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Adsorption kinetics of removal of a toxic dye, Malachite Green, from wastewater by using hen feathers

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Abstract

The paper includes meticulous utilization of hen feather as potential adsorbent to remove a hazardous triphenylmethane dye, Malachite Green from wastewater. The adsorption studies were carried out at 30, 40 and 50 °C and effects of pH, temperature, amount of adsorbent, contact time, concentration of adsorbate, etc. on the adsorption were measured. On the basis of adsorption data Langmuir and Freundlich adsorption isotherm models were also confirmed. The adsorption isotherm constants thus obtained were employed to calculate thermodynamic parameters like Gibb's free energy, change in enthalpy and entropy. The paper also incorporates systematic kinetic studies of the ongoing adsorption process and a first order adsorption kinetics was found to be operative during the adsorption. The specific rate constants at different temperatures were found to be dependent upon the concentration of the dye. The adsorption was found to operate via film and particle diffusion process in the higher and lower concentration ranges, respectively.

Keywords: Hen feather; Adsorption; Kinetics; Malachite Green; Wastewater

1. Introduction

Removal of toxic substances from water has been a challenge since long time and adsorption technique has proved best to minimize this task [1,2]. It is now well established that for the wastewater treatment, adsorption is a much better process than other physical techniques like, flocculation, froth flotation, etc. because of its efficacy and economy [3–7]. Moreover, ability of adsorption to remove toxic chemicals without disturbing the quality of water or leaving behind any toxic degraded products has augmented its usage in comparison to electrochemical, biochemical or photochemical degradation processes [8]. Recovery of costly toxic substances from the wastewater is an added advantage of the adsorption procedure.

For the past few years, the focus of the research is to utilize cheap materials as potential adsorbents and the processes developed so far are based on exploring those solid waste products, which can prove economic and bring cost effectiveness. Recently, this laboratory tested the adsorbing ability of hen feathers and exploited its use as potential biosorbent for the removal of a hazardous dye, Malachite Green. Hen feather, which has so far used adsorbent to remove only metal impurities from the wastewater [9–12] gave encouraging results for the dye adsorption and the same have been documented in the present paper.

The dye under consideration is Malachite Green, which is an important water-soluble dye belonging to triphenylmethane family. It is widely used to dye wool, silk, cotton, leather, etc. materials. In the aquaculture, commercial fish hatchery and animal husbandry it also acts as an antifungal therapeutic agent, while for humans it is used as antiseptic and fungicidal [13–15]. Its oral consumption is carcinogenic and that is why it is applied on the external wounds and ulcers [16]. The available toxicological information reveals that in the tissues of fish and mice Malachite Green easily reduces to persistable leuco-Malachite Green [13,17], which acts as a tumor promoter. Thus, the detection of Malachite Green in fishes, animal milk and other foodstuff, destined for human consumption, alarm the health hazards against human being [14,18]. Studies also confirm that the products formed after degradation of Malachite Green are also not safe and have carcinogenic potential [19,20].

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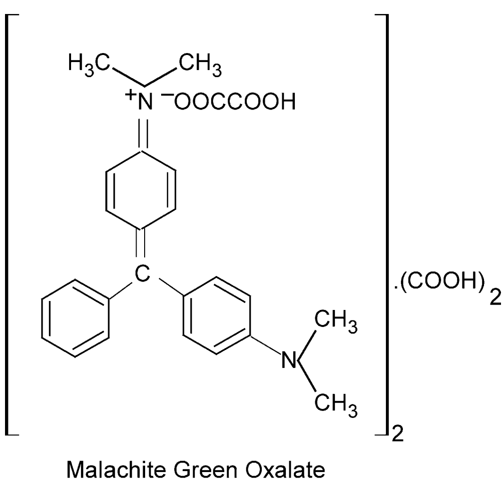
Keeping the toxicity of Malachite Green in view various attempts have been made for its removal from the wastewater. These researches include photo-degradation [21], photocatalytic degradation [22] and adsorption. As far as removal of Malachite Green through adsorption is concern, some solid waste materials like activated products of carbon [23–27], sugar cane dust [28], shale oil ash [29] and magnesium chloride [30], etc. have been tested as adsorbents. But most of these materials are either costly or useful in other purposes, while hen feather is an easily available waste material, which can be obtained at negligible cost.

2. Materials and methods

Malachite Green oxalate (I), *N*-[4-[[4-(dimethylamino) phenyl]phenylmethylene]-2,5-cyclohexadien-1-ylidene]-*N*-methyl-oxalate, (molecular formula $C_{52}H_{54}N_4O_{12}$), was obtained from M/s. Merck and its 1 mM stock solution was prepared in doubly distilled water. All other reagents used were of A.R. grade. Hen feathers were collected from local poultry farm and activated before use.

