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Parametric Evaluation of the Adsorption of Malachite Green and Congo Red on Chitin Flakes

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ABSTRACT

The sorption of synthetic dyes, Congo Red (CR) and Malachite Green (MG) on a low-cost biopolymer, chitin flakes, was investigated in kinetic and equilibrium studies. Factors affecting adsorption such as pH, contact time, adsorbent dose, dye concentration and temperature was studies in batch process. Maximum dye adsorption on chitin occurred within a contact time of 18 hours, adsorbent dose of 5.0 g/L, solution pH of 7.0 for an initial dye concentration of 150 mg/L. Experimental data revealed stronger adsorption of congo red on chitin flakes, compared to malachite green. Congo red sorption on chitin flakes was largely independent of pH, while malachite green sorption was significantly affected by pH. The kinetic data was fitted to pseudo first order, second order and Weber-Morris intra-particle diffusion model. The process of dye removal followed pseudo first-order kinetics for MG and pseudo first order for CR. The adsorption capacities, calculated using Langmuir isotherm, was56.8 mg/g for congo red and 42.1 mg/g for malachite green.

Key words: Dyes, Chitin, Adsorption, Biopolymer, Langmuir

INTRODUCTION

Presence of recalcitrant chemicals such as dyes presents a persistent problems to source water in India, especially rivers and streams. Treatment of such dyes prior to their discharge, is essential to negate environmental and human health risks. Wastewater treatment in textile industries is usually a combination of reverse osmosis systems and aerobic bioreactors [1, 2]. However, high maintenance costs of the treatment units, and decreased degradation efficiency for modern synthetic dyes in bioreactors has resulted in many industrial effluent treatment plants failing to meet the minimum national standards. Conventional municipal wastewater treatment is inefficient in the complete removal of dyes [1, 2]. Use of activated carbon systems, ion-exchange and other treatments suffer from high maintenance costs. Emerging technologies such as UV/hydrogen peroxide and other advanced oxidation processes, while promising, have their own limitations due to the chance of secondary contamination and handling of chemicals [1, 2]. Despite its limitations, adsorption is generally favored as it provides a stable system, and can be cost effective upon use of low-cost adsorbents. Materials such as peat, wood chips and lignin have been used for dye removal [1-7]. Chitin/Chitosan flakes, beads, and composites have been effectively used in the removal of dyes, heavy metals and other recalcitrant compounds [8-14].Adsorption of reactive dyes such as methylene blue on chitin/chitosan was best described by Langmuir adsorption and was observed to have good sorption capacities. The purpose of this study is to evaluate the adsorption characteristics of a low-cost adsorbent, chitin, for the removal of dyes from wastewater.

MATERIALS AND METHODS

Materials and Characterization

Chitin is a high-molecular weight linear polymer of N-acetyl-D-glucosamine (N-acetyl-2-amino-2-deoxy-D-glucopyranose). Chitin ($C_8H_{13}NO_5$) from crushed crab shells (Loba Chemie Pvt., Mumbai, India) in the form of large flakes was used throughout this work without any preliminary treatment. The chitin flakes were characterized for their zeta potential and surface area. The particle size of the chitin flakes ranged from 10-500 µm. The zeta potential was determined using a Laser Zeta Meter^{TM} from PenKem, Inc (Bedford Hills, NY). The zeta potential measurements showed that the isolectric point was at pH = 3.1 (pH_{pzc} = 3.1). The surface area of the carbon particles was assessed by Brunauer-Emmet-Teller (BET) surface area analyzer. Chitin flakes had a high content of nitrogen (6.89%), and a surface area of 9.58 m^2/g.

