART

2.1 Materials

Cresol red 4,4'-(1,1-dioxido-3H-2,1-benzoxathiole-3,3-diyl)bis(2-methylphenol) was purchased from Merck Company. (Soluble dye with melting point 290 °C and density 0.98 g/mL at 25 °C). Bio-degradable nontoxic anionic polysaccharide sodium alginate was obtained from Sigma-Aldrich (type180947). Medium molecular weight poly(D-glucosamine) i.e. chitosan animal origin was obtained from Sigma-Aldrich. (type 448877). Viscosity 200-800 cP, 1 wt. % in 1% acetic acid (25 °C, Brookfield). Chitosan is manufactured commercially by deacetylation of chitin, which is the structural part in the exoskeleton of crabs and shrimp and cell walls of fungi. The chemical structure of chitosan is given in the Figure 1. On average, the molecular weight of commercially prepared chitosan is in the range from 3800 to 20,000 Daltons. The synthesis of chitosan is in general the deacetylation of chitin using sodium hydroxide in excess as a reagent and water as a solvent. This reaction pathway at complete deacetylation)yields up to 98% product. Magnetite (Fe_3O_4) was purchased from Merck Company. It is a mineral and a member of the spinel group. Magnetite is the most magnetic of all the naturally occurring minerals. Numerous natural and synthetic adsorbents were used, out of which magnetic composites (MCs) and magnetic nanocomposites (MNCs) have gained much attention presently in the removal of dyes from aqueous solution.
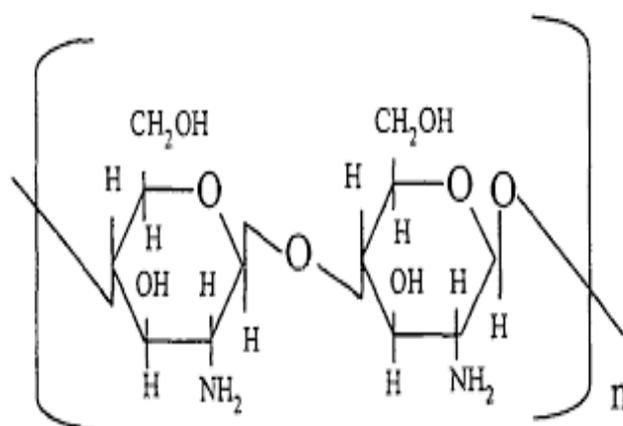

Figure 1. The chemical structure of chitosan

2.2. Preparation of chitosan-coated beads

The beads prepared from alginate nanocomposites coated with chitosan were obtained using layer by layer (LbL) method. In the first step, sodium alginate (0.3035 g) was dissolved in 10 ml of distilled water by continuous stirring until a homogeneous mixture was obtained. Fe_3O_4 (1% mass) was added into this solution and in the ultrasonic bath. After 30 minutes the solution was kept in the sonicator for further 15 min. The final

solution was dropped into the $CaCl_2$ (2% mass) solution with a proper syringe at 300 K and completely dispersed magnetite beads were obtained. The spherical beads were formed for 30 minutes in the gelling solution with gentle stirring. The beads were collected by filtration and washed several times with distilled water. Magnetic alginate nanobeads were incubated in the the solution of chitosan which was previously prepared by dissolving of 3 grams of chitosan in 1L of acetate buffer solution (0.02 mol/L of sodium acetate/acetic acid 1%) at pH 5.0. Then, the beads were taken out and washed several times with distilled water. The samples were dried in an oven at 60 ºC until constant weight.

2.3. Adsorption experiments

For adsorption process determination the dye stock solution was obtained by dissolving weighted cresol red in distilled water (concentration $1gL^{-1}$). The cresol red solutions were obtained by diluting the dye stock solution in accurate proportions to required initial concentrations (50ppm; 25ppm; 12.5ppm). The samples including magnetite powder and bio-degradable polymer blend were used as the adsorbent. 25 ppm dye solution was used to follow the effect of the temperature on adsorption. The adsorption was followed using spectrophotometer at the wavelength (λ_{max}=376, 440 and 574 nm for pH of 6, 8 and 10), respectively. The uptake percent (%) of dye was calculated from the experimental results. The solution of cresol red was prepared with different pH values (6, 8, 10) to study the effect of pH adjusting by NaOH and HCl solutions. Adsorption experiments were carried out with and without magnetic field. Magnetometer was used to investigate the effect of the magnetic field on the adsorption. During the adsorption process, the concentrations of red dye wwas determined according to general spectrophotometer method at its maximum wavelength over working concentration range as given in method. The uptake percentage of dye was estimated using the equation given below:

$$\text{Uptake } \% = \frac{c_o - c_t}{c_o} \times 100 \qquad (1)$$

where C_o (mgL^{-1}) and C_t (mgL^{-1}) are the concentrations of cresol red in the solution at the initial time (t = 0) and any time (t = t), respectively.

