CELLULOSE CHEMISTRY AND TECHNOLOGY

LIGNIN REMOVAL FROM AQUEOUS SOLUTIONS USING Fe_3O_4 MAGNETIC NANOPARTICLES AS RECOVERABLE ADSORBENT

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In the present study, the use of Fe_3O_4 magnetic nanoparticles as recoverable adsorbent for lignin removal from aqueous solutions has been investigated. Fe_3O_4 magnetic nanoparticles (MNPs) were chemically synthesized. The size and cross-section shapes of the synthesized particles were determined by scanning electron microscope (SEM) and X-ray diffraction analysis (XRD). The effects of some different parameters, including the amount of adsorbent, pH of solution, salt effect and adsorption time, on the removal efficiency of lignin were investigated and optimized.
The kinetic studies on lignin showed rapid sorption dynamics by a pseudo-second order kinetic model. According to the isotherm studies, lignin adsorption equilibrium data were fitted well to the Langmuir isotherm. The maximum monolayer capacity (q_{max}) and the Langmuir constant (K_L) were obtained from the Langmuir model as 2554.42 mg g^{-1} and 0.812 L mg^{-1}, respectively. The simple synthesis method and the recoverability of Fe_3O_4MNPs recommend it as a good adsorbent for lignin removal from aqueous solutions.

Keywords: lignin, Fe_3O_4 magnetic nanoparticles, adsorption, Langmuir isotherm

INTRODUCTION

Wood contains approximately 50 percent of cellulose, which is combined with lignin, a high molecular weight aromatic compound of phenolic character. Different sources of wood have various percentages of lignin. Lignin contains methoxy and phenolic hydroxyl groups and it is believed that there is some kind of linkage between cellulose and lignin molecules. In the plant, lignin serves as a matrix in which the fibrous cellulosic cells and specialized structures are embedded.[1,2] Approximately 50-106 tons of the lignin produced as a by-product of the pulp and paper industry are burned; only small amounts are used as additives in several industrial processes. A large volume of expensive petrochemicals could be substituted in the production of engineering plastics, if there existed an economical way to transform lignin into a marketable product.[3-5]

Large quantities of lignin compounds are obtained as industrial wastes.[6] Lignin, as a recalcitrant aromatic biopolymer, could be degraded in the environment by white rot fungi, especially by the concerted action of their extracellular phenol oxidase and the subsequent radical process initiated by them caused by the coupling of generated phenoxy radicals.[7-8]

The pulping of wood produces considerable amounts of waste liquors containing lignin derivatives and others in dissolved form. The lignin derivatives are very resistant to biological degradation; however after decomposition, natural color appears. Colored wastes are not acceptable for domestic or some industrial uses without treatment to remove the color preventive and remedial measures should be incorporated for the treatment of refinery liquid effluent streams.[9] The effluents from kraft pulping are highly polluted[10] and cause considerable damage to the receiving waters if discharged untreated, since they have high levels of biological oxygen demand (BOD), chemical oxygen demand (COD), chlorinated compounds, suspended solids (mainly fibres), fatty acids, tannins, resin acids, lignin and its derivatives, sulphur and sulphur compounds, etc.[11-13] Traditional methods for dealing with the wastewater consist in biological, physical, chemical processes and various combinations of these.[14] Recently, several physical and chemical processes for colour removal in paper mill effluents have been extensively studied, including rapid filtration through soil, ultrafiltration, ion-exchange chromatography, lime precipitation, modified bleaching sequences, such as peroxide addition during extraction and the replacement of chlorine by hypochlorite, and sorption on hypo and alum sludge, activated carbon and allophonic compounds.[15]

The present research investigates the applicability of Fe_3O_4 magnetic nanoparticles as a cheap and effective adsorbent for trapping and removing lignin from aqueous samples.

EXPERIMENTAL

Chemicals

Lignin, ferric chloride ($FeCl_3.6H_2O$), ferrous chloride ($FeCl_2.4H_2O$), sodium hydroxide (NaOH), ammonia (NH_3 25%) and hydrochloric acid (HCl 37%) with high purity were purchased from Merck (Darmstadt, Germany), Sigma-Aldrich (Taufkirchen, Germany) and Acros (New Jersey, USA). A stock standard solution of lignin with a concentration of 1000 mg L^{-1} was prepared in double distilled water. The stock solution of lignin was diluted with double distilled water to prepare standard solutions with concentrations in the range of 5-50 mg L^{-1} of lignin.