Adsorption Experiments

Stock solutions (500 mg L^{-1}) of Congo red (CR) and Malachite green (MG) were prepared in de-ionized water and maintained at near neutral pH (~7.0). Dye sorption envelopes (removal as a function of pH) were determined using 0.1-0.15mM for CR and 0.1-0.15 mM for MG. The starting pH of the selenium solutions was adjusted between 2.5 and 10.5 using either 0.01N HCl or NaOH. The final pH of the suspension was recorded after 24 hours. The pH of the suspension was relatively stable throughout the experiment, with a marginal change of ±0.5 pH units compared to the initial pH. A control sample (dye solution without any adsorbent) was maintained for 24hrs. The samples were subsequently centrifuged and filtered through 0.45 µm Nylon filters. Additional batch experiments performed were: (1) adsorption isotherm plots using increasing dye (CR and MG) concentrations from 0.04 – 0.44 mM at pH 7.0 ± 0.2 using 2 g $L^{-1}$of sorbent; and (2) adsorption kinetics for 72 hours using 0.23 mM CR and 0.17 mM MG at a adsorbent dosage of 1,2 and 5 g/L. Experiments were performed in triplicate and average values reported. Concentration of dyes was measured using UV-Vis spectrophotometer and the wavelength for CR and MG were 498 nm and 621 nm, respectively. The detection limit was 0.5 mg L^{-1}.

RESULTS AND DISCUSSION

Equilibrium pH Studies

Figures 1 (A & B) illustrate the dye removal as a function of pH. The percentage dye removal was calculated by the following relation:

$$\%\, dye\ removal = \frac{[dye]_{initial} - [dye]_{final}}{[dye]_{initial}} \times 100 \qquad (1)$$

Where $dye_{initial}$ and dye_{final} are the initial and the final dye concentrations in solution. The surface coverage (Γ, mg m^{-2}) was calculated as the amount of dye removed per unit surface area of the sorbent, and is shown in Figures 2 (A & B). At equilibrium conditions, the percent removal of CR appeared to increase with pH up to a pH of 7.5-8, and then slightly decreased with increasing pH (Figure 1 A). With 0.1 mM CR, the percent removal was observed to reach almost 99 % with no significant shifts in percent removal across pH. With increase in concentration from 0.1 to 0.15 mM, the percent removal reduced significantly with maximum reducing from 99% to 69% at same pH, as expected. If the surface of the adsorbent is saturated with the solute (particularly in the case of mono-layer adsorption), increase in solute concentration would result in lower removal %. With increasing pH from 3 to 7.5, CR removal increased from 30% to 59%, before slightly decreasing to 55% with a further pH increase. The plot of surface coverage vs. pH mimicked the sorption envelope curves. At lower CR concentration, the surface coverage of the dye on chitin was almost similar across pH (ranging from 2.07 – 2.35 mg/m^2 for 0.1 mM). With increase in CR concentration to 0.15 mM, the amount of dye adsorbed on chitin increase with maximum coverage of 3.15 mg/m^2. Congo red is a dipolar molecule, existing in anionic form at basic pH and cationic form in acidic pH [5]. Sorption of CR on chitin can best be explained via the forces of electrostatic attraction. In acidic pH below 3, surface charge density on chitin is mostly positive which repulses the cationic CR molecule. As the pH increases toward basic pH, the surface charge on chitin becomes increasingly negative, which results in the attraction of the cationic form of CR to the chitin surface. With further increase in pH, the surface charge density of chitin is increasingly negative and the CR ion is also negatively charged, resulting in electrostatic repulsion and therefore, a slight decrease in percent removal was observed.

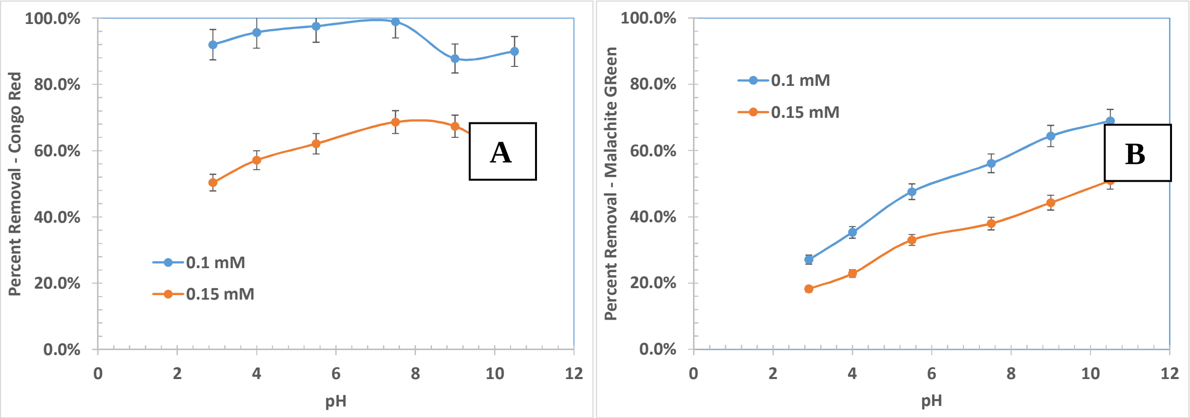

Figure 1. Sorption percent removal of Congo red (A) and Malachite green (B) on Chitin vs. solution pH