$$\text{Max uptake } \% = \frac{c_o - c_e}{c_o} \times 100 \qquad (2)$$

where C_e represents the concentration of cresol red in the solution at equilibrium and used for the calculation of maximum uptaken value. The mass of cresol red adsorbed at any time (C = C_t) and at equilibrium (C = C_e) per unit mass of the adsorbents (q) was calculated from the Eq 2.

$$q = \frac{c_o - c}{W} \times V \qquad (3)$$

where q is the adsorbed amount of cresol red in the solid phase at equilibrium (q=q_e) and time t (min) (q=q_t), respectively. V (L) indicates the volume of dye solution and W (g) is the weight of the adsorbent. Adsorption experiments were carried out in the glass-stoppered flasks immersed in a thermostatic shaker bath. Samples were kept for 25 ml of different concentrations of cresol red solutions. During the adsorption process, the samples were taken at the pre-determined time intervals and adsorbents were separated from the solution using a magnet. The difference between the concentrations of cresol red solutions before and after adsorption gives the adsorbed amount of dye on the adsorbents. 25 ppm of dye solution was used at different temperatures and pH to follow the effect of temperature and pH on the adsorption.

3. RESULTS AND DISCUSSION

The image and size of magnetic beads before and after adsorption are given in the Figure 2. The removal of cresol red by the adsorbent as a function of contact time was studied (Table 1). When the initial concentration of cresol red increased from 12.5 to 50 ppm, the uptaken value increased from 8% to 18% . If a magnetic field was applied during the adsorption process, the uptake amount of cresol red increased from 21% to 33%, with the concentration of cresol red varying from 12.5 to 50 ppm. Rapid adsorption (in 100 min) was observed using a magnetic field. The effect of initial pH on the adsorption of cresol red onto magnetic beads is shown in Figure 3. The adsorption capacity increases when the pH increases. The presence of hydroxyl and amino groups in chitosan serve on the adsorption active sides. High adsorption values were obtained at pH = 10. The comparison of the adsorption of 25 ppm dye solution as related to the magnetic field presence at the same conditions is shown in Figure 4. Kinetic study of adsorption of cresol red from an aqueous solution onto the adsorbent was carried out, by the well-known Lagergren's pseudo first-order and pseudo second-order model.

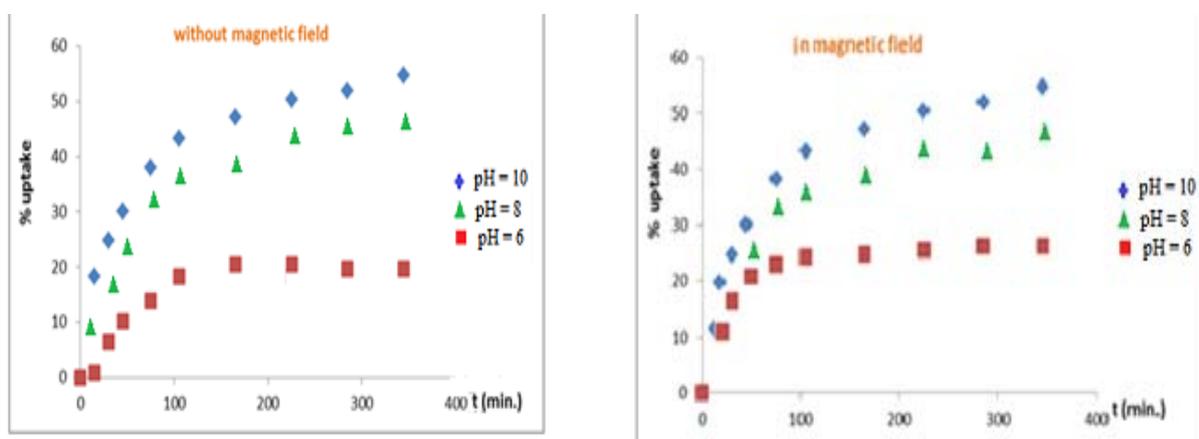*Figure 2. The size of nanocomposite beads a) after and (b) before adsorption process*

Figure 3. Adsorption of cresol red at different pH values, at 25ºC and solution concentration,
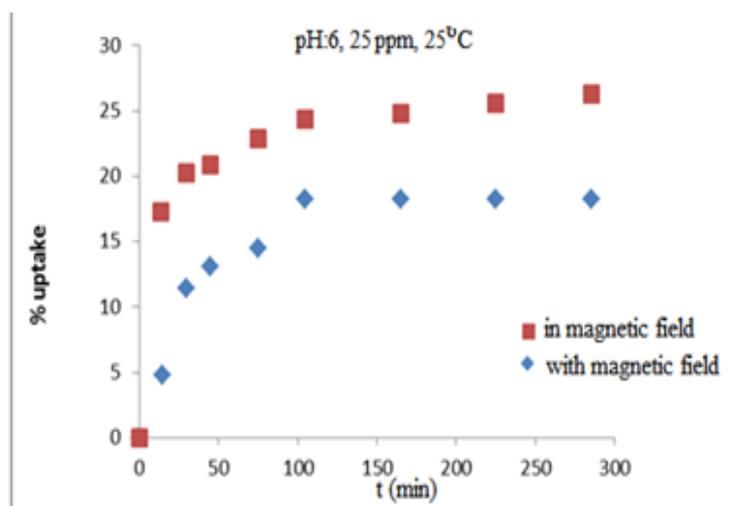*25 ppm (with and without magnetic field)*