Equipment

UV-Vis and diffuse reflectance spectra (DRS) of lignin were obtained using a double-beam Sinco spectrophotometer (S-4100, Korea). All absorbance measurements were obtained using an Apel UV-Vis spectrophotometer (PD-303UV, Japan). For absorbance measurements, 280 nm was chosen as the maximum absorbance wavelength (λ_{max}) of lignin. X-ray diffraction (XRD) measurements were performed using a Philips diffractometer (PW1830, Holland) with monochromatized Cu K_α radiation. The pH of the solutions was adjusted with a Jenway pH meter (model 3320, Staffordshire ST15 0SA, England) supplied with a combined glass electrode. A Stuart CB162 motor-stirrer (Staffordshire ST150SA, England) was used to stir the solutions by a magnet. Magnetic separation was done using a strong super magnet with 1.4 Tesla magnetic fields (2.5 ×5 × 5 cm). The morphology of the synthesized samples was characterized with a scanning electron microscope (SEM) from Philips Company (XL30 ESEM, Holland).

Synthesis of magnetic nanoparticles

To prepare a stock solution of ferrous and ferric ions, 6.3 g of $FeCl_3.6H_2O$, 4.0 g of $FeCl_2.4H_2O$ and 3 mL of HCl (12 mol L^{-1}) were dissolved in 50 mL of deionized water in a beaker and the solution was degassed with argon gas for 20 min before use. Also, 500 mL of 1.5 mol L^{-1} NH_3 solution was degassed (for 15 min) and heated to 80 °C in the reactor. This solution was added to the ferrous and ferric solution dropwise, using a dropping funnel during 30 min under argon gas protection and vigorous stirring (1000 rpm). During the whole process, the solution was maintained at temperatures above 80 °C and argon gas was used to prevent the intrusion of oxygen. After the reaction, the obtained Fe_3O_4 MNPs were separated from the reaction medium by magnetic field (with 1.4 Tesla magnetic strength), and then they were washed four times with 500 mL deionized water. Finally, the obtained MNPs were resuspended in 500 mL of 1.5 mol L^{-1} NaOH to prevent agglomeration. The pH of the suspension was 11.0 and the concentration of the generated MNPs in suspension was estimated to be about 6.2 mg mL^{-1}.

For lignin separation from aquoues solutions, a proper amount of Fe_3O_4 MNPs (6.2 mg) was used to remove lignin from 40 mL of solution under optimized conditions (solution pH: 2-3, stirring for 10 min at room temperature).

RESULTS AND DISCUSSION

Characterization of MNPs

The characterization of Fe_3O_4 MNPs was performed using FT-IR and SEM techniques. An SEM image of the prepared MNPs is shown in Fig.1.

Fe_3O_4 surface morphology analysis demonstrated the agglomeration of many ultrafine particles with diameters below 43 nmFig. 2 shows the XRD pattern of the synthesized MNPs. The peaks at 2θ angles ranging from 30° to 40° and the absence of peaks at 2θ angles of 20° to 30° proved that the black synthesized powder was Fe_3O_4. In the proposed procedure, to achieve maximum adsorption efficiency, various parameters affecting the removal of lignin were studied and optimized with a univariate method.

Lignin adsorption using synthesized MNPs

In order to find the maximum absorption wavelength of lignin, the adsorption spectrum of lignin was obtained. According to the spectrum, 280 nm was selected as the best wavelength for quantitative measurements. To assess the stability of lignin at different pHs, the adsorption spectrum of a 100 mg L^{-1} lignin solution was obtained at various pHs.