The pH meter, model number HI 8424 (M/s. Henna Instruments, Italy) was used for monitoring the pH of solutions and absorbance measurements were carried out in the wavelength range 200–710 nm using UV–vis spectrophotometer, model number 117 (M/s. Systronics, Ahmedabad, India).



(I)

Collected hen feathers were of about 1 cm length, which were first agitated and rinsed thoroughly in the pool of doubly distilled water and then dried. Soft barbs of every dried feather were now cut into small pieces of about less than 0.1 mm length and hard middle rachis was removed and discarded. Barbs were then treated with hydrogen peroxide (30%, v/v) for about 24 h to oxidize the adhering organic material. The material thus obtained was kept in an oven at 100 °C for 12 h for the removal of moisture and finally stored in a vacuum desiccator.

All the adsorption studies were carried out at 30, 40 and 50 °C temperatures by batch technique. Adsorption of the 25 mL of dye solutions of varying concentrations was carried out in a series of 100 mL graduated conical flasks after adding required amount hen feather at a desired pH and temperature. Conical flasks were intermittently agitated for about 3 h to achieve equilibration and no change in the amount of adsorbed dye was found by agitating the flask for 3–10 h. Thus to achieve equilibrium each flask was shaked for about 3 h only. Feathers were now removed by carefully filtering the mixture and concentration of the dye in the equilibrated solution was determined spectrophotmetrically by measuring the absorbance at λ_{max} of 620 nm. It is important to note that no shift in the peak was observed when wavelength was recorded before and after the adsorption.

All kinetic measurements were carried out in a 100 mL airtight conical flasks using 25 mL solution of the dye of known concentration and a known amount of adsorbent and flasks were mechanically agitated in a water bath. The dye filtrate was removed after a definite interval of time and analyzed spectrophotometrically.

3. Results and discussion

3.1. Adsorption studies

The amount of Malachite Green adsorbed over hen feathers was monitored in the pH range 3–7 and the adsorption was found to increase with increasing pH (Fig. 1). Since at pH 5.0, sufficient uptake of the dye takes place, hence all further studies were carried at pH 5.0. The pH profile clearly indicates that the protonation of Malachite Green ($pK_a = 10.3$) easily takes place in the high acidic medium; while with decrease in acidity of the solution the dye becomes more de-protonated. The low adsorption of dye in highly acidic solution also shows possibility of development of positive charge on the adsorbent, which inhibits the adsorption of dye over it. However, on moving towards the basic range the uptake of dye increases due to change in its polarity, which might have developed electric double layer around the adsorbent.

Concentration versus amount of the adsorbed dye graph (Fig. 2) at 30, 40 and 50 °C indicates that the uptake of the dye increases at each temperature by varying the concentration from 1×10^{-5} to 1×10^{-4} M at pH 5.0. Fig. 2 indicates that

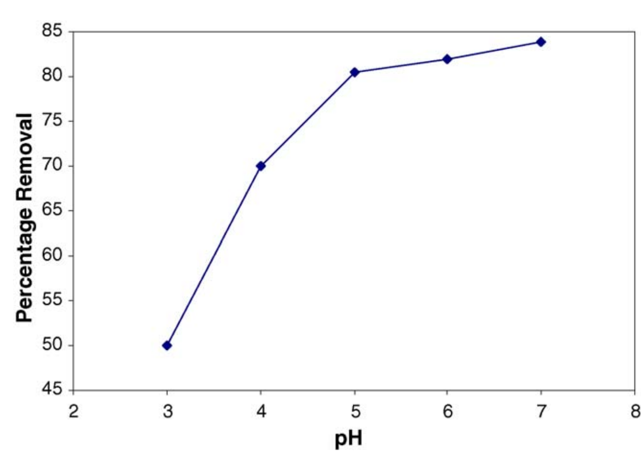


Fig. 1. Effect of pH on uptake of Malachite Green (4×10^{-4} M) by hen feathers (0.1 g) at 30 °C.

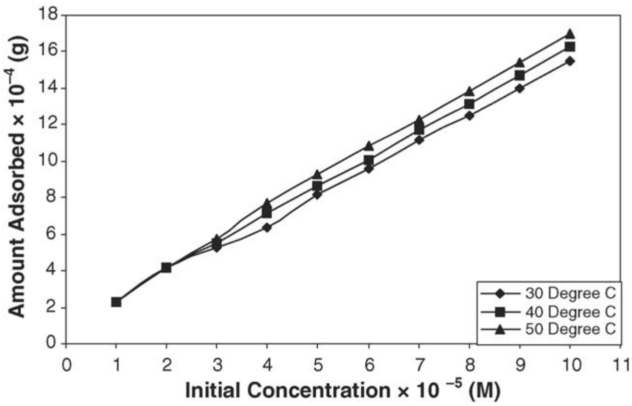


Fig. 2. Effect of concentration for the removal of Malachite Green by hen feathers (0.1 g) at pH 5.0 and at different temperatures.

adsorption of the dye also increases with increase in temperature and suggests possibility of endothermic process during the course of adsorption.

