

# Adsorption mechanism of malachite green onto activated phosphate rock: a kinetics and theoretical study

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## Abstract

Adsorption kinetics of malachite green onto the Algerian activated phosphate rock was studied for better removal of the dye from wastewater. The prepared sorbent displayed a good surface area of 42.2 m<sup>2</sup>/g. The adsorption process appeared to be of physisorption nature and it took less than 60 min to get equilibrium whereas the kinetics indicated that the adsorption is likely a second order reaction, which is further proved with the high  $R^2$  value. The intra-particle diffusion model confirms an adsorption mechanism limited on two steps, i.e., (1) surface adsorption, and (2) pore diffusion with a diffusion parameter of  $D_1=10^{-18}$  cm<sup>2</sup>/s. Besides, semi-empirical theoretical calculations provide a new insight into adsorption mechanism as a principle of hydrogen bonding and ionic interaction.

**Keywords:** Adsorption; Dye Removal; Kinetics; Phosphate; PM3

## Introduction

Today, synthetic dyes are found in all spheres of our daily lives as more than 100,000 of commercial dyes have been produced as a factor of  $7 \times 10^5$  to  $10^6$  tons per year (McMullan et al., 2001). Among them, 10-15% of are estimated to be discharged as effluents by textile industry (Ncibi et al., 2007). Even in smaller amounts, xenobiotic nature of dyes makes them resistant to deterioration and hence are persistent in flowing water resulting into inhibition of aquatic biota (Patil et al., 2011). The compounds are therefore required to be removed from the aquatic system. Several methods have been employed for remediation of dye-containing effluents including biological, physicochemical, and chemical techniques (Forgacs et al., 2004).

For the removal of dyes from wastewater, adsorption has been proven to be one of the effective procedure due to its high efficiency, adsorbent recyclability and less harmful effects on environment as compared to others conventional remediation techniques (Ertaş et al., 2010). Since commercially available synthetic adsorbent are expensive and are difficult to regenerate (Rubin et al., 2005), research is focusing on use of natural and low cost adsorbents especially phosphate containing compounds which possess great potential to remove dyes from solutions (Keleş et al., 2010; Elouear et al., 2008; Young et al., 2005; Aklil et al., 2004; Baraka et al., 2009; Alzaydien, 2009; Achkoun et al., 2012).

In order to develop an accurate understanding of the adsorption process, theoretical modelling of the physicochemical properties

resulting from the interaction between adsorbent and adsorbate in terms of various computations quantum chemistry approaches is therefore an important issue. Recently, quantum chemical methods have profoundly changed the science of designing, developing and interpreting structure–property relationships of different organic and inorganic materials (Pang and Xu, 2012; Wick et al., 2010; Vysotsky et al., 2015; Chernyshova et al., 2011). For experimentalists, exploitation of deep insights provided by the computational quantum chemistry may present an effective guide for the adsorption studies in terms of comprehension and interpretation.

The aim of the current study is to study the mechanistic nature of malachite green adsorption onto low-cost Algerian activated phosphate rock. For this purpose, a combination of theoretical and kinetic model is used, i.e., general adsorption, adsorption diffusion, and semi-empirical modelling.

## Materials and Methods

### Adsorbent

The phosphate used in this study was obtained from the region of Djebel onk (FERPHOS Mining Company, Algeria); whose basin is located about 100 km south of Tebessa city and 20 km from the Algerian-Tunisian border. The mountainous massive of Djebel Onk forms a set of 20 km length, which rises to 1198 m altitude in Djebel Tarfaya. The geographical coordinates are recorded as 34.4300° N, 8.0000° E (Mezghache et al., 2002).

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As phosphate rock was received in the form of brown-coloured powder, prior purification was undergone to remove all impurities associated with the phosphate material. Particles fraction, having a particle size less than 80  $\mu\text{m}$ , was abundantly washed with distilled water and then dried in an oven overnight at 105  $^{\circ}\text{C}$ . Subsequently, the fraction of the phosphate obtained was subjected to chemical activation (acid/base) in order to obtain an activated phosphate rock-support according to the protocol described by Elouearet al., (2008). Spectrometric and gravimetric methods were carried out for the chemical analysis and the specific surface area was measured by Sear's method (Sears., 1956).

## Sorbate dye

Malachite green dye was purchased from Sigma-Aldrich. A stock solution of dye was prepared by dissolving 1 gram dye in 1000 ml distilled water. Afterwards, the solution diluted using distilled water as per the required concentration range of 1-100 mg/L.