All optimization studies were carried out according to the following procedure: (1) 40 mL aqueous solution of liquid (100 mg L^{-1}) was poured in a 50 mL beaker, and its pH was adjusted in the range of 2-3; (2) 1.0 mL of the Fe_3O_4 MNPs suspension (containing 6.2 mg of Fe_3O_4 MNPs) was added to the solution, (3) the mixture was stirred for 10 min, (4) after dye adsorption, Fe_3O_4 MNPs were quickly separated from the sample solution using a super magnet (1.4 T), (5) the residual dye concentration in the supernatant clear solution was determined spectrophotometrically using a direct calibration curve.

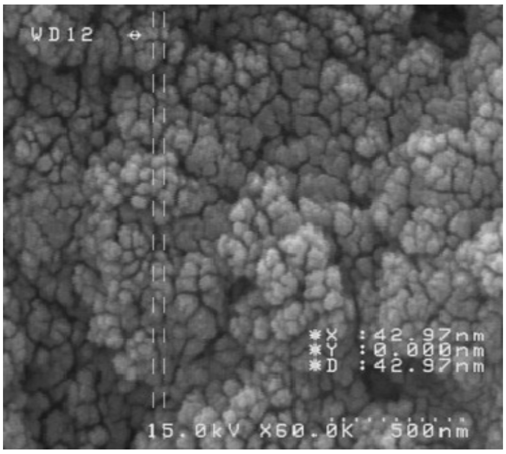

Figure 1: SEM image of Fe_3O_4 magnetic nanoparticles

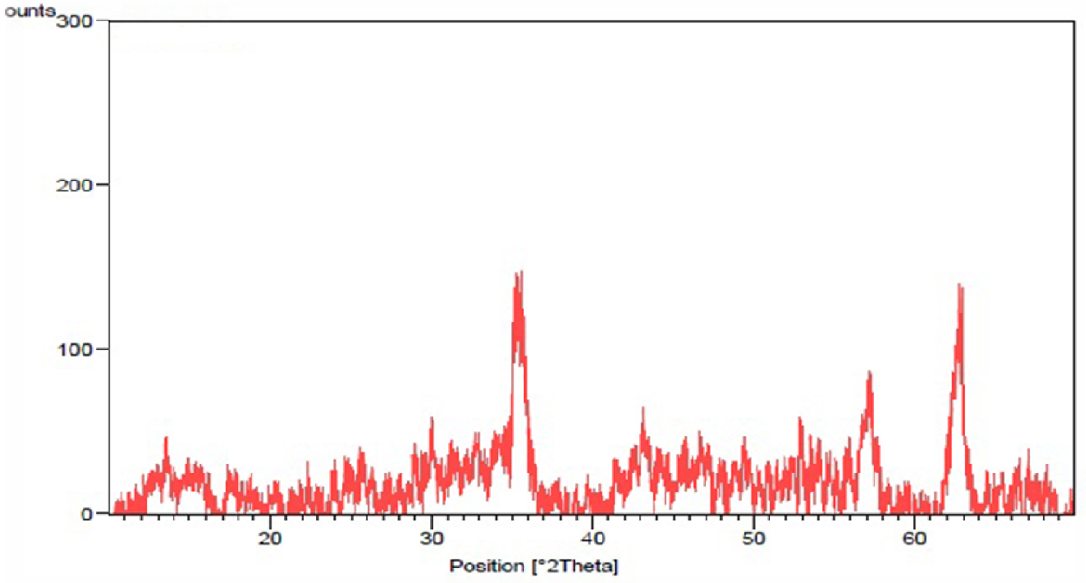

Figure 2: XRD pattern of synthesized Fe_3O_4 MNPs

The removal efficiency was calculated according to the equationbelow:

$$\text{Lignin removal efficiency } (\%) = \frac{C_0 - C_r}{C_0} 100$$

where C_0 and C_r are the initial and residual concentrations of lignin in the solution (mg L^{-1}), respectively.

For the study of lignin adsorbed onto the surface of magnetic nanoparticles, XRD and DRS spectra were obtained. The XRD pattern of Fe_3O_4 MNPs after lignin adsorption is shown in Fig. 3. Also, DRS studies (Fig. 4) strongly confirmed the lignin adsorption onto the surface of MNPs.

