

## **Acid-thermal Activated Nanobentonite as an Economic Industrial Adsorbent for Malachite Green from Aqueous Solutions. Optimization, Isotherm, and Thermodynamic Studies**

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**ABSTRACT:** The limited adsorption capacity of natural clays is a crucial and economic issue which confined their applications in industry as cheap adsorbents to remove toxic contaminants from wastewaters. Here, the adsorption capacity of a natural nano bentonite was enhanced by a simple acid and thermal activation and the manufactured nano-adsorbent was characterized by FESEM, BET, FT-IR, and XRD. Effects of pH, temperature, sorbent capacity, and the initial concentration of malachite green were examined. The isotherm behavior of the adsorption system was investigated by the Langmuir and Freundlich isotherm models. Also, the kinetic inspections demonstrated that the adsorption of malachite green matched with the pseudo-second-order kinetic and the obtained thermodynamic parameters H, S, and G showed that the adsorption of malachite green was a spontaneous and endothermic process. The results indicated that the acid-thermal activated nano bentonite, with an enhanced surface area of  $>220 \text{ m}^2/\text{g}$ , can be depleted as a powerful and low-cost adsorbent to expel malachite green from aqueous solutions.

**Keywords:** *Adsorption, Isotherm, Malachite Green, Nanobentonite, Removal, Thermodynamic.*

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Table S1: Details of the dye used.

Dyestuff	Basic Green 4 (BG 4)
IUPAC name	N-[4-[[4- dimethylamino phenyl]phenylmethylene]-2,5-cyclohexadien-1-ylidene]-Nmethyl-oxalate
Commercial name	Malachite Green oxalate
Appearance	Green crystalline powder
Empirical formula	C <sub>52</sub> H <sub>54</sub> N <sub>4</sub> O <sub>12</sub>
Molecular weight	926g
$\lambda_{\max}$	619nm
Formula	

Table S2: Pseudo-first-order and pseudo-second-order rate constants for three different MG concentrations.

[MG]	Pseudo-first-order			Pseudo-second-order				
ppm	q <sub>cal</sub> (mg/g)	k <sub>1</sub> (1/min)	R <sub>2</sub>	q <sub>cal</sub> (mg/g)	k <sub>2</sub> (g/mg.min)	h (mg/g.min)	R <sub>2</sub>	q <sub>exp</sub>
20	163.11	0.7553	0.84	102	0.0057	0.57	0.99	99
40	185	0.649	0.91	156	0.0035	0.537	0.99	150
60	162.2	0.7150	0.89	208	0.0025	0.51	0.99	198
80	138	0.6807	0.98	263	0.0019	0.473	0.99	249
100	176	0.5716	0.93	322	0.0014	0.424	0.99	300