## Kinetics study

The adsorption kinetics of malachite green was performed using 100 mg/L dye concentration and an activated phosphate rock mass of 1 gram. The agitation speed was kept constant at 250 rpm for 85 min at 30  $^{\circ}\text{C}$ . At programmed intervals of time, malachite green concentrations were measured using the UV-visible spectrometric method at a wavelength of 674 nm. Blanks containing distilled water were used as negative controls.

## Theoretical calculation (modelling approach)

The computations were made with a P4 Duo Proc X64 (8G0 RAM) microcomputer in Windows 8.0 environment. All calculations were made using HyperChem v7 software (<http://www.hyperchem.com>). The geometry of malachite green was optimized at the MM+ level of theory (r.m.s = 0.0001 Kcal/ $\text{\AA}$ ). Mulliken atomic charges and electrostatic potential were assessed by the semi-empirical parametric method 3 (PM3) being derived from the Hartree-Fock theory (Stewart., 2004).

We studied possible interaction sites through computation of electronic charge distribution and electrostatic potential. The interactions between phosphate groups ( $\text{PO}_4^{-3}$ ) of activated phosphate rock and malachite green dye is considered as background knowledge due to (a) acid–base interaction due to hydrogen bonding; (b) adsorption by dispersion forces as a principle of electrostatic interactions; and (c) ion pairing by adsorption onto opposite-ly unoccupied charged sites.

**Table 1:** Chemical composition of natural and activated phosphate rock

Samples	Composition (% by weight)							
	CaO	P <sub>2</sub> O <sub>5</sub>	MgO	Fe <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	F <sub>2</sub>	CO <sub>2</sub>	SO <sub>4</sub>
Phosphate rock	42.80	23.05	2.01	0.70	2.90	2.80	9.83	3.13
Activated phosphate rock	42.72	23.89	1.99	0.67	2.70	2.04	3.83	3.04

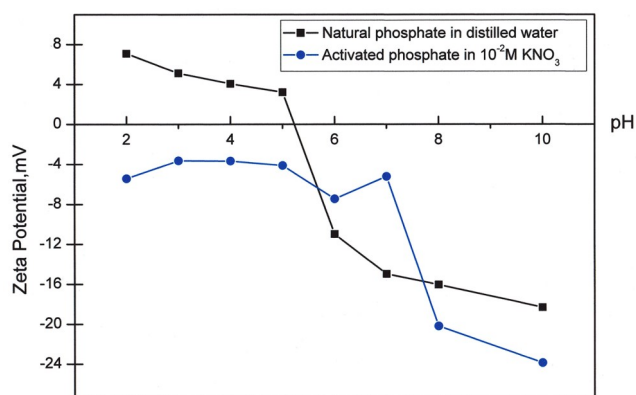
# Results and Discussion

## Phosphate rock characterization

The chemical analysis revealed that the main components in phosphate rock are CaO, P<sub>2</sub>O<sub>5</sub>, and CO<sub>2</sub> followed by flour and quartz (Table 1). The phosphate rock powders showed different chemical composition before and after the activation due to acid/base treatment. A reduction in the mass fraction of CO<sub>2</sub>, CaO and F<sub>2</sub> after chemical treatment is observed, which was further decreased from 9.83%, 42.8% and 2.8 % (w/w) to 3.83%, 42.72% and 2.04 % (w/w), respectively. However, the percentage of P<sub>2</sub>O<sub>5</sub> content increased from 23.05% to 23.89%.

The surface area of activated phosphate rock is observed to be 42.20 m<sup>2</sup>/g, which is greater than the natural phosphate rock whose initial surface area was of 27.67 m<sup>2</sup>/g. This value indicates that the phosphate has low porosity.

The pH measurements are an important factor in adsorption study, as it indicates surface charge properties of phosphate particles and in turn can suggest the ability of the compound to get adsorb, penetrate and adhere onto the surface of the adsorbent. In distilled water, phosphate particles had an isoelectric point for pH ranging between 4-6, while the surface charge is appeared to be negative above this pH. The activated phosphate rock used in this study had a pH of 8.58 that confirms the negative charge of activated phosphate rock over the surface area (Figure 1).



**Fig. 1:** Zeta potential of phosphate particles as a function of pH. (Ionic strength maintained by addition of 10<sup>-2</sup> M KNO<sub>3</sub>, T=30 $^{\circ}\text{C}$ ).

