

Removal of Methylene Blue dye from aqueous solutions Using Lagerstroemia indica seed (LIS) activated carbon

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Abstract

The feasibility of using Lagerstroemia indica seed (LIS) activated carbon for the cationic dye (methylene blue MB) adsorption from aqueous solution has been investigated as a low cost and an eco-friendly adsorbent. Adsorption studies were conducted on a batch process, to study the effects of contact time, initial dye concentration, Carbon dosage and pH. Maximum colour removal was observed at higher pH. The present dye removal decreased from 93% to 85% as the dye concentration has been increased from 10 mg/l to 40 mg/l. A maximum removal of 93% is obtained at higher pH. Kinetic models, the pseudo-first and pseudo-second order rate equations were applied. The obtained results show that the sorption of MB by LIS was best described by the pseudo- second order kinetic model. Sorption equilibrium isotherms of MB at different temperatures was determined and correlated with common isotherm equations such as Langmuir and Freundlich models. The results indicate that the Langmuir and Freundlich model fits the data better. The results suggest that LIS is a potential low-cost adsorbent for the MB dye removal from aqueous solutions.

Keywords- Methylene blue, Adsorption, Kinetics, Acid treatment

I. INTRODUCTION

Color is the first contaminant to be recognized in water. [1] Residual dyes are the major contributors to color in waste waters generated from textile, pulps, paint, printing, dyeing and cosmetics [1-3]. Color impedes light penetration, retards photosynthetic activity, inhibits the growth of biota and also has a tendency to chelate metal ions which result in micro-toxicity to fish and other organisms [4]. Most of the dyes are toxic, carcinogenic and can cause allergic dermatitis, skin irritation, mutation, etc. [5-7]. It is difficult to remove the dyes from effluents since they are stable to light, heat and oxidizing agents and are biologically non-degradable. Currently, several physical or chemical processes are used to treat dye-laden waste waters, such as these include chemical coagulation/flocculation, ozonation, oxidation, ion exchange, irradiation, precipitation, reverse osmosis, membrane separation [1-2, 4,7-9].

The aim of the present investigations has been to evaluate the efficiency of the removal of methylene blue from aqueous solutions using *Lagerstroemia indica* seeds as an easily available and cheap adsorbent. The effects of contact time, initial dye concentration, pH, ionic strength and temperature of dye solution and adsorbent dose on the adsorption percentage have been investigated to optimize the conditions leading to maximum removal efficiency. The obtained results may provide useful data for future scale up using this material as a low-cost adsorbent for the removal of cationic dye.

II. EXPERIMENTAL

A. Materials and methods

Fresh *Lagerstroemia indica* seeds are used for adsorption experiments with Sulphuric acid treatment. Cut the seeds into small pieces and dry it in sunlight. The dried material soaked in boiling solution of 10% H₂SO₄ for 1h and kept at room temperature. After 24h the seed material was separated, air dried and carbonized in muffle furnace at 400°C for 20min. The carbonized material was powdered and activated in a muffle furnace at 800°C for a period of 10min. Then the material was washed with plenty of distilled water to remove residual acid, dried, sieved into 300 µm size and then preserved in the desiccator for further adsorption studies.

B. Preparation of MB solution

The dye methylene blue (MB) was obtained from Sigma-Aldrich and their stock solutions (1000 mg/L) were prepared in double distilled water. All reagents used in the present work were of analytical grade. To prepare various solutions at desired concentrations from the stock solution, double distilled water was used for the necessary dilutions. MB concentration was analyzed by measuring the absorbance values after and before each experiment with UV-Visible spectrophotometer at 664 nm respectively.

C. Adsorption studies

Sorption studies were performed by the batch technique to obtain equilibrium data. In each experiment, 0.1 g of adsorbent was added to a 50 ml dye solution of known concentration. All the experiments were carried out in duplicate. After equilibrium, the final dye concentration (C_e) was measured and the percentage removal of dye was calculated using the following relationship:

$$\% \text{Dye removal} = (C_i - C_e) / C_i \times 100 \quad (1)$$

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

The amount of dye adsorbed q_e (mg/g), onto LIS was calculated from the mass balance equation as follows:

$$q_e = (C_i - C_e)V / M \quad (2)$$

where V is the volume of dye solution (L), and M is the mass of the adsorbent used (g).