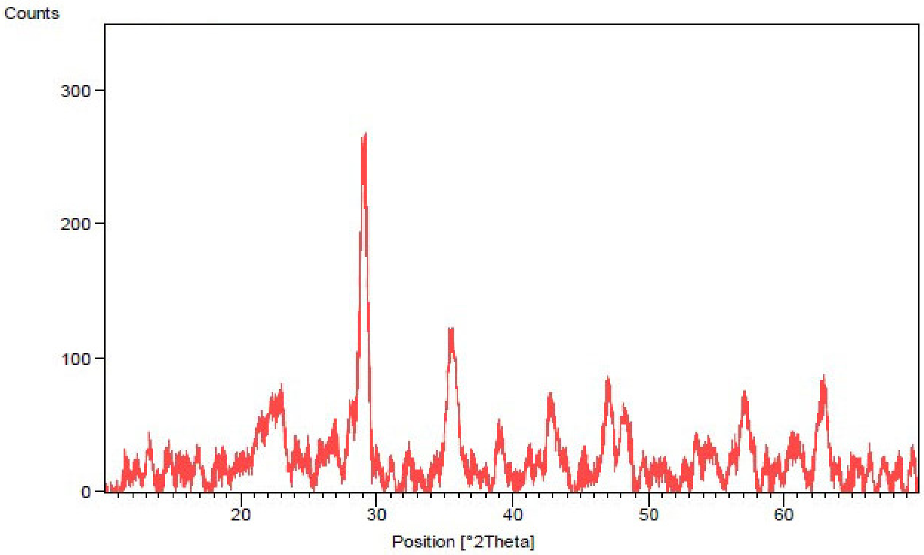

Figure 3: XRD pattern of the adsorbed lignin on synthesized Fe_3O_4 MNPs

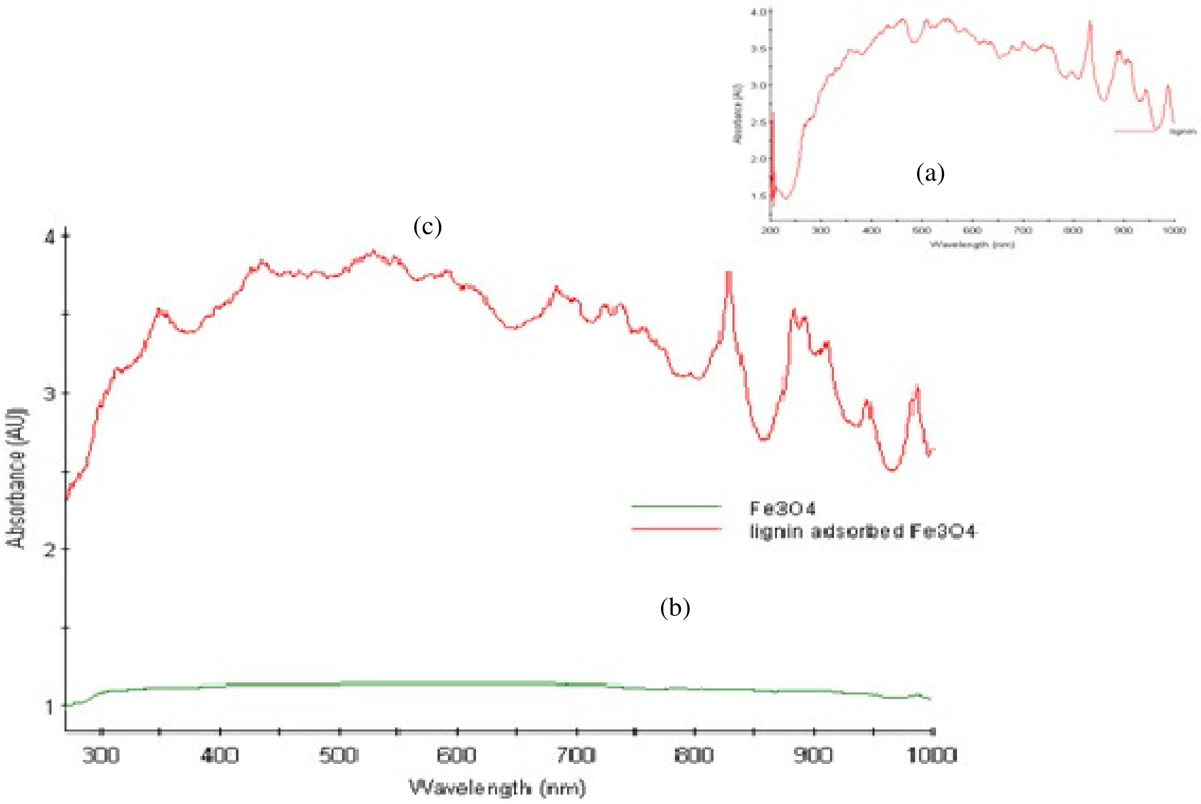

Figure 4: DRS spectrum of pure lignin (a), Fe_3O_4 before (b) and after lignin adsorption (c)

Influence of pH

The pH of the solution exerts a deep influence on the adsorptive uptake of lignin, presumably due to its influence on the surface properties of the adsorbent and ionization/dissociation of lignin. The effect of pH on the adsorption of lignin onto the surface of Fe_3O_4 MNPs was studied in the pH range of 2.0-9.0 and it was found that the adsorption decreased with an increase in pH, as can be seen from Fig. 5. The variation in the lignin removal efficiency with solution pH can be explained by considering the surface charge of the adsorbent. According to the zeta potential of Fe_3O_4 MNPs, their isoelectric point is at pH 7.[16]

Therefore, it is concluded that the surface of these particles has a positive charge at acidic pHs. The positively charged surface of Fe_3O_4 MNPs in acidic solutions was favorable for the adsorption. As pH increases, the positive charge density decreases.[16,17] Therefore, electrostatic attraction between the negatively charged lignin and the positively charged MNPs decreases. At pHs higher than 3, the charge density of the outer surface of the adsorbent and consequently the adsorption capacity decreases. The maximum adsorption capacity of the lignin is recorded at acidic pHs (pH: 2-3). Therefore, pH 2 was selected for all further adsorption experiments.At this pH, lignin is properly adsorbed onto the surface of Fe_3O_4 MNPs.

Effects of ionic strength and contact time

The effect of ionic strength on the adsorption of lignin (C_{lig}= 100 mg L^{-1}, V=40 mL) was investigated by the addition of NaCl to the solution in the range of 0-6% (w/v). The results showed that with the increase of the NaCl concentration, the adsorption capacity of the Fe_3O_4 MNPs decreased significantly (Fig. 6). Thus, the strategy of adding no salt was chosen for further studies. According to the results, the presence of high ionic content in the sample reduces lignin removal efficiency. Real waters, especially dyeing wastewaters, have high salt contents. The reduction of efficiency can be prevented with the addition of higher amounts of Fe_3O_4 MNPs and using longer adsorption times or by separating ions from the solution prior to the decolorization process.

The study of the adsorption capacity of lignin by Fe_3O_4 MNPs in the range of 1-120 min showed that the adsorption capacity of lignin increased with contact time up to 5 min, and then maximum removal is attained. For this reason, the optimum contact time was selected as 10 min.