## Adsorption equilibrium – effect of contact time

The adsorption experiments were performed using two systems with natural and activated phosphate rock. The adsorption capacity

of malachite green in both systems was measured using 1 g of the prepared phosphate combined with an initial solution of 20 mg/L at adjusted pH of 8. The solutions were continuously agitated at 250 rpm and a temperature of 30 °C.

Figure 2 illustrates that the adsorption rate was fast in the beginning of the process which became slower during the stirring time, and reached to the equilibrium state in less than an hour. It is observed that the adsorption capacity of the activated phosphate rock was larger than that of natural phosphate rock. In addition, as adsorption rate was faster with activated phosphate rock compared to the phosphate rock; the difference could be due to the nature of the interactions of each phosphate surface with the malachite green dye and to the changes in phosphate surface area (Elouear et al., 2008).

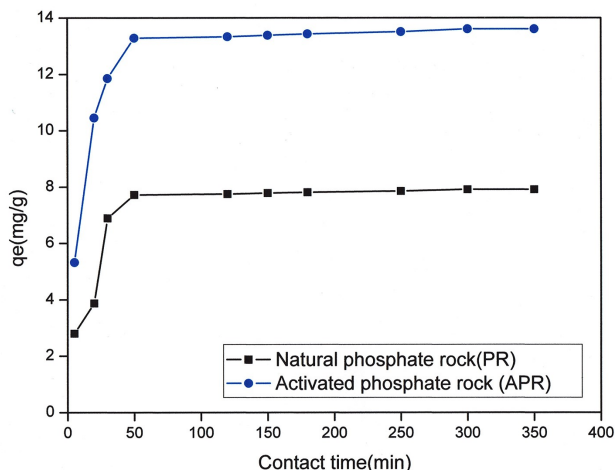


Fig. 2: Effect of contact time on the removal of malachite green by phosphate rock and activated phosphate rock (T=30°C, C0 = 20 mg L<sup>-1</sup> and amount of phosphate rock =1g).

### Adsorption kinetics

The adsorption reaction and adsorption diffusion models are well established methods to describe the adsorption kinetics. Hereby, we considered the kinetic laws of the pseudo-first-order (Ho and McKay, 1999), and the pseudo-second-order (Ho et al., 2000) for intraparticle diffusions as described earlier (Manlin et al., 2014).

**Pseudo first-order kinetic model:** The pseudo first-order equation, proposed by Lagergren (Ho and McKay, 1999), can be expressed as follows:

$$\log(q_e - q_t) = \log(q_e) - \frac{K_1}{2.303} t \quad (1)$$

where  $q_e$  and  $q_t$  are the quantities of dye adsorbed at “equilibrium” and at time “t”, respectively (mg/g) while  $K_1$  is the adsorption rate constant ( $\text{min}^{-1}$ ).

The straight line obtained by plotting  $\log(q_e - q_t)$  versus  $t$  gives  $\log q_e$  as the intercept and  $K_1/2.303$  as the slope. Thus, the amount of solute adsorbed at equilibrium ( $q_e$ ) and the first order kinetic constant ( $K_1$ ) can be obtained from the intercept and the slope.

The values of the kinetic model parameters and the correlation coefficient are presented in Table 2. Figure 3 showed the pseudo-first order kinetics modelling of malachite green dye adsorption onto activated phosphate rock. The equilibrium rate constant of pseudo-first order sorption ( $K_1$ ) was recorded to be of  $2.543 \times 10^{-2} \text{ min}^{-1}$ . The correlation coefficients  $R^2$  was below than 0.930 and the calculated amount of solute adsorbed  $q_e$  did not appear to be good in agreement with the experimental data. Therefore, it is confirmed that the adsorption of malachite green onto activated phosphate rock is not a first order kinetics.

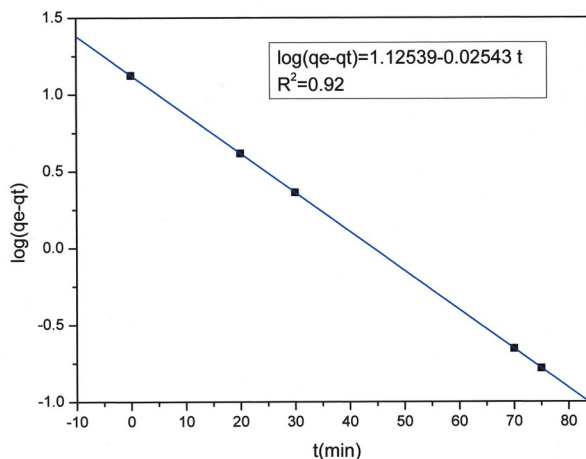


Fig. 3: Pseudo first-order kinetics for adsorption of malachite green onto activated phosphate rock.