Figure 4. Comparing the adsorption with and without the influence of the magnetic field

Pseudo first-order rate expression is given as,

$$dq_t/dt = k_1(q_e - q_t) \tag{4}$$

Integrating of Eq (4) for the boundary conditions, at t=0, q_t =0 and t=t, $q_t=q_t$ gives the following equation:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{5}$$

where, k_1 is the pseudo first-order rate constant of the adsorption (min^{-1}).

It was estimated that for obtained curves the correlation coefficients, R^2, have high values, 0.995, 0.997 and 0.998 for the concentration of 50 ppm, 25 ppm, 12.5 ppm, respectively. The results indicate the applicability of this kinetic equation on the adsorption process. The calculated ($q_{e,cal}$) values for all adsorbents are much closer to the experimental ($q_{e,exp}$) values in the case of pseudo first-order kinetic model (Table 1). These results verify the adequacy of the pseudo first order model. The experimental data were also applied to the pseudo second order kinetic model based on the adsorption capacity. The correlation coefficients, R^2 obtained from the second order kinetic model depicted low values and the experimental values of ($q_{e,exp}$) do not agree well with the calculated values ($q_{e,cal}$) for this model. This result shows that the second order kinetic model does not fit well with the whole range of contact time. The effect of temperature on the adsorption capacity of magnetic nanoparticles was studied for different temperatures, 25 ºC, 40 ºC, 60 ºC for the same concentration of 25 ppm. The adsorption capacity decreases with the increasing temperature, indicating that the adsorption is an exothermic process. Using these results the date thermodynamic parameters were estimated.

Table 1. Kinetic parameters for cresol red adsorption obtained at 25 ºC for solutions with different concentration.

Parameters	50 ppm	25 ppm	12,5 ppm
$q_{e,cal}$	24.47	12.75	3.24
$q_{e,exp}$	28.36	12.71	4.45
K_1	0.0149	0.0188	0.0133

4. CONCLUSIONS

The efficient composite materials for dyes removal from aqueous solution based on medium molecular weights chitosan and a bio-degradable nontoxic anionic polysaccharide sodium alginate filled with magnetite nanoparticles were synthesiyed. Alginate composite beads coated with chitosan were prepared using layer-by-layer deposition method. During the adsorption process the concentrations of dyes in solution waste determined according to the general spectrophotometer method. The uptake value of cresol red on the magnetic beads adsorbent, in the magnetic field was higher than in the non-magnetic field. The adsorption percentage of dye on the adsorbent increases with increasing dye concentration. The adsorption equilibrium was obtained in 100 minutes in magnetic field. The pseudo first order and second order model were used to determine the kinetics of adsorption process. First order kinetic model provides good correlation for the dye adsorption. The themperature effect studies assessed that the adsorption of cresol red on the magnetic nanobeads increased with the temperature ranging from 25 °C to 60 °C. This result shows that this adsorption process is endothermic.

5. ACKNOWLEDGEMENT

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ДОБИЈАЊЕ КОМПОЗИТНИХ МАТЕРИЈАЛА ОД НАНОЧЕСТИЦА МАГНЕТИТА И НАТРИЈУМ АЛГИНАТА ЗА ПРЕЧИШЋАВАЊЕ ОТПАДНИХ ВОДА

Сажетак: Примена синтетичких боја у разним индустријским гранама, укључујући пластику, производњу папира, бојење одеће, штампарство и третирање коже, последњих година значајно је порасла, што је резултирало отпуштањем отпадних вода које садржи боје у еко-системе вода и земљишта. Постоји велики број метода за уклањање отпада након технолошких поступака бојења (коагулација, хемијско таложење, реверзибилна осмоза, екстракција, филтрација, биолошки третман и адсорпција). Уклањање боја код већине индустријских постројења је еколошки опасно. Најважнији корак код пречишћавања отпадних вода је обезбедити адсорбенте велике селективности који имају ниску цену и дуг век трајања. Циљ нашег рада је био да се за уклањање боја из водених раствора припреме ефикасни композитни материјали на основу деацетилованог хитина, то јест поли(Д-глукосамина) средњих молекулских маса и био-деградабилног нетоксичног полисахарида натријум алгината са наночестицама магнетита. Композитне алгинатне грануле су прекриване поли(Д-глукозамином), методом наношења слој по слој (LbL). У току процеса адсорпције, концентрација боја је праћена применом опште спектрофотометријске методе.

Кључне речи: отпадне воде, адсорпција, нанотехнологије, полимерни композити.

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