Linear forms of Langmuir Eq. (1) and Freundlich Eq. (2) adsorption isotherm models were employed for the verification of the sorption data and with the help of these models thermodynamic parameters were also calculated.

$$\frac{1}{q_e} = \frac{1}{Q_o} + \left(\frac{1}{bQ_o}\right)\left(\frac{1}{C_e}\right) \quad (1)$$

$$\log q_e = \log K_f + \frac{1}{n}\log C_e \quad (2)$$

where C_e is measured molar concentration in solution at equilibrium, Q_o the number of moles of solute adsorbed per unit weight of adsorbent, q_e the number of moles of solute adsorbed per unit weight of adsorbent at concentration C_e and b, K_f and n are constants.

Linearity obtained in case of both the models (Figs. 3 and 4) confirms their applicability in the adsorption of Malachite Green over hen feathers, at each temperature. Straight lines obtained for both the models were used to calculate Langmuir and Freundlich constants and given in Table 1. The values Langmuir constants Q_o and b are found to increase with increasing temperature,

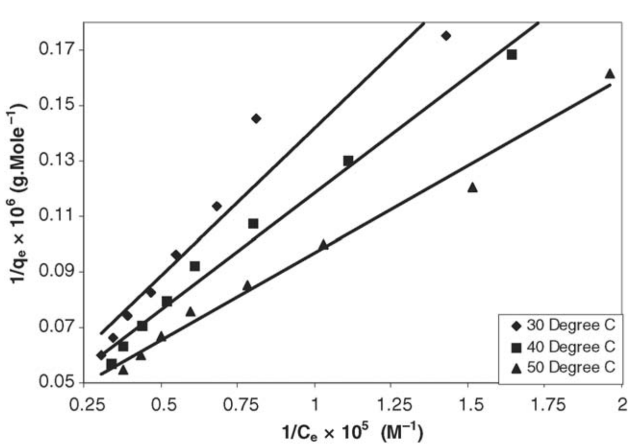


Fig. 3. Langmuir adsorption isotherms for adsorption of Malachite Green over hen feathers (0.1 g) at pH 5.0.

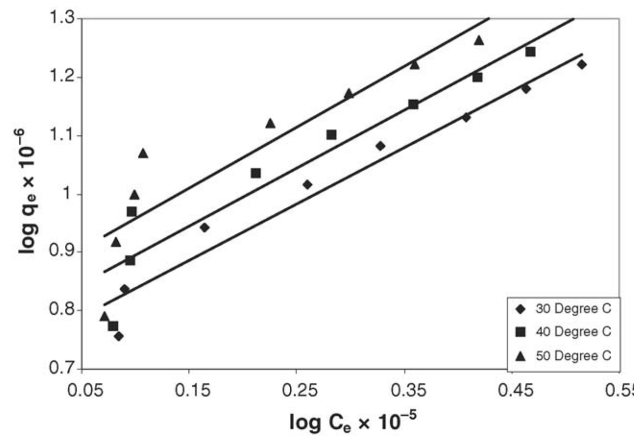


Fig. 4. Freundlich adsorption isotherms for adsorption of Malachite Green over hen feathers (0.1 g) at pH 5.0.

while that of Freundlich constants, K_f and n are almost similar. The increase in value of Q_o with temperature further indicates the endothermic nature of the ongoing processes.

To confirm the favorablility of the process method of Weber and Chakravorti [31] was adopted by calculating separation factor r [32], a dimensionless constant, using following equation:

$$r = \frac{1}{1 + bC_o} \quad (3)$$

where values b and C_o were obtained from Langmuir isotherm. At all temperatures the values of r were found between zero to unity (Table 1) and indicate that the ongoing adsorption is highly favorable.

Thermodynamic parameters were also calculated by using following equations:

$$\Delta G^o = -RT \ln b \quad (4)$$

$$\Delta H^o = -R\left(\frac{T_2 T_1}{T_2 - T_1}\right)\ln\left(\frac{b_2}{b_1}\right) \quad (5)$$

$$\Delta S^o = \frac{\Delta H^o - \Delta G^o}{T} \quad (6)$$

where b, b_1, b_2 are the equilibrium constants at different temperatures as presented in Table 1.