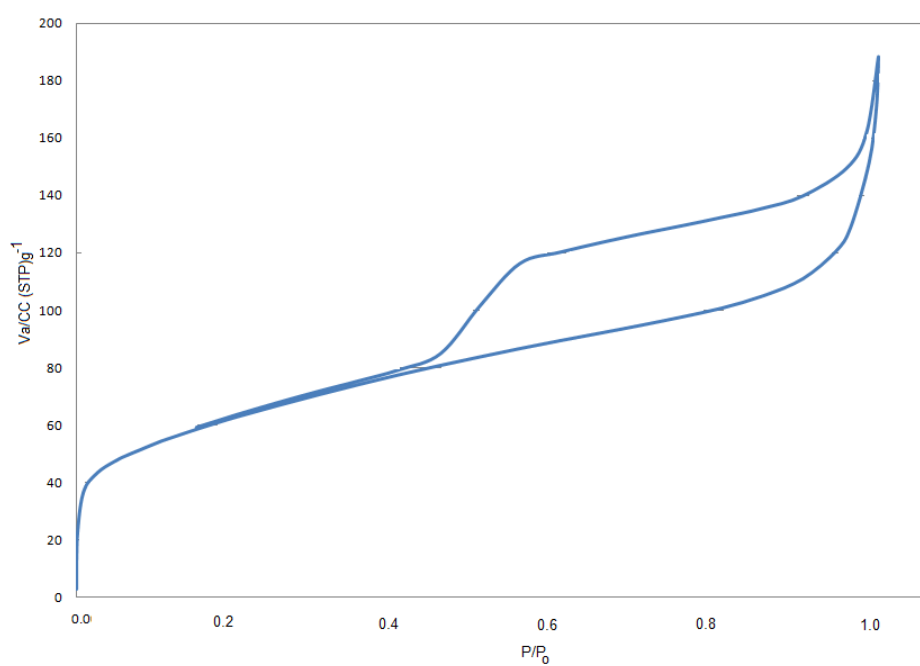
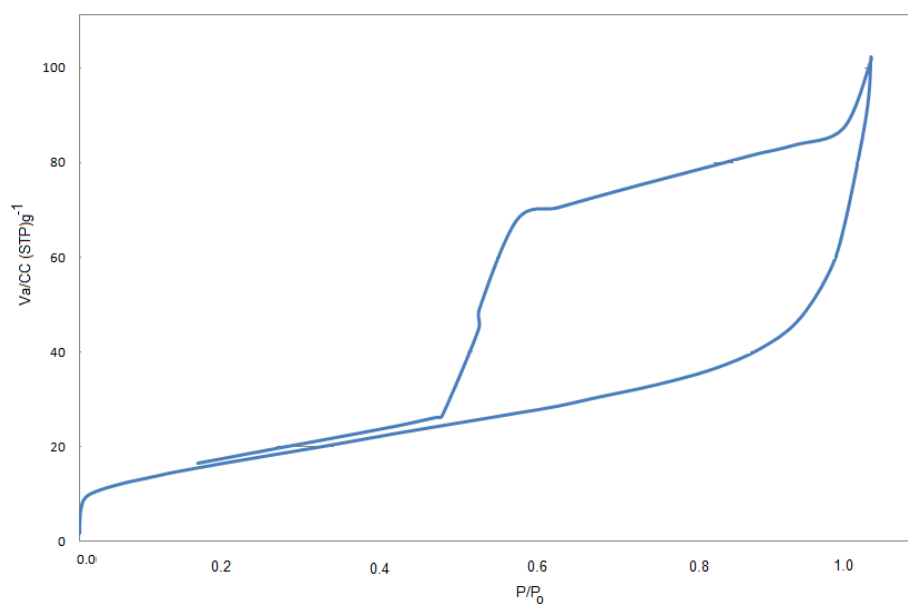


Fig. S1:  $N_2$  adsorption/desorption isotherms for nanobentonite (up) and acid/thermal activated nanobentonite (bottom).

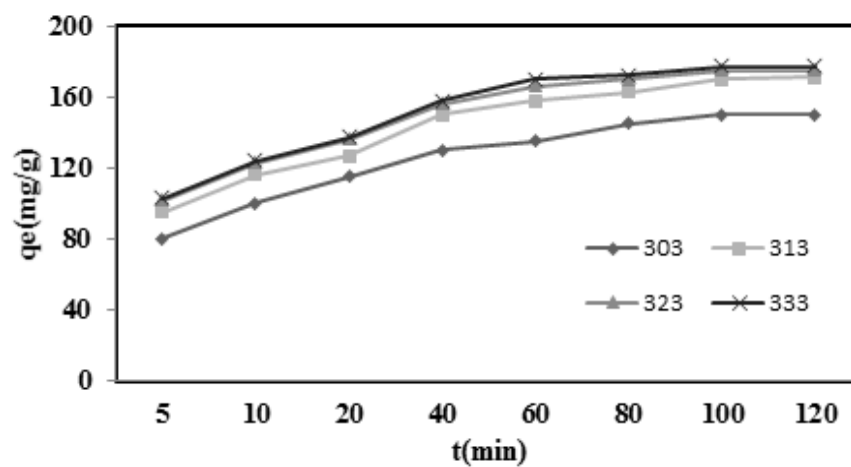


Fig. S2: Effect of temperature on the adsorption of MG by acid-thermal nanobenonite. Conditions: initial dye concentration: 40 mg/L, pH=6, adsorbent dose: 0.01mg