Batch adsorption experiments were carried out at initial pH values ranging from about 2 to 12; initial pH was adjusted by addition of dilute HCl or NaOH solutions. The pH values were measured by using a Elico make pH-meter. The effects of temperature on the adsorption data were carried out by performing the adsorption experiments at various temperatures (30, 40, 50 and 60°C). The equilibrium data have been analyzed using the Langmuir, and Freundlich isotherms and the characteristics parameters for each isotherm have been determined.

III. RESULT AND DISCUSSION

A. Effect of contact time

The effect of contact time on adsorption of MB onto LIS is shown in Fig. 1. The results show that adsorption process reached equilibrium within 90 minutes and percentage dye removal increased with increase in contact time. LIS rapidly adsorbed over 67 % of the dye within the first 5 minutes of contact time. The changes in percentage adsorption after the 5th minute became relatively gradual with the equilibrium being reached within 90 minutes with 93% dye removal achieved. The high removal rate at the start of the contact time was due to the large amount of surface area available for adsorption of the dye during the initial stage and the capacity of the adsorbent became gradually exhausted with time since the few remaining vacant surface sites became difficult to be occupied due to repulsive forces between the solute molecules on the solid and bulk phases. Similar results have been previously reported in the literature for dye removal [10].

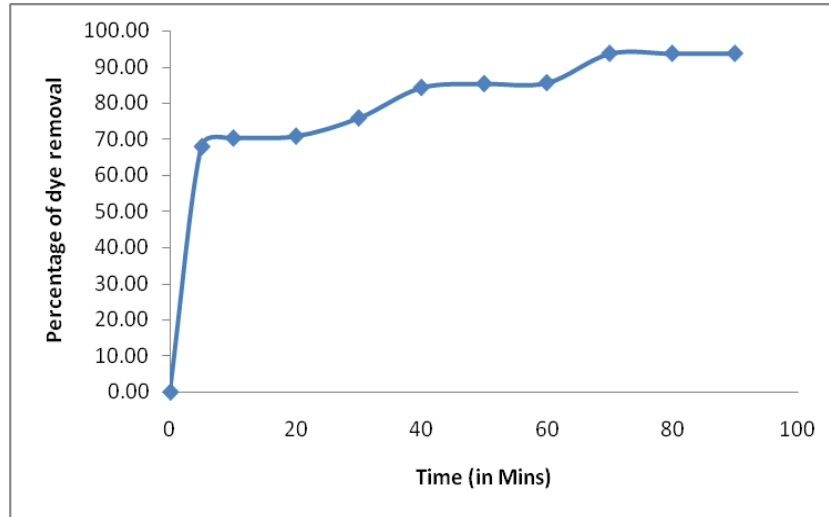


Fig.1 Effect of contact time on MB dye sorption

B. Effect of adsorbent dose

The removal of MB with LIS was studied at different adsorbent dosages (0.1-0.3 g/50 mL) of dye solution at a constant dye concentration (30 and 40 mg/L), pH (7.2) and contact time (60 min). The results (Fig. 2) indicate that an increase in the adsorbent dose resulted in a higher removal of MB dyes. Maximum removal was observed with an adsorbent dose of 0.30 g/ 50 mL for MB. The increase in the percentage removal with an increase in the adsorbent dosage is due to the increase in the number of adsorption sites. The adsorption capacity was lesser at higher adsorbent doses. This is due to greater availability of the exchangeable sites or surface area at a higher concentration of the adsorbent [11].