Obtained thermodynamic parameters, Gibb's free energy (ΔG^o), enthalpy of the process (ΔH^o) and entropy (ΔH^o) are presented in Table 2. Negative value of ΔG^o at each temperature indicates the feasiblity and spontaneity of the ongoing adsorption. A decrease in values of ΔG^o with the increasing

Table 1
Freundlich constants, Langmuir constants and separation factor for the adsorption of Malachite Green over hen feathers (0.1 g) at pH 5.0 and different temperatures

Temperature (°C)	$Q_o \times 10^{-5}$ (mol g^{-1})	$b \times 10^4$ (L mol^{-1})	n	K_f	r
30	2.82	3.33	10.31	1.000	0.75
40	2.91	4.09	10.06	1.000	0.71
50	2.93	5.43	9.58	1.000	0.65

Table 2
Thermodynamic parameters for the uptake of Malachite Green over hen feathers (0.1 g) at pH 5.0

$-\Delta G^{o}$ (kJ mol^{-1})	
30 °C	26.23
40 °C	27.63
50 °C	29.28
ΔS^{o} (J K^{-1} mol^{-1})	20.01
ΔH^{o} (kJ mol^{-1})	152

temperature suggests more adsorption of the dye at higher temperature. The endothermic nature of the process was once again confirmed due to positive values of enthalpy change (ΔH^{o}). Positive value of entropy change (ΔS^{o}) indicates good affinity of the feathers with Malachite Green.

3.2. Kinetic studies

To design an effective and quick adsorption model it was considered necessary to carry out adsorption with kinetics viewpoint and effects of contact time, amount of adsorbent and concentration of adsorbate solution on the uptake of the dye was monitored very carefully.

Figs. 5 and 6 exhibit contact time versus adsorbed amount graph at 4×10^{-5} and 6×10^{-5} M concentrations of the dye, respectively and indicate that with the increase in temperature the amount of adsorbed dye increases. A further verification of the endothermic nature of the process was done by calculating the half-life of process at each temperature, which was found to decrease with increasing temperatures. Interestingly, at all the temperatures equilibrium was found to establish more rapidly (in just 90 min) in the lower concentration range of the dye than at higher concentrations, where saturation takes place in about 150 min. Hence, it was considered necessary to present the kinetic data obtained at 4×10^{-5} and 6×10^{-5} M concentrations.

Effect of amount of adsorbent on the uptake of the dye was also observed (Fig. 7) and it was found that the adsorption of the dye increases with increase in the amount of the hen feathers from 0.01 to 0.15 g. A further increase in the amount of the dye did not affect the adsorbed dye's amount. The rate of uptake of the dye over adsorbent was also found to follow the same pattern. As fairly good adsorption was achieved at 0.1 g of feathers, hence studies were carried out on this amount only. At all the temperatures, the half-life decreases with increasing amount of adsorbent, which confirms dependency of amount of adsorbent on rate of adsorption.

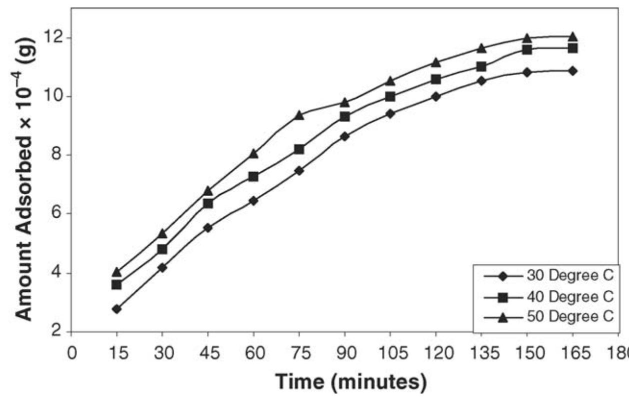


Fig. 6. Effect of contact time for the uptake of Malachite Green (6×10^{-5} M) by hen feathers (0.1 g) at pH 5.0 and at different temperatures.

3.3. Adsorption rate constant study

To evaluate specific rate constants of Malachite Green—hen feather adsorption at different temperatures following Lagergren's first order rate expression [33] was applied:

$$\log (q_e - q_t) = \log q_e - \frac{k_{ads}}{2.303} \times t \qquad (7)$$

where q_e and q_t are the amount adsorbed at equilibrium and time t, respectively.