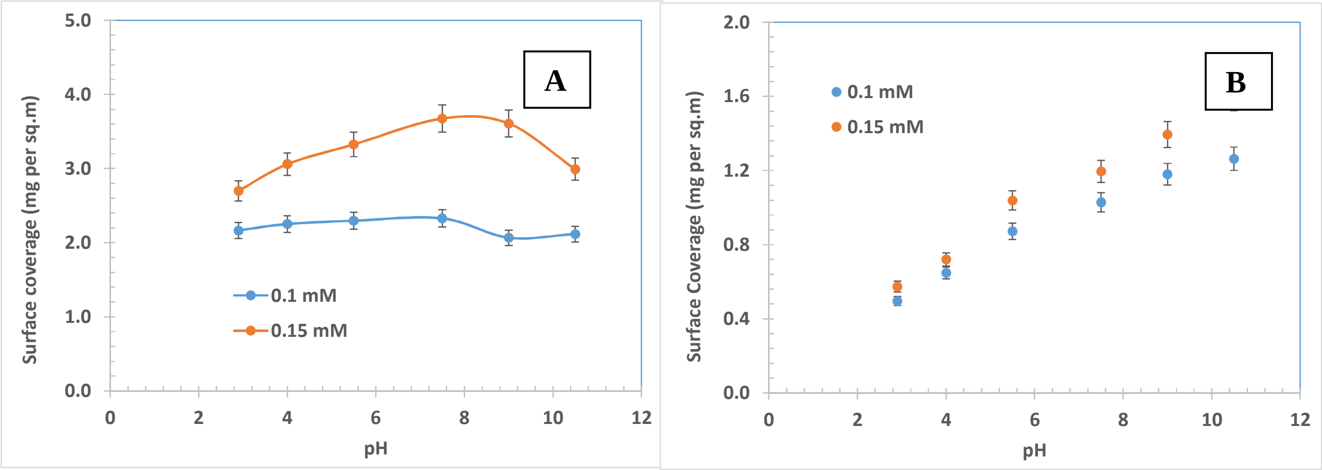

Figure 2. Sorption surface coverage (mg m^{-2}) of Congo red (A) and Malachite green (B) on Chitin vs. solution pH

While the percent removal and surface coverage plots for MG were also similar, the effect of pH on adsorption of MG on chitin was more pronounced. As can be seen in Figure 1 B, percent removal increased with increasing pH, with the maximum removal obtained at basic pH (70% at pH = 10.5). Malachite Green is a cationic dye, and carboxylic groups of MG (pKa = 10.3) are protonated and therefore, have high positive charge density at a lower pH [6]. At low pH, the surface charge density on chitin is also positive, resulting in electrostatic repulsion between the dye and the surface. As the pH increases, OH$^-$ attaches to the sorbent surface, and attracts the negatively charged MG cation, and explains the increase in percent removal with pH. Nevertheless, it was observed that CR is adsorbed more on chitin flakes, compared to MG.

Kinetic Studies

Adsorption of CR and MG as a function of time was performed at pH 7.0±0.5. The sorption capacity of dyes on chitin was calculated at various time intervals (q_t) and also at equilibrium (q_e). The sorption capacity (mg per gm) was fitted to the Lagergren equation (equation 3), which assumes a pseudo first order adsorption rate, pseudo second order rate expression (equation 4) and Weber Morris intraparticle diffusion expression (equation 5) [5-6].

$$q_t \ or \ q_e = \frac{[dye]_{initial} - [dye]_{final}}{amount\ of\ sorbent} \tag{2}$$

$$\ln\left(\frac{q_e}{q_e - q_t}\right) = kt \quad Lagergen\ Equation \tag{3}$$

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{kq_e^2} \quad Pseudo\ Second\ order\ Equation \tag{4}$$

$$q_t = k_i\sqrt{(t)}\ \mathit{Intraparticle\ Diffusion\ Equation} \qquad (5)$$

Effect of Adsorbent Dose

Dye degradation kinetics is presented in Figure 3 A and B for various adsorbent dosages. As can be seen, CR is reduced completely upon using 5 g/L of chitin flakes. With reduced dosage, the percent dye reduction is decreased as expected. Adsorption is generally a function of the number of active sites on the sorbent surface. Increased number of adsorption sites increased with adsorbent dosage, resulting in more sorption. Similar kinetic curves were also observed for MG, albeit the difference in adsorption upon increasing dosage was not as pronounced when compared to that for CR.