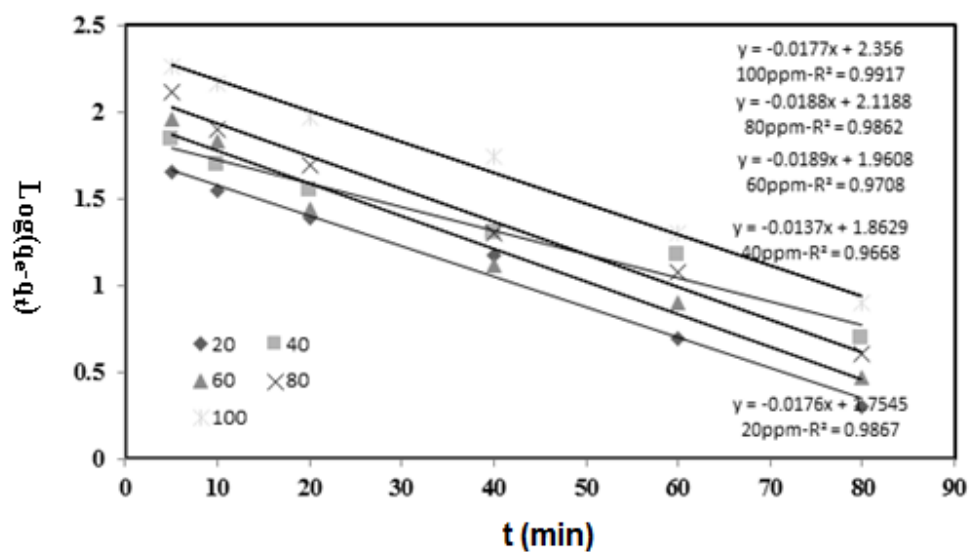


Fig. S3: Pseudo-first-order kinetic models for the dye adsorption onto the nanobentonite. Conditions: initial dye concentration: 40 mg/L, dose 0.01g, temperature: 303 K, contact time: 100 min.

