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RESEARCH ARTICLE

Adsorption of malachite green using NPP-modified bentonite in synthetic medium and textile wastewater

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SUMMARY : Adsorption of malachite green (MG) using sodium pyrophosphate modified bentonite (NPP-bentonite) in synthetic medium and textile wastewater was investigated in batch method. The effect of pH, adsorbent dose, contact time and initial dye concentration on MG adsorption was studied. XRF technique was employed for composition study of NPP-bentonite. The adsorption equilibrium was attained at 60 min and adsorption efficiency reached maximum of 94.90 % at pH 7.0 with adsorbent dose of 1 g/L and initial dye concentration of 50 mg/L. The equilibrium data showed good fitting for Langmuir isotherm model. The result showed applicability of NPP-bentonite as an effective low cost adsorbent for adsorption of MG from textile wastewater.

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Key Words :
Malachite green, Bentonite, Sodum pyrophosphate, Isotherm, Wastewater

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Discharge of wastewater containing dyes into water bodies causes environmental disposal problems due to non – biodegradable and persistent nature. Malachite green is one of the toxic dyes used in textile, leather, paper and paint industries (Hameed and El-Khaiary, 2008). Effects on humans mainly include carcinogenesis, mutagenesis, respiratory toxicity and reduction in fertility (Srivastava *et al.*, 2004).

Chemical and biological treatments for removal of dyes from wastewater are either ineffective or costly process. Adsorption is one of the simple and cost effective techniques provided that the adsorbents used are of low cost. A number of low cost adsorbents are being used for the removal of dyes from wastewater, which mainly include bottom ash (Gupta *et al.*, 2004), degreased coffee bean (Baek *et al.*, 2010), neem sawdust (Khattria and Singh, 2009), bentonite (Bulut *et al.*, 2008), montmorillonite (Tahir *et al.*, 2010) and Moroccan clay (Bennani Karim *et al.*, 2011).

Clay minerals are considered to be excellent adsorbents because of their large surface area, chemical and mechanical stability, layered structure and high cation exchange capacity (Sarma *et al.*, 2011). Modification of clay has received attention due to characteristics changes effected on natural clay which improves its performance compared to natural clay. The modified clays employed as adsorbents for removal of dyes include Reactive blue 19 by dodecyltrimethylammonium bromide (DTMA) modified bentonite (Ozcan *et al.*, 2007), Aniline blue by sodium tetraborate (NTB) modified kaolinite (Unuabonah *et al.*, 2008) and hexadecyltrimethylammonium bromide (HDTMA) modified montmorillonite (Arellano-Cardenas *et al.*, 2013) have been reported.

The present study was done on the adsorption of synthetic MG using NPP-bentonite as adsorbent. Detailed study was carried out covering effect of pH, contact time, adsorbent dose and initial dye concentration on the performance of adsorbent. Langmuir and Freundlich isotherm models were used for analyzing the equilibrium data. The practical applicability of NPP-bentonite was assessed using textile wastewater containing MG.

EXPERIMENTAL METHODOLOGY

The malachite green (MG) dye stock solution (1000 mg/L) was prepared by dissolving a known amount of MG (Merck, A.R grade, India) in deionised water and further diluted to obtain working solutions of lower concentration. The pH adjustment of the solutions was carried out using 0.01N HCl and 0.01N NaOH.

The natural bentonite was procured from S.B. Patil Minerals Limited, Gulbarga (Karnataka), India. The powdered sample was washed with deionised water and dried at room temperature. The dried sample was treated with 0.01% sodium pyrophosphate solution for 24 h. The resulting NPP-bentonite was centrifuged and washed several times with deionised water, oven dried at 110°C for 24 h, cooled and stored in air tight container for further use. The chemical composition of NPP-bentonite was found out using X-ray fluorescence spectrometer (Philips PW 2404, Netherlands).

The wastewater containing dyes was collected from textile industry located in Bangalore, Karnataka, India. Standard methods (Clesceri *et al.*, 1998) were employed to determine the physico-chemical characteristics of textile wastewater and results are presented in Table A.

Table A : Physico-chemical characteristics of textile wastewater

Parameters	Results
pH	8.64
Colour	Greenish blue
TDS(mg/L)	3572
COD(mg/L)	719

Batch experiments were carried out at room temperature; for experimental run 100 ml of 50 mg/L dye solution at the desired pH were taken in 250 ml Erlenmeyer flasks. A known amount of adsorbent was added and the mixture was shaken at a constant stirring speed of 200 rpm on a mechanical shaker (KEMI KRS 110, India) for a fixed time period. The mixture was centrifuged at 5000 rpm for 10 min and concentration of dye remaining in the supernatant solution was determined by UV-Visible spectrophotometer (Systronics 108, India) at λ_{max} of 620 nm. All experiments were conducted in triplicate and average values were considered. The percentage adsorption was calculated by the following equation :

$$\%A = \frac{(C_i - C_e)}{C_i} \times 100 \quad (1)$$

where, C_i and C_e are initial and final dye concentrations (mg/L), respectively.