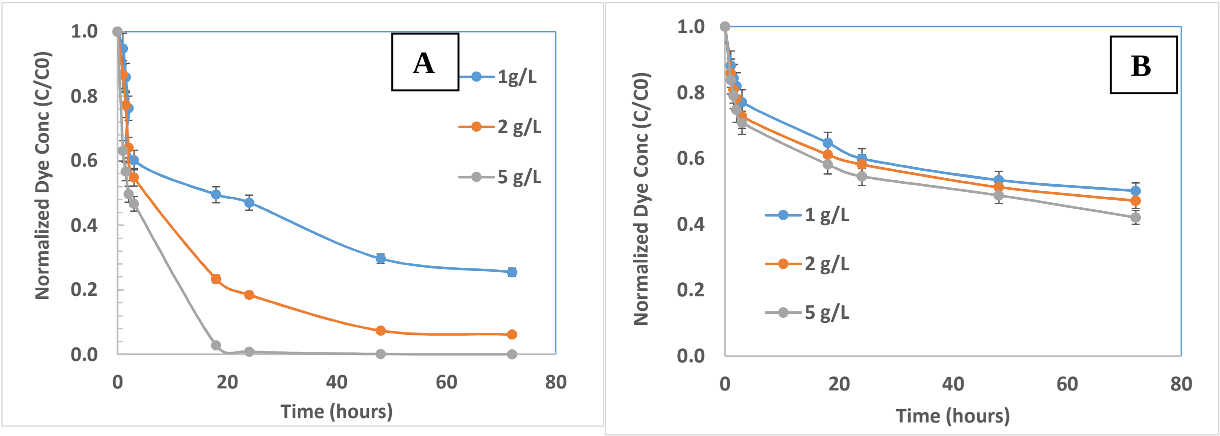

Figure 3. Degradation kinetics of Congo red (A) and Malachite green (B) on Chitin flakes

The kinetic data was fitted to the linear forms of the equations 3, 4 and 5 and the rate constants were determined. Table 1 presents the rate constants for the fit to Lagergen equation, pseudo second order equation and Weber-Morris intraparticle diffusion equations. It was observed that adsorption of CR was best described by pseudo first order kinetics, while that of MG was best represented by pseudo second order kinetics. In other studies [5-6], CR and MG sorption on activated carbon and neem sawdust was described by pseudo second order and pseudo first order, respectively. Intraparticle diffusion model did not fit well to both the adsorption data. Irrespective of the kinetic rate expression, it was observed that the rate constants increased with increased dosage, suggesting that the adsorption of dye was controlled by the number of active surface sites.

Table 1. Rate Constants for Dye Degradation

Lagergen Equation (Pseudo First Order)	**Adsorbent Dosage**					
	1 g/L		**2 g/L**		**5 g/L**	
	K (L/min)	**R^2**	**K (g/ mg-min)**	**R^2**	**K (mg/g-min)**	**R^2**
Congo Red	0.06	0.93	0.11	0.98	0.16	0.95
Malachite Green	0.06	0.92	0.06	0.82	0.07	0.83
Pseudo Second Order Equation	**K (L/min)**	**R^2**	**K (g/ mg-min)**	**R^2**	**K (mg/g-min)**	**R^2**
Congo Red	0.002	0.81	0.02	0.72	0.11	0.83
Malachite Green	0.009	0.92	0.014	0.95	0.02	0.98
Weber Morris Intraparticle Diffusion Expression	**K (L/min)**	**R^2**	**K (g/ mg-min)**	**R^2**	**K (mg/g-min)**	**R^2**
Congo Red	18.35	0.85	12.98	0.84	5.23	0.51
Malachite Green	4.77	0.85	2.56	0.74	1.1	0.65