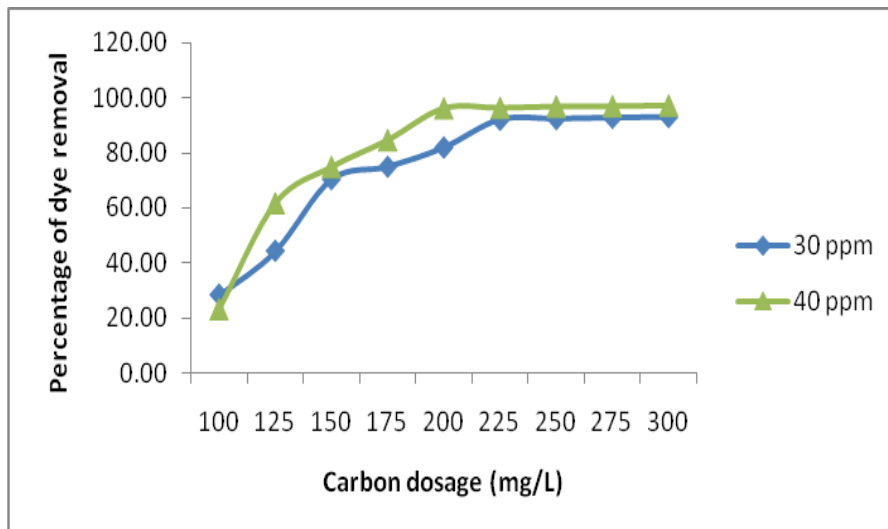


Fig.2 Effect of adsorbent dose on MB dye sorption

C. Adsorption kinetics

Adsorption kinetic models are used to explain the adsorption mechanism and adsorption characteristics. The pseudo-first-order kinetic model and pseudo-second-order kinetic model are often used to predict the adsorption process.

The pseudo-first-order kinetic model (fig.3) is expressed as [12]:

$$\log(q_e - q_t) = \log q_e - k_1 / 2.303 t \quad (3)$$

The pseudo-second-order kinetic model (fig.4) is expressed as [12]:

$$t/q_t = 1/(k_2 q_e^2) + 1/q_e t \quad (4)$$

where q_e and q_t are the amount of solute adsorbed (mg g^{-1}) at equilibrium and time t (min), respectively, k_1 is the rate constant of the pseudo-first-order adsorption (min^{-1}), and k_2 is the rate constant of the pseudo-second-order adsorption ($\text{mg g}^{-1} \text{min}^{-1}$).

The values of q_e , k_1 , and k_2 were determined using nonlinear regressive analysis by least square sum of difference between calculated values and experimental values according to Eqs. (3) and (4), respectively. The parameters were listed in Table 1.

From Table 1, the value of R^2 (0.999) from the pseudo-second order kinetic model was higher than that from the pseudo-first-order kinetic model. The fitted curve from the pseudo second-order kinetic model was very close to the experimental curve. So it was concluded that the pseudo-second-order kinetic model is better to fit the experimental data and the process may be chemical process [12].

The half-adsorption time $t_{1/2}$ was another parameter which can be calculated from the equilibrium concentration and the diffusion coefficient rate values. This was calculated by using the following equation [13]:

$$t_{1/2} = 1/(k_2 q_e) \quad (5)$$

where k_2 and q_e can be obtained from Table 1.