The effect of pH on MG adsorption was studied as follows: NPP-bentonite (1 g/L) was added to each of 250 ml Erlenmeyer flasks containing 100 ml of 50 mg/L MG solution. The initial pH of the solution was adjusted to 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0 and 10.0 using 0.01N HCl and 0.01N NaOH solution. After 60 min of shaking, the solution was centrifuged and MG was estimated by UV-Visible spectrophotometer.

The effect of adsorbent dose on MG adsorption was studied as follows: NPP-bentonite in doses of 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5 and 5.0 g/L was taken in different 250 ml Erlenmeyer flasks. To this 100 ml of 50 mg/L MG solution was added and pH was adjusted to 7.0. The resulting solution was agitated for 60 min and the unabsorbed MG in filtrate was found using UV-Visible spectrophotometer.

The effect of contact time on MG adsorption was studied as follows: MG solution (100 ml of 50 mg/L) was added into 1 g/L NPP-bentonite containing Erlenmeyer flasks and pH was adjusted to 7.0. The resulting solution was shaken on a mechanical shaker for different time intervals of 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 110 and 120 min. The residual concentration of MG in filtrate was determined by UV-Visible spectrophotometer.

The effect of initial dye concentration on MG adsorption was studied as follows: Hundred ml of MG dye solution in 10, 20, 30, 40 and 50 mg/L concentration were taken in separate Erlenmeyer flasks. NPP-bentonite (1 g/L) was added and pH was maintained at 7.0 with contact time of 60 min. The unabsorbed MG concentration in supernatant solution was determined by UV-Visible spectrophotometer.

EXPERIMENTAL FINDINGS AND DISCUSSION

The chemical composition of NPP-bentonite is shown in Table 2.The pH of dye solution is one of the most important parameters for adsorption of MG. The effect of pH on adsorption of MG by NPP-bentonite is depicted in Fig. 1. The per cent adsorption of MG increased from 73.40 to 94.90 per cent with increase in pH from 2.0 to 7.0. The maximum adsorption occurred at pH 10.0. This is because, at lower pH, NPP-bentonite is covered with more number of H_3O^+ ions which get replaced by OH^- ions as the pH increases making the surface negatively charged (Sarma *et al.*, 2011). Eventhough maximum adsorption efficiency was at pH 10.0; all studies were carried out at neutral pH 7.0, keeping in mind the colour stability of MG. The effect of adsorbent dose on

Table 1 : Chemical composition of NPP-bentonit

Constituents	% Weight
SiO_2	62.10
Al_2O_3	16.83
Fe_2O_3	3.67
CaO	2.98
MgO	1.35
Na_2O	2.16
K_2O	0.54
LOI*	10.11

*Loss of ignition

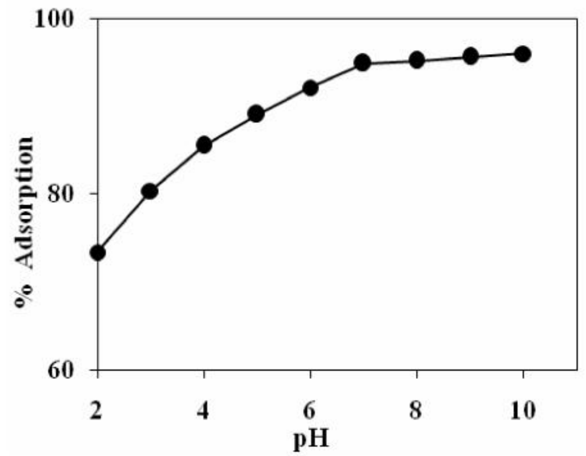

Fig. 1 : **Effect of pH on MG adsorption by NPP-bentonit**

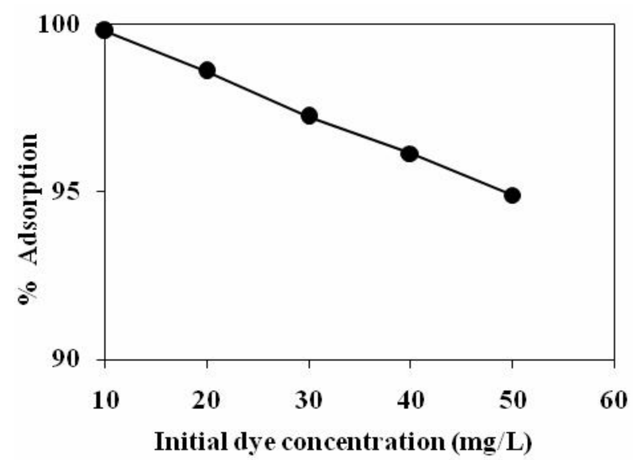

Fig. 4 : **Effect of initial dye concentration on MG adsorption by NPP-bentonit**

