

## A comparative study of malachite green removal from an aqueous solution using raw and chemically modified expanded perlite

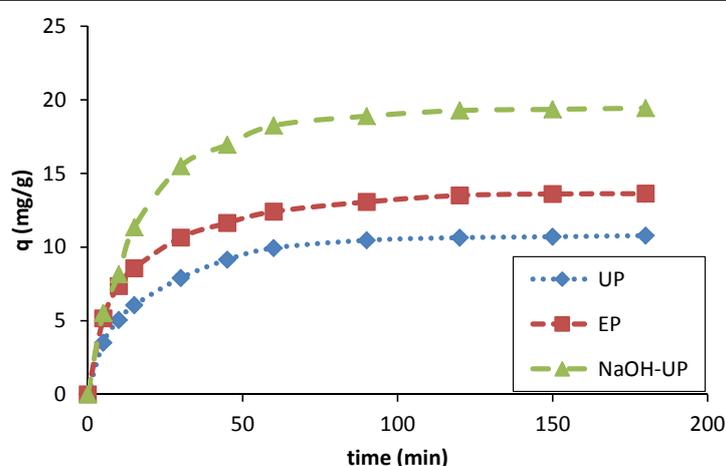
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### HIGHLIGHTS

- An easily available low-cost mineral (Perlite) is modified for adsorption.
- Chemically modified perlite was used to remove malachite green from an aqueous solution for the first time.
- Modified adsorbents were characterized by FTIR and SEM analyses.
- Adsorption kinetics, isotherm and effects of the influential parameters were studied.

### GRAPHICAL ABSTRACT



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### ABSTRACT

Adsorption of malachite green (MG) from an aqueous solution onto unexpanded perlite (UP), expanded perlite (EP) and NaOH-modified unexpanded perlite (NaOH-UP) powders has been investigated. The effects of contact time, pH, initial dye concentration, adsorbent dosage and temperature have been evaluated. The adsorbents were characterized by Brunauer-Emmett-Teller (BET) analysis, Fourier transform infrared (FTIR) spectroscopy, and scanning electron microscopy (SEM). The obtained results proved that the three examined powders can be used successfully for removal of MG from aqueous solutions as low cost mineral adsorbents. The maximum adsorption capacities of UP, EP and NaOH-UP were 23.81 mg/g, 29.41 mg/g and 39.68 mg/g, respectively. Kinetic studies show that the kinetics of the MG adsorption onto the adsorbents followed the second order model. The MG equilibrium adsorption data were best described by the Langmuir isotherm model for all adsorbents.

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## 1. Introduction

The wastewater of some common industries, which are usually discharged into the environment, contain a large amount of dyes, heavy metal, surfactants and other hazardous chemicals. Synthetic dyes are used in many industries such as textile, printers, paper production, food technology, hair colourings, etc. Accordingly, the removal of dyes from contaminated wastewaters is an urgent global requirement [1,2]. Malachite green (MG) is a cationic dye that has many applications such as fungicide in the aquaculture industry [3]. This dye has adverse carcinogenic properties and its usage has been banned in such industries [4]. However considering its low cost, high efficiency, and lack of alternative material, MG is still applied in some regions [5,6]. As a result, the presence of MG in foodstuffs and environment, even at low concentrations, has become an important concern.

Dyes are almost stable compounds and conventional physicochemical and biological treatment methods are generally proposed to remove them from industrial wastewaters. Among all of the applied methods, the adsorption process is one of the most popular routes due to its simplicity of design and operation, high removal efficiency and economic advantageous if low cost adsorbents are applied [7]. Various types of dye can be completely removed even in very low concentrations [8]. Up to now, several different adsorbents have been used for the removal of MG such as rice husk bio-char produced by liquefaction [9], carboxylate functionalized multi-walled carbon nanotubes [10,11], zeolite [12], zeolitic imidazole framework [13], clay [14], bentonite [15], activated red mud [16] and walnut shell [17].