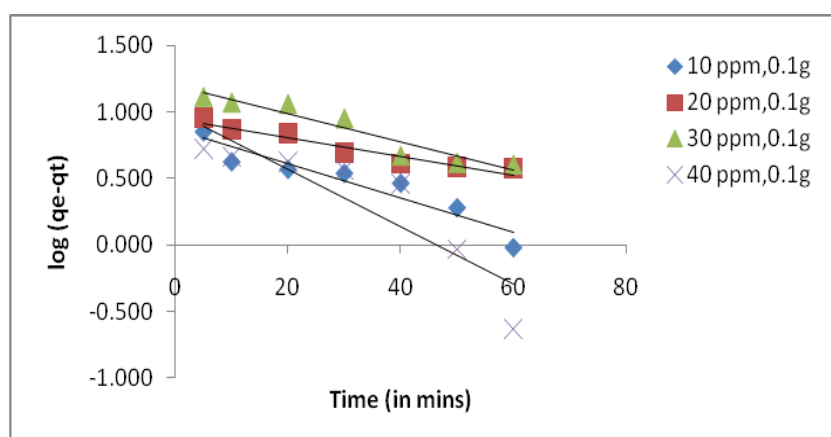


Fig. 3 Pseudo-first-order kinetics plot for the adsorption of MB dye by LIS

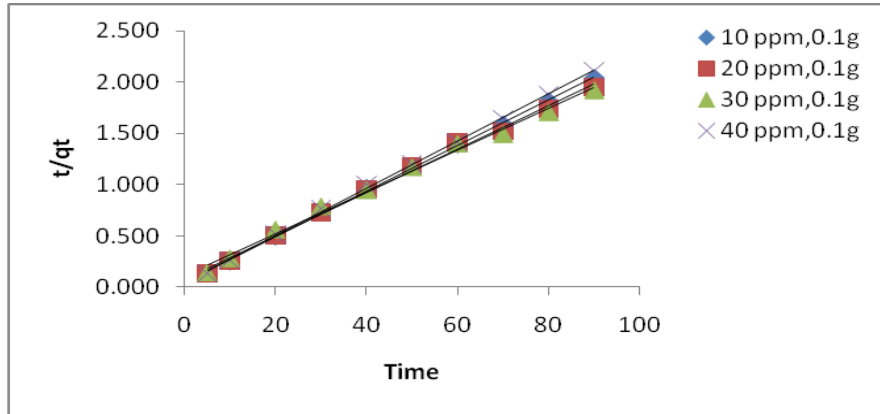


Fig. 4 Pseudo-second-order kinetics plot for the adsorption of MB dye by LIS

Table 1. Kinetic model values for adsorption of methylene blue onto activated LIS carbon

Concentration (mg/L)	10	20	30	40
Pseudo first order kinetics				
$K_1 \times 10^{-2} (\text{min}^{-1})$	2.95	1.61	2.23	4.84
$q_{e,cal} (\text{mg/L})$	7.83	8.96	15.66	10.03
R^2	0.8936	0.9277	0.9148	0.7898
Pseudo second order kinetics				
$K_1 \times 10^{-3} (\text{min}^{-1})$	10.12	5.93	3.31	9.7
$q_{e,cal} (\text{mg/L})$	44.14	46.04	46.81	42.69
R^2	0.9990	0.9956	0.9931	0.9990

D. Adsorption isotherms

The adsorption isotherm indicates how the adsorption molecules distribute between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state. The time required to attain this equilibrium state is termed the equilibrium time, and the amount of dye adsorbed at equilibrium reflects the maximum adsorption capacity of the adsorbent under the operating conditions. The analysis of the isotherm data by fitting them to different isotherm models is an important step to find the suitable model for the case studied [14]. The Langmuir and Freundlich were used to describe the data derived from the adsorption of the dye by LIS over the entire concentration range studied. The Langmuir model assumes monolayer sorption on a surface with a finite number of identical sites [15]. While, the Freundlich isotherm model assumes heterogeneous surface energies, in which the energy term in the Langmuir equation varies as a function of the surface coverage and

hence does not assume monolayer capacity [16]. The applicability of the two isotherm equations were compared by evaluating the correlation coefficients, R^2 .

E. Langmuir isotherm

The linear form of the Langmuir's isotherm model is given by the following equation:

$$C_e/q_e = 1/(Q_0 \cdot b) + C_e/Q_0 \tag{6}$$

where C_e is the equilibrium concentration of the dye (mg/L), q_e is the amount of adsorbate adsorbed per unit mass of adsorbent (mg/g), and Q_0 and b are the Langmuir constants related to adsorption capacity and rate of adsorption, respectively. The plot of C_e/q_e against C_e (fig. 5) gave straight lines with slope $1/Q_0$ for MB. This result indicated that the adsorption of MB on LIS follows the Langmuir isotherm and demonstrated the formation of monolayer coverage of dye molecules at the outer surface of LIS. The Langmuir constants b and Q_0 for MB was calculated from this isotherm and their values are given in Table 2. The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless equilibrium parameter (R_L) [17], which is defined by:

$$R_L = 1/(1 + b \cdot C_0) \tag{7}$$

where, b is the Langmuir constant and C_0 is the highest dye concentration (mg/L). The value of R_L indicates the type of the isotherm to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$). Values of R_L were found to be 0.8906–0.3608 for MB in the concentration range studied. These results confirmed that the LIS is favorable for the adsorption of MB dye under the experimental conditions used.