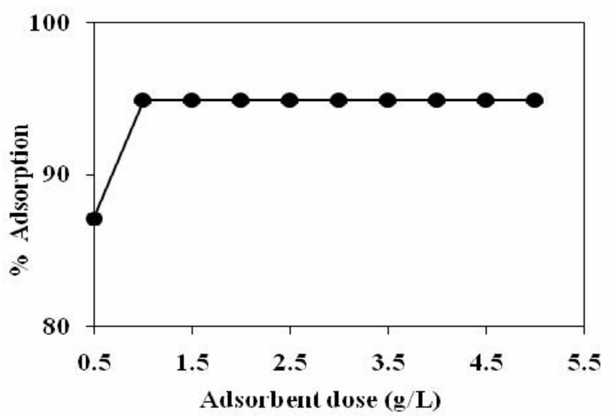

Fig. 2 : **Effect of adsorbent dose on MG adsorption by NPP-bentonit**

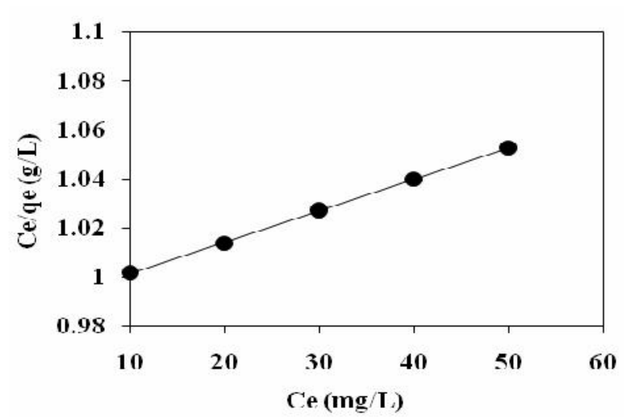

Fig. 5 : **Langmuir isotherm plots for MG adsorption by NPP-bentonit**

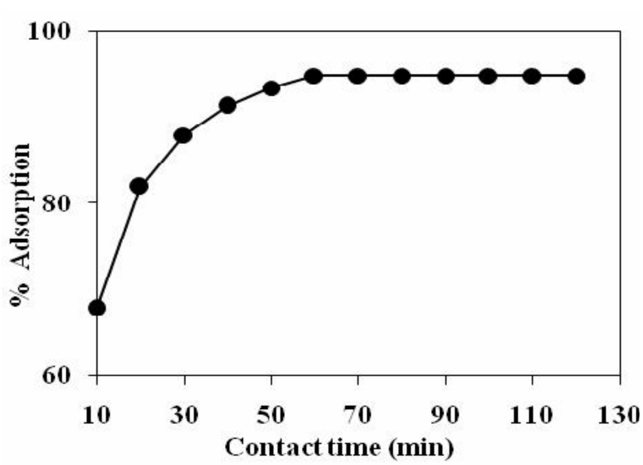

Fig. 3 : **Effect of contact time on MG adsorption by NPP-bentonit**

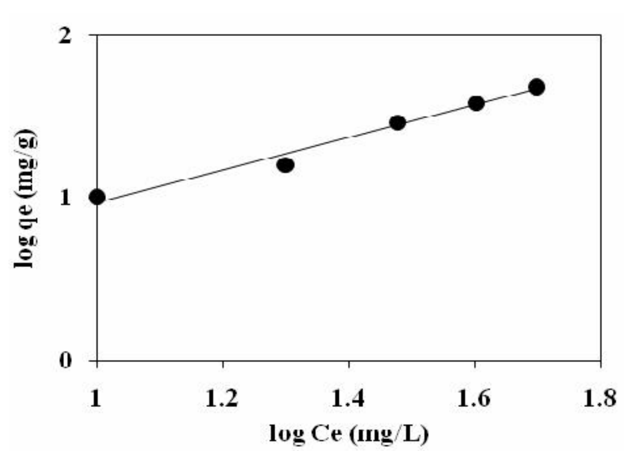

Fig. 6 : **Freundlich isotherm plots for MG adsorption by NPP-bentonit**

adsorption of MG by NPP-bentonite is presented in Fig. 2. The per cent adsorption increased from 87.10 to 94.90 % with the increase in adsorbent dose from 0.5 to 1 g/L. This is because initially adsorbent consists of more number of adsorption sites which in turn increases the binding capacity. Further increase in adsorbent dose beyond 1 g/L keeps MG adsorption static which may be attributed to attainment of equilibrium between liquid and solid phase.