Dye Adsorption Isotherms

Langmuir and Freundlich adsorption isotherm were used to determine the maximum adsorption capacity of the chitin flakes, according to equations 6 and 7 respectively [5-12].

$$q_e = \frac{q_{max}K_aC_e}{1+K_aC_e}\ \mathit{Langmuir\ Equation} \qquad (6)$$

$$q_e = K_f C_e^{1/n} \ Freundlich\ Equation \qquad (7)$$

Figure 4 below shows the sorption isotherms for CR and MG. With increasing equilibrium concentration, the uptake of dyes on chitin increased, before stabilizing to asymptotic curve. The data from the isotherm was fitted to linearized form of equations 6 and 7, and the maximum capacities are presented in Table 2. Both CR and MG adsorption isotherms were best described by Langmuir isotherm. The maximum capacity deduced from the isotherm showed a higher capacity for CR (56.8 mg/g), when compared to MG (42.1 mg/g). The constant K_a, constant related to the energy or net enthalpy, or adsorption potential was also observed to be higher for CR, compared to MG. The maximum capacity of chitin for CR and MG sorption was compared to other materials and is presented in Table 3. As can be seen in the table, sorption of CR was higher in chitin flakes compared to activated carbon [5, 6, 13]. Similarly, sorption of MG was comparable to other adsorbents.

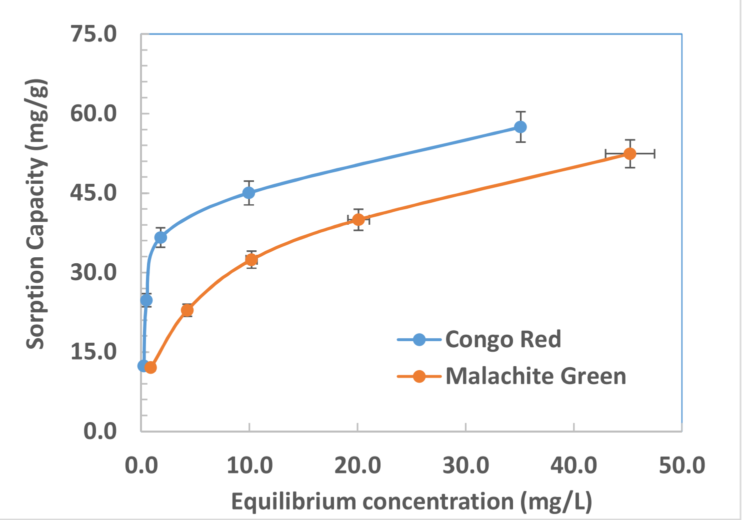

Figure 4. Adsorption isotherm of Congo red and Malachite Green on Chitin flakes

Table 2. Maximum capacity of chitin for dye removal

Langmuir Isotherm	**Q_{max} (mg/g)**	**K_a**	**R^2**
Congo Red	56.8	1.17	0.98
Malachite Green	42.1	0.44	0.96
Freundlich Isotherm	**K_f**	**n**	**R^2**
Congo Red	24.5	3.7	0.9
Malachite Green	12.9	2.7	0.99

Table 3. Comparison of the adsorbent capacities for dye removal

Adsorbent	**Adsorption Capacity (Q_{max}- mg/g)**		
	Congo Red	**Malachite Green**	**Reference**
Activated carbon	6.7	149	[5-7]
Mesoporous carbon	45-53	476.1	[7, 12]
MCM-48	-	158.7	[7]
Chitosan Beads	-	93.55	[7]
Bentonite clay/Kaolin/Zeolite	3.7 – 35.4	0.18	[7, 13]
Activated charcoal	-	7.7	[7]
Chitin flakes	56.8	42.1	This work
Neem saw dust	-	4.35	[6]

CONCLUSION

The adsorption of dipolar CR and cationic MG on chitin was studied. The conclusions are:
1. Adsorption of CR on chitin is significantly higher than that of MG. Maximum capacity of chitin for CR was higher than that for chitin.

2. Adsorption of CR on chitin was not greatly affected by change in pH. However, sorption of MG on chitin increased significantly with increasing pH.
3. Adsorption kinetics of CR and MG was best described by pseudo first order and second order kinetics, respectively.

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