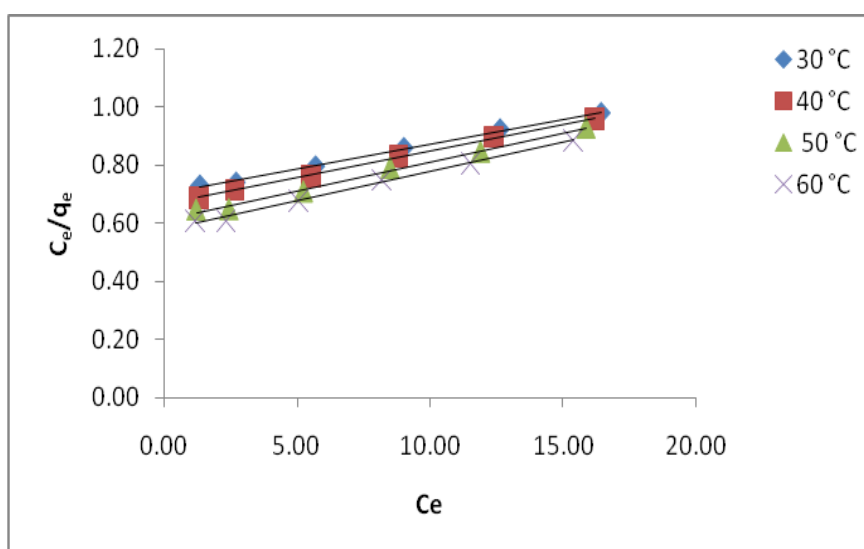


Fig.5. Langmuir isotherm for the adsorption MB on to LIS

F. Freundlich isotherm

The linear form of the Freundlich isotherm model can be defined by the following equation [16]:

$$\log q_e = \log k_f + \frac{1}{n} \log C_e \tag{8}$$

where K_f [mg/g (L/mg)ⁿ] is the Freundlich isotherm constant related to adsorption capacity (represents the quantity of dye adsorbed onto the adsorbent) and n is the Freundlich isotherm constant related to adsorption intensity (giving an indication of how favorable the adsorption process). The applicability of the Freundlich sorption isotherm was analyzed by plotting $\log q_e$ versus $\log C_e$ is given in fig.6. This plot gives straight lines for the dye with slope ‘1/n’, indicating that the adsorption of MB follow the Freundlich isotherm. The slope 1/n ranging between 0 and 1, is a measure of adsorption intensity or surface heterogeneity. It becomes more heterogeneous as its value gets closer to zero and a value for 1/n below one indicates a normal Langmuir isotherm while 1/n above one is indicative of cooperative adsorption [18]. Accordingly, the Freundlich constants (K_f and n) and the related correlation coefficients were calculated and recorded in Table 2.

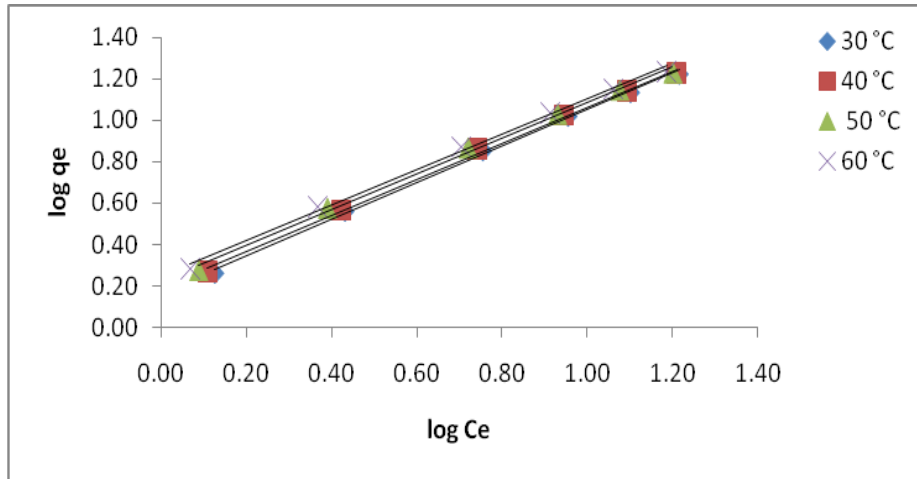


Fig.6. Freundlich isotherm for the adsorption MB on to LIS

Table 2 Constants of adsorption isotherms of MB on LIS.