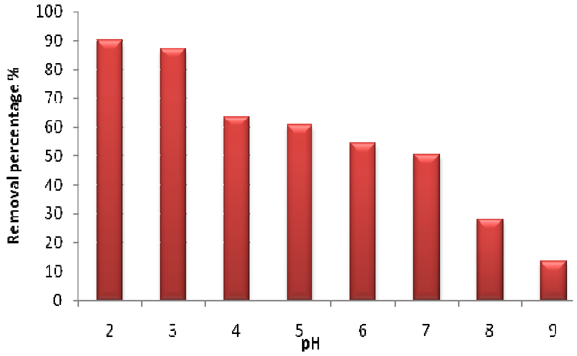

Figure 5: Effect of sample pH on lignin removal efficiency

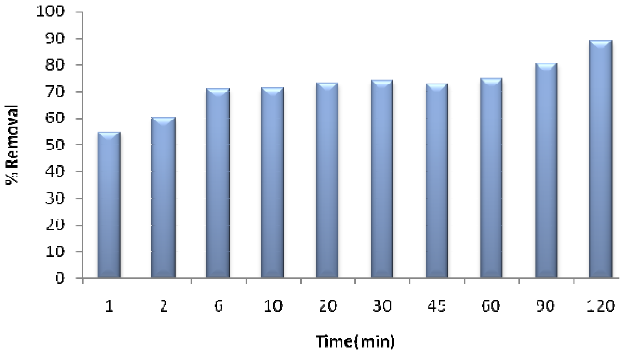

Figure 6: Effect of time on removal percent

Desorption and regeneration studies

Since lignin adsorption onto Fe_3O_4 MNPs is a reversible process, it is possible to regenerate or reuse Fe_3O_4 MNPs. The primary objective of regeneration is to restore the adsorption capacity of an exhausted adsorbent, while the secondary objective is to recover valuable components present in the adsorbed phase. Desorption of lignin from the Fe_3O_4 MNPs was studied using deionized water and different kinds of organic solvents, including acetonitrile, ethanol, and methanol. According to the results, the desorption ability of acetonitrile was found to be the highestof all the solvents.

The results showed that a desorption efficiency above 80% can be achieved in a short time of 10 min and in a one-step elution using 5 mL of acetonitrile. The recovery for deionized water, EtOH and MeOH was lower than 40%, 50% and 65%, respectively. The further studies showed that Fe_3O_4 MNPs can be regenerated by acetonitrile and reused for at least six successive removal processes with a removal efficiency above 80% (Fig.7).

Study of kinetic and adsorption isotherm

The kineticstudy of lignin adsorption onto Fe_3O_4 MNPs is required for selecting the optimum operating conditions for the full-scale bath processes. The kinetic parameters, which are helpful for the prediction of the adsorption rate, provide important information for designing and modeling the adsorption processes. Kinetic studies were performed in a 1.0 L glass beaker, where 5 mL of Fe_3O_4 MNPs (6.2 mg L^{-1}) was added into 400 mL of the lignin solution with 100 mg L^{-1} concentration at ambient temperature. The agitation speed of the motor stirrer was fixed at 300 rpm during the experiments. At time intervals ranging from 1 to 120 min, 10 mL of the samples were taken from the solution and were analyzed spectrophotometrically for residual lignin concentration in the solution. The kinetic data on the adsorption of the lignin onto Fe_3O_4 MNPs were studied using pseudo-first order,[18] pseudo-second order [19] and intra-particle diffusion[20] models to find out the adsorption rate expression. The conformity between experimental data and the model-predicted values was expressed by the correlation coefficients (R^2).

According to the results, the removal rate was very fast during the initial stages of the adsorption processes. The adsorption process followed the pseudo-second order kinetics. The rate of the pseudo-second order reaction may be dependent on the amount of the solute sorbed on the surface of the adsorbent and the amount of sorption at equilibrium. The kinetic rate equations can be rewritten as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e{}^2} + \left(\frac{1}{q_e}\right) t$$

where q_t and q_e are the values of adsorbed lignin at each time and at equilibrium, respectively, and k_2 is the pseudo-second order rate constant. The fitting of kinetic data to the pseudo-second order kinetic model is shown in Fig. 8.

Fig. 9 shows the equilibrium concentrations of lignin versus time after sorption by Fe_3O_4 MNPs at various initial concentrations.

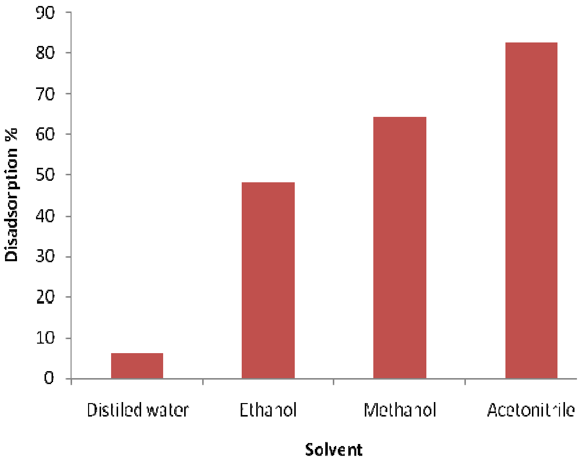

Figure 7: Desorption of lignin from Fe_3O_4 MNPs (5 mL desorption solvent)