At all the temperatures the time versus $\log(q_e - q_t)$ graphs exhibit a straight line (Figs. 8 and 9) and confirm the first order nature of the process. The slop of these lines gave the value of the rate constant, k_{ads} at each temperature, which were found as 1.34×10^{-2}, 1.36×10^{-2} and 1.43×10^{-2} min^{-1} at 30, 40 and 50 °C, respectively at 4×10^{-5} M concentration and 1.91×10^{-2}, 1.93×10^{-2} and 2.12×10^{-2} min^{-1} at 30, 40 and

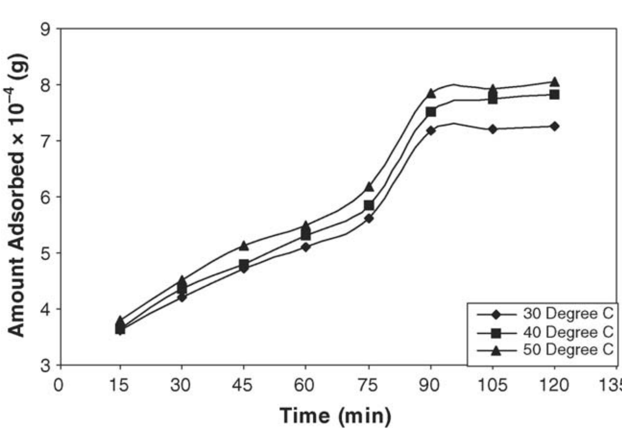


Fig. 5. Effect of contact time for the uptake of Malachite Green (4×10^{-5} M) by hen feathers (0.1 g) at pH 5.0 and at different temperatures.

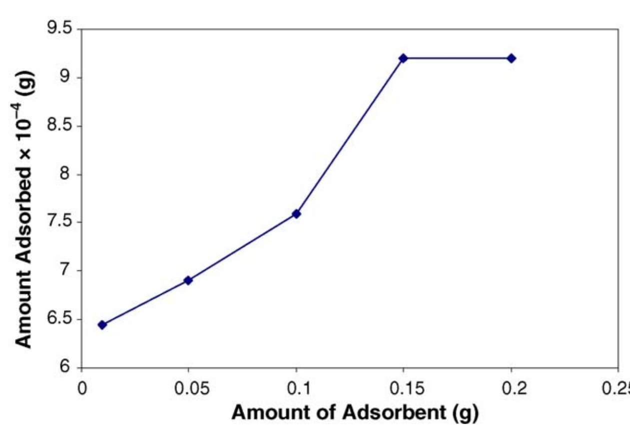


Fig. 7. Effect of amount of adsorbent for the removal of Malachite Green (4×10^{-4} M) at 30 °C and pH 5.0.

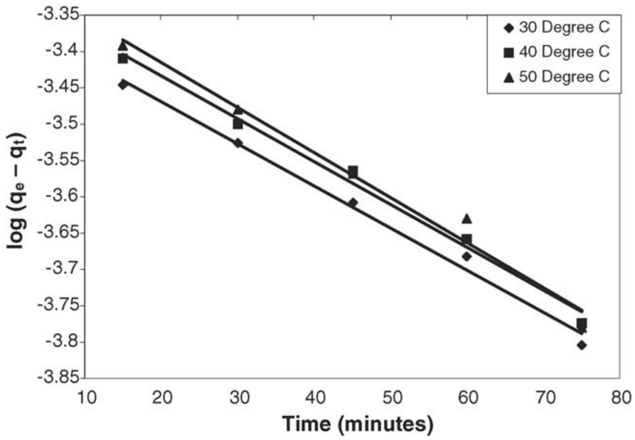


Fig. 8. Lagergren plot for Malachite Green (4×10^{-5} M)—hen feather system at different temperatures.

50 °C, respectively at 5×10^{-5} M concentration of Malachite Green. This also confirms the increase in uptake of the dye by increasing temperature.

3.4. Rate expression and treatment of data

The kinetic data thus obtained has also been treated by ingenious mathematical treatment given by Boyd et al. [34] and Reichenberg [35]. The treatment helps in predicting the mechanistic steps involved in the ongoing adsorption process, i.e. whether the rate of removal of the dye takes place via particle diffusion or film diffusion mechanism.

During the adsorption of an organic/inorganic substance over a porous adsorbent, following three possible cases exist, particle diffusion governance of rate, when external transport > internal transport; film diffusion governance of rate, when external transport < internal transport; and a third case, when external transport ≈ internal transport. The third case will give rise to formation of a liquid film surrounding the adsorbent particles with a proper concentration gradient, as transport of ions to the boundary may not be possible at a significant rate [36]. Thus the third case may be excluded for the consideration in the present discussion and possibility can be explored for the rate determine step out of film or particle diffusion.