**Pseudo-second-order kinetic model:** The pseudo-second-order kinetic equation is expressed as follows (Ho et al., 2000);

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \left(\frac{1}{q_e}\right)t \quad (2)$$

where  $K_2$  ( $\text{g/mg} \cdot \text{min}$ ) is the second order kinetic constant for the adsorption reaction.

The results in Figure 4 showed a linear relationship with a correlation coefficient closer to the unity ( $R^2=0.997$ ), hence indicating an adequate model to correctly describe the adsorption kinetics. Hereby, calculated  $q_e$  values found to agree the experimental data set and therefore it can be concluded that the adsorption of malachite green dye onto activated phosphate rock was likely a second order reaction. Similar results were found in the adsorption of malachite green onto different adsorbents such as a chitosan bead, degraded

Table 2: Kinetics parameters of malachite green adsorption onto activated phosphate rock

Pseudo-first order			Pseudo-second order			
$q_e$ (mg/g)	$K_1(\text{min}^{-1})$	$R^2$	$q_e$ (mg/g)	$K_2$ (g/mg.min)	$R^2$	$D$ ( $\text{cm}^2 \cdot \text{s}^{-1}$ )
13.347	$2.543 \times 10^{-2}$	0.920	15.188	$5.890 \times 10^{-3}$	0.997	$2.898 \times 10^{-18}$

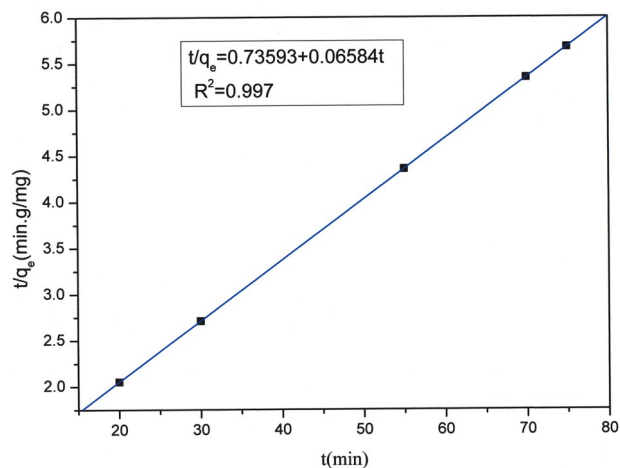


Fig. 4: Pseudo second-order kinetics for adsorption of malachite green onto activated phosphate rock.

coffee bean, modified rice husk and maize cob (Bekçi et al., 2008; Baek et al., 2010; Zou et al., 2011; Sonawane et al., 2009).

**Intraparticle diffusion model:** The intraparticle diffusion model is presented by the following equation (Manlin et al., 2014);

$$q_t = K_t t^{1/2} \quad (3)$$

where  $K_t$  is the intraparticle diffusion rate constant ( $\text{g/mg}\cdot\text{min}^{1/2}$ ), which is derived from the slope of the linear part of the equation for this model. The  $q_t$  is the quantity of the dye adsorbed at “equilibrium” and at time “t”.

The values of the diffusion parameter ( $D_i$ ) are deduced from the following formula;

$$D_i = \frac{0.03 \cdot r_0}{t^{1/2}} \quad (4)$$

where  $t_{1/2}$  is a half-time reaction (s) (adsorption equilibrium reaction),  $r_0$  is the particle diameter of the adsorbent in (cm), and  $D$  is intraparticle diffusion parameter ( $\text{cm}^2/\text{s}$ ).

The introduction of the equation 3 to the experimental data indicated that the plot of  $q_t$  versus  $t_{1/2}$  exhibit two separate regions with two straight lines, implying the existence of several steps that may have controlled the adsorption reaction process. The intraparticle diffusion constants observed to have decreasing values, i.e.,  $K_{t1}=1.42$  ( $\text{g/mg}\cdot\text{min}^{1/2}$ ) and  $K_{t2}=0.023$  ( $\text{g/mg}\cdot\text{min}^{1/2}$ ), successively; which are directly related to the nature of the internal porosity of activated phosphates (Zou et al., 2011).

In Figure 5, two plateau are observed, indicating that the diffusion of malachite green onto the activated phosphate rock surface is carried out in two stages. In addition, deviations of the straight lines from the origin and the calculated values of the diffusion parameter are estimated to be of  $D_i = 10^{-18}$   $\text{cm}^2/\text{s}$ , hence, suggesting that the intraparticle diffusion was not the only rate limiting mechanism in the adsorption mechanism.