Temperature (°C)	Langmuir			Freundlich		
	Q _o	b	R ²	n	K _f	R ²
30	58.13	0.0245	0.9969	1.1344	1.1797	0.9982
40	53.64	0.0274	0.9983	1.1473	1.5556	0.9982
50	50.5	0.0322	0.9938	1.1636	1.678	0.9969
60	49.01	0.0354	0.9932	1.1735	1.7803	0.9967

IV. CONCLUSION

The adsorption of methylene blue from aqueous solution onto *Lagerstroemia indica* seed has been studied. Adsorption experiments were carried out as a function of contact time, adsorbent dosage, solution temperature, pH and dye concentration. The adsorption experiments indicated that *Lagerstroemia indica* seeds were effective in removing basic dye such as methylene blue from aqueous solutions. The removal percent decreased with the increasing initial concentration of dye in the solution and increased with the increasing adsorbent dosage. The results also indicated that with temperature increasing, the ability of adsorption increased indicating an endothermic process. The adsorption data was well described by the Langmuir and Freundlich isotherm equation. The rates of sorption were found to conform to pseudo-second-order kinetics with good correlation. The present study concludes that *Lagerstroemia indica* seed could be employed as a low-cost adsorbent for the removal of basic dye from aqueous solutions.

REFERENCES

- [1] R. Malik, D.S. Ramteke, S.R. Wate, Adsorption of malachite green on groundnut shell waste based powdered activated carbon, *Waste Manag.* 27 (9) (2007) 1129-1138.
- [2] Z. Aksu, Application of biosorption for the removal of organic pollutants: a review, *Process Biochem.* 40 (2005) 997-1026.
- [3] C. Namasivayam, R. Radhika, S. Suba, Uptake of dyes by a promising locally available agricultural solid waste: coir pith, *Waste Manage.* 21 (2001) 381-387.
- [4] V.K. Garg, M. Amita, R. Kumar, R. Gupta, Basic dye (methylene blue) removal from simulated wastewater by adsorption using Indian rosewood saw dust: a timber industry waste, *Dyes Pig.* 63 (2004) 243-250.
- [5] K.G. Bhattacharyya, A. Sharma, *Azadirachta indica* leaf powder as an effective biosorbent for dyes: a case study with aqueous congo red solutions, *J. Environ. Manage.* 71 (2004) 217-229.
- [6] K.C. Chen, J.Y. Wu, C.C. Huang, Y.M. Liang, S.C.J. Hwang, Decolorization of azo dye using PVA-immobilized microorganisms, *J. Biotechnol.* 101 (2003) 241-252.
- [7] M.I. Banat, P. Nigam, D. Singh, R. Marchant microbial decolorization of textile-dye containing effluents: a review, *Bioresource Technology* 58 (1996) 217-227.
- [8] Y. Fu, T. Viraraghavan, Fungal decolorization of wastewaters: a review. *Biores Technol.* 79 (2001) 251-62.
- [9] T. Robinson, G. McMullan, R. Marchant, P. Nigam, Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative. *Biores Technol.* 77(2001):247-55.

- [10] Chanzu HA, Onyari JM, Shiundu PM. Biosorption of malachite green from aqueous solutions onto polylactide/spent brewery grains films: kinetic and equilibrium studies. *J Polym Environ* (2012); 20(3): 665 – 672
- [11] R. Ahmad, Studies on adsorption of crystal violet dye from aqueous solution onto coniferous pinus bark powder (CPBP), *J. Hazard. Mater.* 171 (2009) 767–773.
- [12] Y.S. Ho, J.C.Y. Ng, G. McKay, Kinetics of pollutant sorption by biosorbents: review, *Sep. Purif. Method.* 29 (2000) 189–232.
- [13] M. Dogan, Y. Ozdemir, M. Alkan, Adsorption kinetics and mechanism of cationic methyl violet and methylene blue dyes onto sepiolite, *Dyes Pigments* 75 (2007) 701–713
- [14] M. El-Guendi, Homogeneous surface diffusion model of basic dyestuffs onto natural clay in batch adsorbers, *Adsorpt. Sci. Technol.* 8 (1991) 217–225.
- [15] I. Langmuir, Adsorption of gases on plain surfaces of glass mica platinum, *J. Am. Chem. Soc.* 40 (1918) 1361–1403.
- [16] H.M.F. Freundlich, Over the adsorption in solution, *J. Phys. Chem.* 57 (1906) 385–471.
- [17] K.M. Parida, A.C. Pradhan, Removal of phenolic compounds from aqueous solutions by adsorption onto manganese nodule leached residue, *J. Hazard. Mater.* 173 (2010) 758–764.
- [18] K. Fytianos, E. Voudrias, E. Kokkalis, Sorption–desorption behavior of 2,4 dichlorophenol by marine sediments, *Chemosphere* 40 (2000) 3–6.