Hence, to examine the actual process involved in the present adsorption, mathematical Eq. (8) of the adsorption dynamics can be employed.

$$F = 1 - \frac{6}{\pi^2}\sum_{1}^{\infty}\left(\frac{1}{n^2}\right)\exp(-n^2 B_t) \tag{8}$$

where F is the fractional attainment of equilibrium at time t and is obtained by using Eq. (9), n is Freundlich constant of the adsorbate and B_t is a calculated mathematical function of F (and vice versa) derived from the Reichenberg's table [35].

$$F = \frac{Q_t}{Q_\infty} \tag{9}$$

where Q_t and Q_∞ are amounts adsorbed after time t and after infinite time, respectively.

On the basis of observed values of F corresponding values of B_t was derived from the Reichenberg's table [35] and time versus B_t graph was plotted at 4×10^{-5} and 6×10^{-5} M concentrations of the Malachite Green at different temperatures. Fig. 10 represents a typical time versus B_t plot at 50 °C for both the concentrations and indicates that in the lower concentration a straight line passing through origin is obtained, while at higher concentration the nature of the graph is curvical. These natures of the graph confirm the involvement of particle and film diffusion mechanisms as the rate controlling steps in the lower and higher concentration ranges, respectively.

To reconfirm the above observations time versus $\log(1 - F)$ (Mckay's plots) were plotted at different concentrations of Malachite Green at different temperatures and straight lines deviating from origin were obtained in the lower concentration range, while graphs straight lines almost passing through origin were obtained at higher concentrations. Fig. 11 shows typical Mckay's plots at 50 °C for 4×10^{-5} and 6×10^{-5} M concentrations of the Malachite Green. These observations further support the fact that rate of adsorption of Malachite Green over hen feathers undergo via internal transport mechanism at low concentration

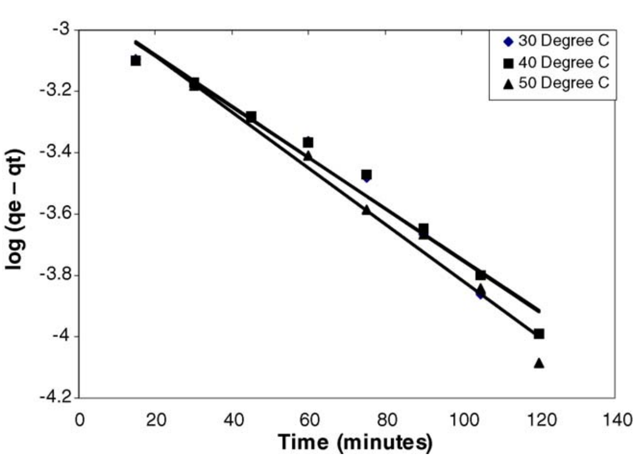


Fig. 9. Lagergren plot for Malachite Green (6×10^{-5} M)—hen feather system at different temperatures.

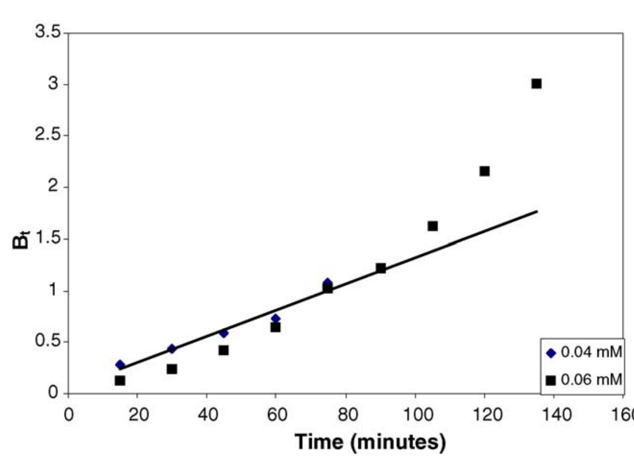


Fig. 10. Time vs. B_t plot for the Malachite Green adsorption over hen feathers at different concentrations and at 50 °C.

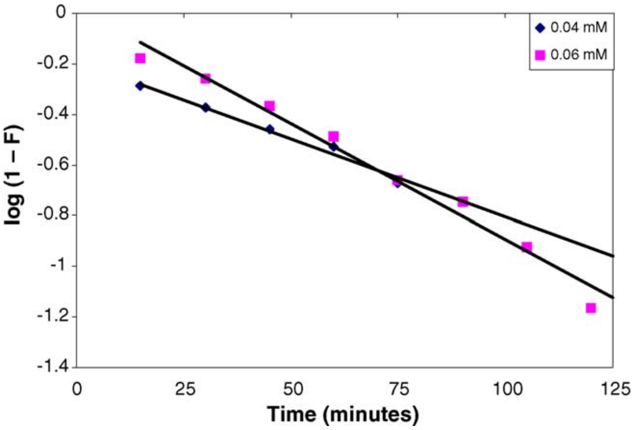


Fig. 11. Time vs. $\log(1-F)$ graph for Malachite Green—hen feather system at different concentrations and at 50 °C.

range while at higher concentrations the external transport of the dye seems to be operative [37].