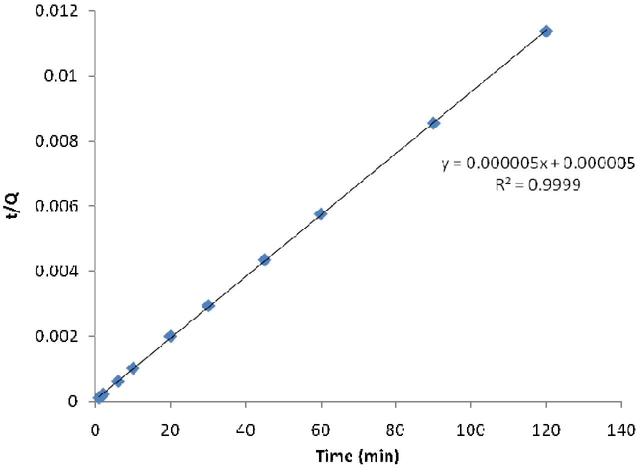

Figure 8: Fitting of kinetic data to pseudo-second order kinetic model (V = 400 mL,C_{lig} = 100 mgL^{-1}, pH = 2.0, 5 ml Fe_3O_4 MNPs)

Table 1
Kinetics of lignin adsorption on Fe_3O_4 MNPs

Intraparticle model			Pseudo-second order kinetic			Pseudo-first order kinetic			Initial concentration
R^2	C	K_p	R^2	K_2	Q_e	R^2	K_1	Q_e	
0.9048	2248.1	34.598	0.9998	86.755	2597.43	0.9411	0.0525	370.169	50
0.781	4159.9	92.655	0.9997	89.59	5025.12	0.9369	0.05988	933.68	100
0.9797	6762.6	117.72	0.9995	112.09	7692.31	0.8893	0.06332	1771.74	150
0.7882	9552.3	106.27	0.9999	116.56	10576.87	0.5959	0.09166	1759.138	200

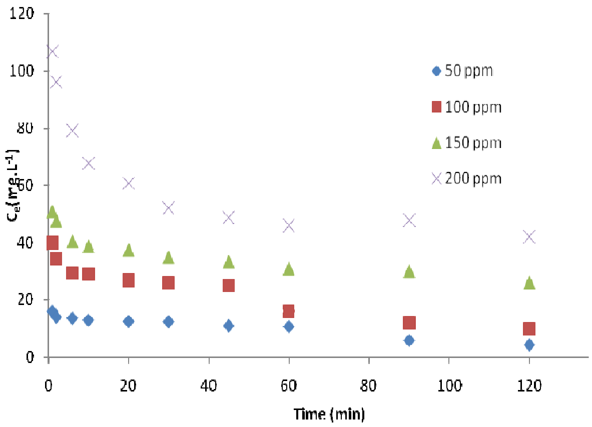

Figure 9: The kinetic curve of lignin adsorption on Fe_3O_4 MNPs for lignin concentration in the range of 50-200 mg L^{-1} (V = 400 mL, pH = 2.0, 5 ml Fe_3O_4 MNPs)

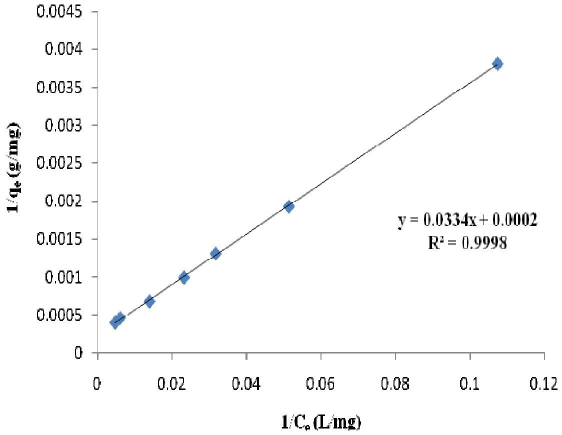

Figure 10: Fitting of isotherm data to the Langmuir model (V = 40 mL, pH = 2.0, 1 ml Fe_3O_4 MNPs)