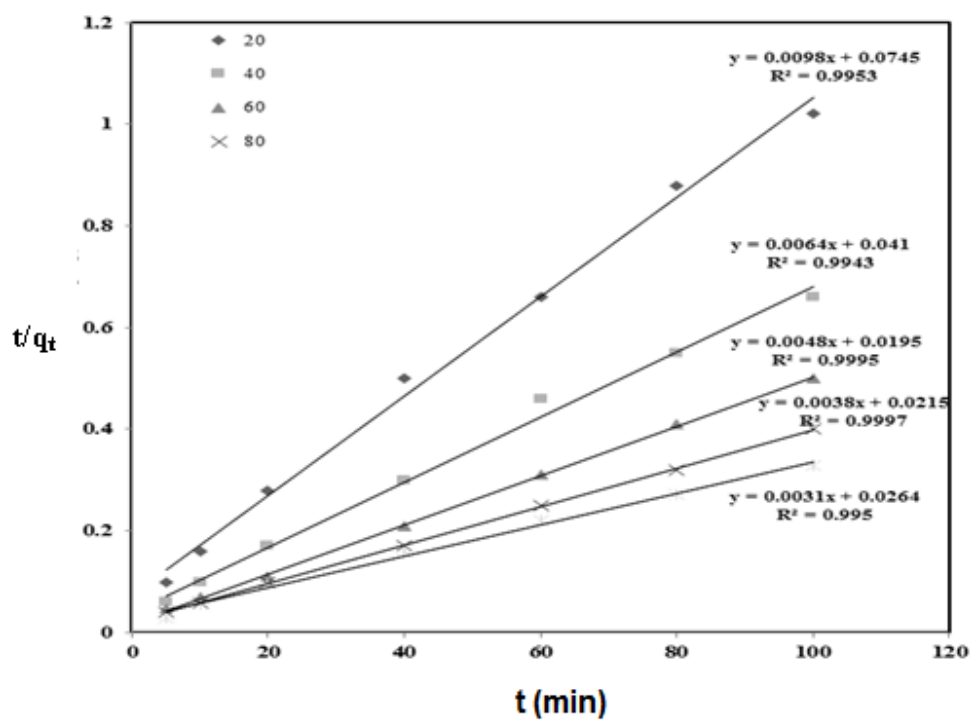


Fig. S4: Pseudo-second-order kinetic models for the dye adsorption onto the nanobentonite.

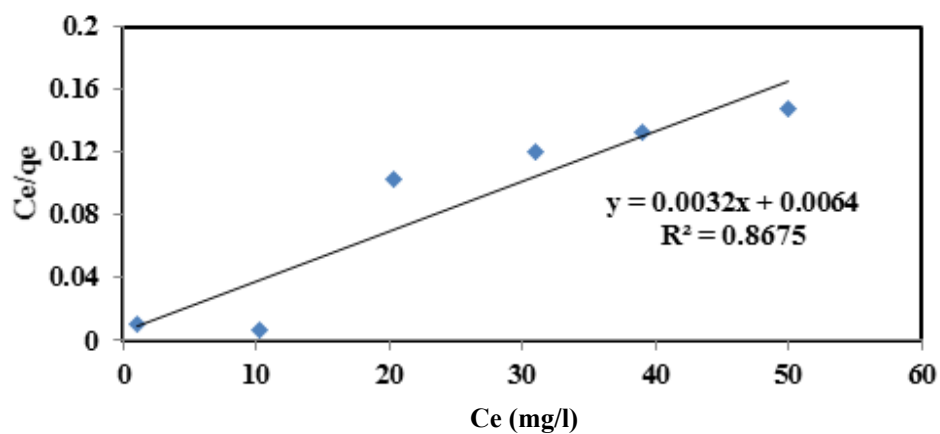
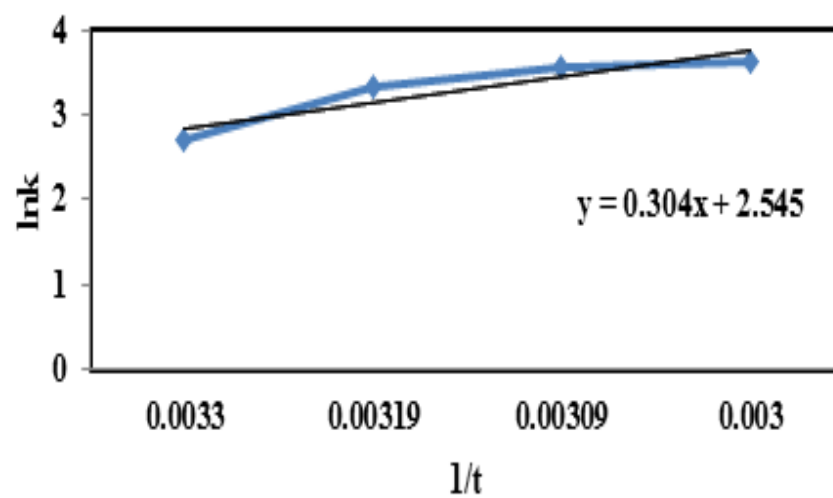


Fig. S5: The linear Langmuir adsorption isotherms for the MG adsorption by the acid-thermal activated nanobentonite. Experimental conditions: dose 0.01g, pH= 6, T: 303 K, contact time 100 min.



**Fig. S6** Effect of temperature on the MG an adsorption by the acid-thermal activated nanobentonite. Experimental conditions: initial dye concentration  $40 \text{ mg l}^{-1}$ , dose  $0.01 \text{ g}$ ,  $\text{pH} = 6$ , temperature  $303 \text{ K}$ .