The behavior may be due to the dimensionality of malachite green dye since the malachite green is a voluminous molecule with a calculated polarizability value of  $42\text{\AA}^3$ . It can be deduced from

here that the dye diffused slowly in the macro-pores of phosphate particles during the adsorption reaction. The phenomenon, therefore, confirms that the mechanism of malachite green adsorption onto the activated phosphate rock could have been due to the contribution of both surface adsorption and intraparticle diffusion. Similar results were reported for slow rate adsorption in case of big molecules such as for methylene blue and malachite green dyes, onto fly ash and activated carbon respectively (Kumar et al., 2005; Hameed and El-Khaiary, 2008).

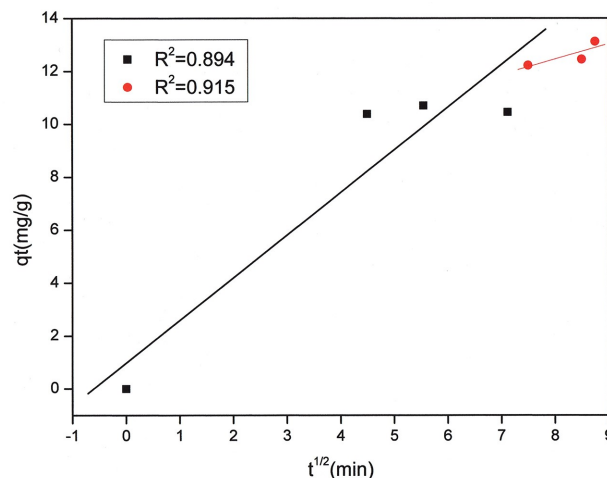


Fig. 5: Intraparticle diffusion plots for malachite green adsorption onto activated phosphate rock.

## Theoretical calculations

Mulliken atomic charges calculated by the semi-empirical PM3 theoretical method are presented in Figure 6. It shows that, for malachite green dye, negative charges were situated onto carbon atoms while positive charges on nitrogen and hydrogen atoms. In addition, malachite green has three extremity sites, i.e., two alkyl amine groups  $-\text{N}(\text{CH}_3)_2$  and  $=\text{N}(\text{CH}_3)_2^+$  with positive charges  $+0.105e$ ,  $+0.103e$ , respectively; and ring with low positive charge ( $+6 \times 10^{-3}e$ ).

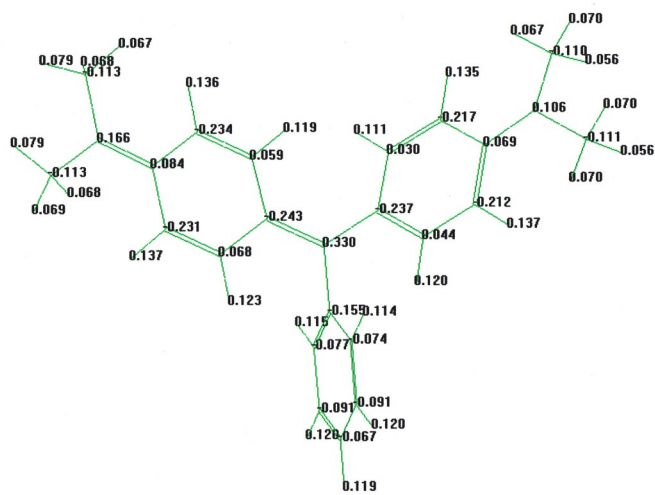


Fig. 6: Mulliken atomic charges on various molecular moieties of malachite green dye as deduced from their optimized PM3 molecular geometries.

From the calculated charges and the electrostatic potential model, it is clear that the negative charge of the phosphate ( $\text{PO}_4^{3-}$ ) onto the surface of activated phosphate rock interacts with malachite greenalkyl amine groups existing in solution by electrostatic attraction (Figure 7). In addition, the negative charges of phosphate groups ( $\text{PO}_4^{3-}$ ) facilitated the formation of hydrogen bonding between the positively charged hydrogen atoms in alkyl amine groups of malachite green dye. Therefore, the cooperative contribution of both hydrogen bonding and electrostatic attraction between alkyl amine groups in malachite green and phosphate groups ( $\text{PO}_4^{3-}$ ) leads to adsorption and enhancement of its capacity. This suggests that the main mechanism for the adsorption behavior of malachite green onto activated phosphate rock is physisorption in nature.