4. Conclusions

Hen feathers were successfully used as adsorbent for the removal of hazardous dye Malachite Green and adsorption of the dye was found to increase with increasing pH, temperature and concentration. The involved adsorption process was endothermic in nature and sorption data validates linear forms of Langmuir and Freundlich adsorption isotherm models. The values Langmuir constants Q_o and b are found to increase with increasing temperature from 2.82×10^{-5} to 2.93×10^{-5} (mol g^{-1}) and 3.33×10^{4} to 5.43×10^{4} (L mol^{-1}), respectively, while that of Freundlich constants, K_f and n were almost constant. To confirm the favorablility of the process separation factor r was also calculated and was found between zero to unity. Thermodynamic parameters, Gibb's free energy (ΔG^o), enthalpy of the process (ΔH^o) and entropy (ΔH^o) were found 26.23–29.28 kJ mol^{-1}, 20.01 kJ mol^{-1} and 152 J K^{-1} mol^{-1}, respectively.

Effect of amount of adsorbent indicates that the uptake of the dye increases with increase in the amount of the hen feathers from 0.01 to 0.15 g. The rate constants, k_{ads} of the ongoing adsorption process were found as 1.34×10^{-2}, 1.36×10^{-2} and 1.43×10^{-2} min^{-1} at 30, 40 and 50 °C, respectively at 4×10^{-5} M concentration and 1.91×10^{-2}, 1.93×10^{-2} and 2.12×10^{-2} min^{-1} at 30, 40 and 50 °C, respectively at 5×10^{-5} M concentration of Malachite Green. Involvement of particle diffusion internal transport mechanism and external transport film diffusion mechanisms were found operative as the rate controlling steps in the lower and higher concentration ranges of the dye, respectively.