Perlite is an inert glassy volcanic rock which has an amorphous structure, light grey colour and high percentage of silica (70-76 %wt.). This low cost mineral can be found almost all around the world especially in USA, Greece, Turkey, Iran, Australia, and New Zealand. Due to the existence of 2-5% H<sub>2</sub>O chemically bounded within its inner microstructure, perlite has the ability to expand from 4 to 20 times its initial volume at temperatures close to its softening point (760-1100 °C). This kind of perlite will be lightweight, high-porosity, and white in colour [18,19]. As a result of this volume increase and obtained porous structure, water adsorption of the expanded perlite is significantly higher than the original raw mineral and obviously the density of the expanded perlite is very low compared to that

of unexpanded perlite [20]. This inorganic compound is almost chemically inert in the environment [21].

Several methods, such as expanded perlite modification by humic acid for methylene blue removal, have been proposed to increase the adsorption capacity of perlite [22]. Sari *et al.* investigated the adsorption capacity of expanded perlite and manganese oxide-modified EP for removal of Sb(III) [23]. Despite its potential for low cost dye removal, chemical modification of perlite has not been studied well. In this study, the adsorption capacities of unexpanded raw perlite (UP), expanded perlite (EP) and NaOH-modified unexpanded perlite (NaOH-UP) were evaluated for the removal of MG from aqueous solutions. Effects of contact time, pH, initial dye concentration and adsorbent dosage on the MG adsorption have been investigated.

## 2. Materials and methods

### 2.1. Chemicals

As adsorbate, MG dye with a molecular formula of C<sub>23</sub>H<sub>25</sub>N<sub>2</sub>Cl and molecular weight of 364.92 g.mol<sup>-1</sup> ( $\lambda_{\text{max}}$ =617 nm) was obtained from Merck company (Germany) and used in the experiments without further purification. The chemical structure of MG is given in Figure 1. As well, its pH was adjusted by addition of HCl and NaOH 0.5 M solutions. Adsorbents, UP and EP perlites were supplied by Omran Mooman Chabahar company from Angooran located in Zanjan province (Iran). The chemical composition of the perlite used is given in Table 1.

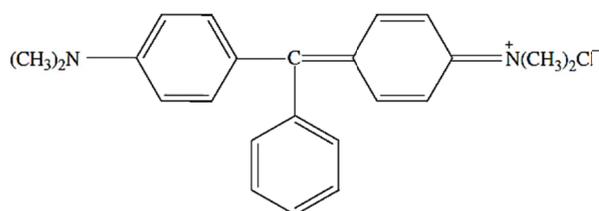


Fig. 1. Molecular structure of MG.

### 2.2. Preparation of the adsorbent

In order to remove dust and soluble impurities, the UP and EP were washed with deionized water three times and then dried in an oven at 80 °C for 24 h. The samples were sieved into #100 mesh size.

**Table 1.** The chemical composition of perlite.

Constituent	Percentage (%)
SiO <sub>2</sub>	72.8
Al <sub>2</sub> O <sub>3</sub>	12.951
Na <sub>2</sub> O	0.321
K <sub>2</sub> O	3.843
Fe <sub>2</sub> O <sub>3</sub>	0.92
TiO <sub>2</sub>	0.015
CaO	1.834
MgO	2.396
H <sub>2</sub> O	4.66
L.O.I	0.26

### 2.3. Preparation of NaOH-modified unexpanded perlite (NaOH-UP)

For preparation of the NaOH-UP sorbent, 2 g of UP were added to a 200 ml solution containing NaOH (0.7 M) and the reaction mixture was stirred at a speed of 120 rpm for 24 h at room temperature. The mixture then was filtered and washed several times with deionized water until the sample became free of NaOH and the pH of the solution was about natural. Finally, the prepared NaOH-UP was dried in an electrical oven (100 °C, 24 h) and sieved through a standard mesh (#100).

### 2.4. Characterization of perlite

In order to determine the surface functional groups of the perlite, FTIR analysis was applied at wavelengths in the range of 4000 and 400 cm<sup>-1</sup> (Perkin Elmer Spectrum, RX1, Germany). The surface morphology of the adsorbents were investigated by scanning electron microscope (SEM) analysis using a VEGA TESCAN scanning electron microscope operated at 30 kV accelerated voltage. The specific surface area, average pore size, and pore volume of the adsorbents were determined using the Brunauer-Emmet-Teller (BET) N<sub>2</sub> sorption method using a PHS-1020 (PHSCHINA, China) analyzer.