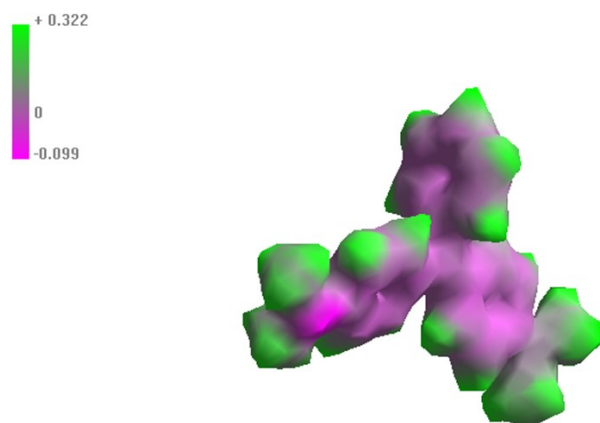


Fig. 7: PM3 calculated electrostatic potential of malachite green showing negative and positive electrostatic potential regions.

To confirm the physical adsorption nature, Dubinin–Radushkevich isotherm is applied and the mean free energy of adsorption ( $E$ , kJ/mol) is calculated as described earlier (Manlin et al., 2014). Following expression used for this purpose;

$$E = \left[ \frac{1}{\sqrt{-2B}} \right] \quad (5)$$

where  $B$  is the constant of sorption energy ( $\text{mol}^2/\text{kJ}^2$ ).

It has been established that, adsorption free energy ranging from 1 to 7 kJ/mol indicate a physisorption process (Li et al., 2004). In this work, we have calculated an adsorption free energy of 0.5 kJ/mol, attesting a physical adsorption reaction (Figure 8). Similar results have been reported for physical adsorption reaction with a free energy  $E=1\text{kJ/mol}$  using layered double hydroxide (HDL) carbon dots composite (Manlin et al., 2014). A previous study mentioned that the hydrogen bonding took an important role in physical adsorption process (Renault et al., 2008).

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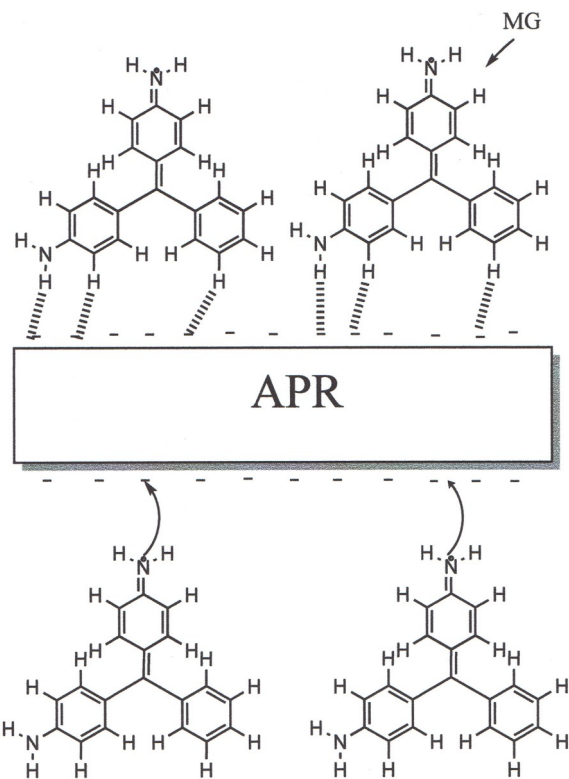


Fig. 8: Schematic presentation of the adsorption process of malachite green onto activated phosphate rock.

## Conclusions

Mechanism study based on the theoretical calculations revealed that the malachite green dye can be adsorbed onto activated phosphate rock by the cooperative contribution of hydrogen bonding and ionic interaction formed between the alkyl amine groups  $-\text{N}(\text{CH}_3)_2$ ,  $=\text{N}(\text{CH}_3)_2^+$  and the negative surface charges of phosphate groups, these double interactions are beneficial to the improvement of adsorption capacities. The calculated Dubinin–Radushkevich means sorption energy ( $E$ ) gives a value of 0.50 kJ/mol, indicating a physical adsorption in nature and further, confirms the proposed mechanism. The kinetics study reveals that the adsorption is described by the pseudo-second-order kinetic model and taking place in two successive steps, firstly surface adsorption and then slow pore diffusion characterized by a small value of effective diffusion parameter.

### Compliance with ethical standards

### Conflict of Interest

The authors declare that they have no conflict of interests.

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