References

[1] D.M. Ruthven, Principles of Adsorption and Desorption Processes, John Wiley and Sons, New York, 1984.
[2] M. Suzuki (Ed.), Fundamentals of Adsorption IV, Kodansha, Tokyo, 1993.
[3] S.E. Bailey, T.J. Plin, R.M. Bricka, D.D. Adrain, A review of potentially low cost sorbents for heavy metals, Water Res. 33 (1999) 2469–2479.
[4] P. MacCarthy, R.W. Klusman, S.W. Cowling, J.A. Rice, Water analysis, Anal. Chem. 67 (1995) 525R–582R.
[5] F.L. Slejko, Adsorption Technology: A Step-by-Step Approach to Process Evaluation and Applications, Marcel Dekker, New York, 1985.
[6] I.H. Suffet, M.J. McGuire, Activated carbon adsorption of organics from aqueous phase, Ann. Arbor Sci. Mich. 1–2 (1980).
[7] L.B. Franklin, Wastewater Engineering: Treatment Disposal and Reuse, McGraw Hill Inc., New York, 1991.
[8] V.K. Gupta, I. Ali, in: A. Hubbard (Ed.), Adsorbents for Water Treatment: Low-cost Alternatives to Carbon, vol. 1, Encyclopedia of Surface and Colloid Science, Marcel Dekker, USA, 2002, pp. 136–166.
[9] S. Al-Asheh, F. Banat, D. Al-Rousan, Adsorption of copper, zinc and nickel ions from single and binary metal ion mixtures on to chicken feathers, Adsorption Sci. Technol. 20 (2002) 849–864.
[10] F. Banat, S. Al-Asheh, D. Al-Rousan, Comparison between different keratin-composed biosorbents for the removal of heavy metal ions from aqueous solutions, Adsorption Sci. Technol. 20 (2002) 393–416.
[11] S. Al-Asheh, F. Banat, D. Al-Rousan, Beneficial reuse of chicken feathers in removal of heavy metals from wastewater, J. Cleaner Prod. 11 (2003) 321–326.
[12] D.I. Ishikawa, K. Suyama, Recovery and refining of au by gold-cyanide ion biosorption using animal fibrous proteins, Appl. Bioche Biotech A: Enzyme Eng. Biotechnol. 70–72 (1998) 719–728.
[13] S.J. Culp, L.R. Blankenship, D.F. Kusewitt, D.R. Doerge, L.T. Mulligan, F.A. Beland, Toxicity and metabolism of malachite green and leucomalachite green during short-term feeding to Fischer 344 rats and B6C3F(1) mice, Chem.-Biol. Interact. 122 (3) (1999) 153–170.
[14] D.J. Alderman, Malachite green—a review, J. Fish Dis. 8 (3) (1985) 289–298.
[15] Y. Sawa, M. Hoten, Antibacterial activity of basic dyes on the dyed acrylic fibers, Sen-I Gakkaishi 57 (5) (2001) 153–158.
[16] R.S. Clifton-Hadley, D.J. Alderman, The effects of malachite green upon proliferative kidney-disease, J. Fish Dis. 10 (2) (1987) 101–107.
[17] S.J. Culp, F.A. Beland, Malachite green: a toxicological review, J. Am. Coll. Toxicol. 15 (3) (1996) 219–238.
[18] S.J. Srivastava, N.D. Singh, A.K. Srivastava, R. Sinha, Acute toxicity of malachite green and its effects on certain blood parameters of a catfish, Heteropneustes Fossilis, Aquat. Toxicol. 31 (3) (1995) 241–247.
[19] S. Singh, M. Das, S.K. Khanna, Biodegradation of malachite green and rhodamine-b by cecal microflora of rats, Biochem. Biophys. Res. Commun. 200 (3) (1994) 1544–1550.
[20] S. Srivastava, R. Sinha, D. Roy, Toxicological effects of malachite green, Aquat. Toxicol. 66 (2004) 319–329.
[21] K. Wu, T. Zhang, J. Zhao, H. Hidaka, Photodegradation of malachite green in the presence of Fe^{3+}/H_2O_2 under visible irradiation, Chem. Lett. 8 (1998) 857–858.
[22] C. Hachem, F. Bocquillon, O. Zahraa, M. Bouchy, Decolourization of textile industry wastewater by the photocatalytic degradation process, Dyes Pigments 49 (2) (2001) 117–125.
[23] G.M. Walker, L.R. Weatherley, Kinetics of acid dye adsorption on GAC, Water Res. 33 (8) (1999) 1895–1899.
[24] V.K. Gupta, S.K. Srivastava, D. Mohan, Equilibrium uptake, sorption dynamics, process optimization and column operations for the removal and recovery of malachite green from wastewater using activated carbon and iron slag, Ind. Eng. Chem. Res. 36 (6) (1997) 2207–2218.
[25] V.K. Gupta, A. Mittal, L. Krishnan, V. Gajbe, Adsorption kinetics and column operations for the removal and recovery of malachite green from wastewater using bottom ash, Sep. Purif. Technol. 40 (2004) 87–96.
[26] Y. Al-Degs, M.A.M. Khraisheh, S.J. Allen, M.N. Ahmad, Effect of carbon surface chemistry on the removal of reactive dyes from textile effluent, Water Res. 34 (3) (2000) 927–935.
[27] A.R. Shawwa, D.W. Smith, D.C. Sego, Color and chlorinated organics removal from pulp mills wastewater using activated petroleum coke, Water Res. 35 (3) (2001) 745–749.
[28] S.D. Khattri, M.K. Singh, Colour removal from dye wastewater using sugar cane dust as an adsorbent, Adsorption Sci. Technol. 17 (4) (1999) 269–282.

[29] Z. Al-Qodah, Adsorption of dyes using shale oil ash, Water Res. 34 (17) (2000) 4295–4303.
[30] B.H. Tan, T.T. Teng, A.K.M. Omar, Removal of dyes and industrial dye wastes by magnesium chloride, Water Res. 34 (2) (2000) 597–601.
[31] T.W. Weber, R.K. Chakravorti, Pore and solid diffusion models for fixed bed adsorbers, J. Am. Inst. Chem. Eng. 20 (1974) 228–238.
[32] K.R. Hall, L.C. Eagleton, A. Acrivers, T. Vermenlem, Pore and solid diffusion kinetics in fixed adsorption constant pattern conditions, Ind. Eng. Chem. Res. 5 (1966) 212–223.
[33] K. Periasamy, C. Namasivayam, Process development for removal and recovery of cadmium from wastewater by a low cost adsorbent: adsorption rates and equilibrium studies, Ind. Eng. Chem. Res. 33 (1994) 317–320.
[34] G.E. Boyd, A.W. Adamson, L.S. Meyers, The exchange adsorption of ions from aqueous solution by organic zeolites. II. Kinetics, J. Am. Chem. Soc. 69 (1947) 2836–2848.
[35] D. Reichenberg, Properties of ion exchange resins in relation to their structure. III. Kinetics of exchange, J. Am. Chem. Soc. 75 (1953) 589–597.
[36] J. Crank, The Mathematics of Diffusion, Clarenden Press, Oxford, 1956.
[37] J.S. Zogoroski, S.D. Fast, J.H. Hass Jr., Phenol removal by activated carbon, J. Colloid Interface Sci. 55 (1976) 329–341.