The pseudo-second order rate constant, k_2, was determined as 89.59 g mg^{-1} min^{-1} and the equilibrium adsorption capacity was obtained as 5025.12 mg g^{-1}. The linear correlation coefficient value (R^2) was found to be the best. The best fit of the pseudo-second order kinetic model in the present system shows the adsorption of the dye followed by the chemisorption mechanism via electrostatic attraction. The obtained values for pseudo-first and -second order kinetics, as well as for intraparticle models, are summarized in Table 1.

The adsorption isotherm is important from both theoretical and practical points of view. In order to optimize the design of an adsorption system for lignin removal, it is important to establish the most appropriate correlations of the equilibrium data of each system. Equilibrium isotherm equations are used to describe the experimental sorption data. The parameters obtained from the different models provide important information on the sorption mechanisms and the surface properties and affinities of the adsorbent. In this study, the two most common isotherms, Langmuir[21] and Freundlich[22] models, were used to describe the experimental adsorption data. The equilibrium adsorption isotherms were determined using batch studies. 40 ml of the lignin solution with various initial lignin concentrations of 50-200 mg L^{-1} were poured into a glass bottle and after pH adjustment in the range of 2-3, 1.0 ml of Fe_3O_4 MNPs (6.2 mg mL^{-1}) was added to the mixture. Then, the mixture was stirred for 60 min. The amount of lignin uptake by the Fe_3O_4 MNPs, q_e (mg g^{-1}), was obtained as follows:

$$q_e = (C_0-C_e)/m_s$$

where C_0 and C_e (mg L^{-1}) are the initial and equilibrium concentrations of lignin in solution, respectively, and m_s is the concentration of Fe_3O_4 MNPs (mg L^{-1}). The Langmuir and Freundlich isotherms can be linearized as follows:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_{max}} + \frac{1}{q_{max}} C_e \qquad \text{Langmuir equation}$$

$$\log q_e = \log K_F + 1/n \log C_e \qquad \text{Freundlich equation}$$

where q_e is the equilibrium lignin concentration on the adsorbent (mg g^{-1}), C_e– the equilibrium lignin concentration in solution (mg L^{-1}), q_{max}– the monolayer capacity of the adsorbent (mg g^{-1}), K_L– the Langmuir constant (L mg^{-1}) and related to the free energy of adsorption, K_F– the Freundlich constant (L mg^{-1}) and n (dimensionless) – the heterogeneity factor.[23]

In the Langmuir model, a plot of $1/q_e$ versus $1/C_e$ should indicate a straight line of the slope $1/q_{max}$ and an intercept of $1/(K_L\ q_{max})$. The correlation coefficient showed strong positive evidence on the adsorption of lignin onto Fe_3O_4 MNPs (R^2=0.9998), following the Langmuir isotherm. The maximum monolayer capacity q_{max} and the Langmuir constant, K_L (L mg^{-1}), were calculated from the Langmuir model as 2554.422 mg g^{-1} and 0.812 L mg^{-1}, respectively. The fittingof the data for lignin adsorption onto the Fe_3O_4 MNPs suggested that the Langmuir model (Fig. 10) gave a better fit than the Freundlich model (R^2 = 0.9842, n = 0.563).[24]

CONCLUSION

The sorption of pollutants from aqueous solutions plays a significant role in water pollution control. In this context, the utilization of Fe_3O_4 MNPs as an efficient sorbent was successful in removing the lignin from the wastewater samples. The adsorption followed the pseudo-second order kinetic model, suggesting chemisorption. The Fe_3O_4 MNPs are synthesized easily and can be regenerated. Due to their very high surface areas, high adsorption capacity can be achieved using Fe_3O_4 MNPs in short times. The data reported here should be useful for the design and fabrication of an economical treatment process for dye adsorption in industrial effluents. In addition, it should be noted that the Fe_3O_4 MNPs adsorbents are magnetically recoverable, which would be very useful and time-savingin their practical applications.

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