The effect of contact time on adsorption of MG by NPP-bentonite is illustrated in Fig. 3. It can be observed that rapid adsorption takes place within 30 min (87.96 %) and equilibrium is reached at 60 min with maximum adsorption of 94.90 % which is attributed to availability of maximum number of adsorption sites. After 60 min the rate of adsorption becomes constant due to gradual filling of adsorption sites which in turn decreases the number of available adsorption sites. The effect of initial dye concentration on adsorption of MG by NPP-bentonite is depicted in Fig. 4. The per cent adsorption decreased from 99.80 to 94.90 % with increase in initial dye concentration from 10 to 50 mg/L. This reveals that increase in dye concentration causes saturation of adsorption sites on NPP-bentonite and as a result the adsorption efficiency decreases.

The adsorption data were fitted to two isotherms namely, Langmuir and Freundlich. The Langmuir (Langmuir, 1918) and Freundlich isotherms (Freundlich, 1906) are given in equation (2) and (3), respectively.

$$C_e/q_e = 1/bq_m + C_e/q_m \quad (2)$$

$$q_e = K_f C_e^n \quad (3)$$

where, q_e is the equilibrium concentration of adsorbate in solid phase (mg/g), C_e is the equilibrium concentration of adsorbate in liquid phase (mg/L), q_m (mg/g) and b (L/g) are Langmuir constants, and K_f [(mg/g)/(mg/L)$^{1/n}$] and n are Freundlich constants.

Fig. 5 shows the linear plot obtained by plotting C_e/q_e versus C_e. The values of q_m (mg/g) and b (L/g) are shown in Table 3. The Langmuir model effectively describes the adsorption data with R^2 value of 0.999.This behaviur indicates a monolayer adsorption. The q_m value of 62.50 mg/g indicates the homogeneous adsorption of MG on NPP-bentonite. Fig. 6 shows the linear plot obtained by plotting log q_e versus log C_e. The values of K_f (mg/g)/(mg/L)$^{1/n}$ and n are given in Table 3. The R^2 value of 0.981 obtained is less compared to that obtained in Langmuir plots. The K_f value of 5.51(mg/g)/(mg/L)$^{1/n}$ indicates higher adsorption capacity and n value of 0.95 indicates favouable adsorption but better fit is obtained with Langmuir isotherm model.

Application to textile wastewater :

The practical applicability of NPP-bentonite for adsorption of MG from textile wastewater was assessed with experiments carried out as follows: 100 ml of wastewater sample was taken in an Erlenmeyer flask containing 1 g/L of NPP-bentonite and pH was adjusted to 7.0. After 60 min of shaking, the wastewater sample was centrifuged and concentration of unabsorbed dye was determined by UV-Visible spectrophotometer. The result showed that MG adsorption from textile wastewater was 95.14 % and this indicates the effectiveness of NPP-bentonite in adsorbing MG from textile wastewater.

Conclusion :

NPP-bentonite acts as an effective adsorbent for adsorption of MG from synthetic medium and textile wastewater. The results indicated that adsorption process was governed by parameters such as pH, adsorbent dose, contact time and initial dye concentration. The optimal pH, adsorbent dose and contact time was found to be at 7.0, 1 g/L and 60 min. Isothermal studies showed good fitting to Langmuir isotherm model with monolayer adsorption capacity of 62.50 mg/g. The results of the study showed the efficiency of NPP-

Table 3 : Isotherms parameters for MG adsorption by NPP-bentonit

Dye	Langmuir isotherm model		Freundlich isotherm model	
MG	q_m (mg/g)	62.50	K_f (mg/g)/(mg/L)$^{1/n}$	5.51
	b (g/L)	26.68	n	0.95
	R^2	0.999	R^2	0.981

Table 4: Comparison of sorption capacity of MG adsorption by NPP-bentonit with different adsorbents

Adsorbents	Langmuir sorption capacity (mg/g)	Reference
Decreased coffee bean	55.30	Baek *et al.,* 2010
Moroccan clay	53.78	Bennani Karim *et al.,* 2011
NPP-bentonite	62.50	Present study
HDTMA-montmorillonite	56.82	Arellano-Cardenas *et al.,* 2013
Rattan sawdust	62.71	Hameed and El–Khaiary, *et al.,* 2008

bentonite in adsorbing MG from textile wastewater.

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