### 2.5. Batch adsorption experiments

The batch operation mode was used to investigate the effects of important experimental parameters, such as contact time, pH, initial dye concentration and adsorbent

dosage, in order to ascertain the MG adsorption by UP, EP and NaOH-UP. All adsorption experiments were carried out in 250 ml flasks, containing 100 ml of dye solution (with desired concentration and pH) shaken at a constant temperature (23°C). The solutions were shaken at 120 rpm in an incubator (incubator-CIT53, Teb Azma, Iran) until the adsorption equilibrium was achieved. Finally, the solutions were centrifuged (Hettich EBA 20) at 6000 rpm for 10 min and then the concentration of the remaining MG and C<sub>e</sub> were determined by applying a double beam UV-visible spectrophotometer (T80 UV/VIS spectrometer, PG Instrument Ltd) at the wavelength of λ<sub>max</sub> = 617 nm, which corresponds to the maximum visible light absorbance of MG. Subsequently, the concentration of dye was calculated using a calibration curve. The removal efficiency and the amounts of dye adsorbed per unit mass of the adsorbent (adsorbent capacity), q<sub>e</sub>(mg.g<sup>-1</sup>), were calculated using Eqs. (1) and (2), respectively.

$$\text{Removal Efficiency (\%)} = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

$$q_e = (C_0 - C_e) \frac{V}{M} \quad (2)$$

Where C<sub>0</sub> and C<sub>e</sub> are the initial and equilibrium dye concentrations (mg.l<sup>-1</sup>) respectively, V is the volume of the solution (L), q<sub>e</sub> is adsorption capacity (mg.g<sup>-1</sup>), and M is the weight of the adsorbent (g) used in the experiment.

## 3. Results and discussion

### 3.1. Adsorbent characterization

The FTIR spectra of UP, EP and NaOH-UP are shown in Figure 2 for comparison. The peak at 782 cm<sup>-1</sup> relates to the stretching vibration of Si-OH bonds. The peak at 1044 cm<sup>-1</sup> indicates Si-O-Si asymmetric stretching vibrations [24]. The peak at 1634 cm<sup>-1</sup> is due to the vibration of water molecules adsorbed on the perlite surface (due to the presence of -OH groups). The O-H bonds vibrations of NaOH can be observed at 1634 cm<sup>-1</sup>. Due to water loss in the thermal modification step, this peak decreased slightly in the EP [22]. The peak at 3434 cm<sup>-1</sup> indicates OH<sup>-</sup> vibration in the silanol groups. Modifying UP with NaOH led the Si-OH groups to convert to SiO<sup>-</sup> and increased the adsorption of MG

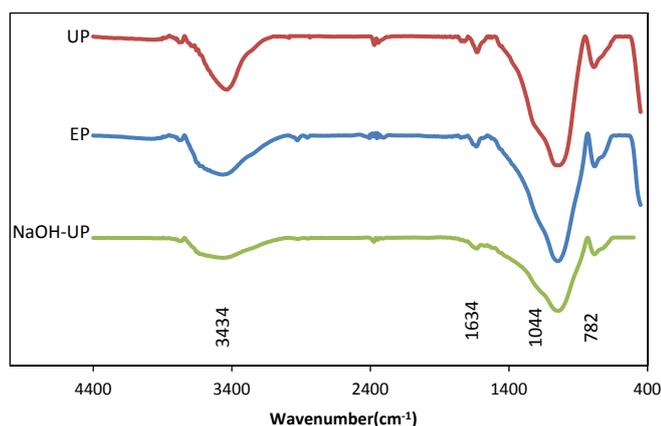


Fig. 2. FTIR spectra of UP, EP and NaOH-UP.

cationic dye. The FTIR spectra show that there is no significant change in the chemical composition of perlite. The  $-\text{SiO}^-$  groups also enhanced electrostatic interactions. Based on the interactions between the delocalized electrons in the MG and local electrons on the surface oxide ( $-\text{SiO}^-$ ), MG can be adsorbed on the NaOH-UP [25].

SEM images of UP, EP and NaOH-UP are shown in Figure 3. Results show the morphology, surface texture, and porosity of the adsorbent. There are significant differences in the surface morphology of the adsorbents. EP has a highly porous structure which may relate to the water desorption during the thermal treatment. UP has a flat surface containing fewer opened pores. As it can be seen, the porosity of perlite has been changed according to the thermal modification step. Similar results were observed by Kabra *et al.* [26].

The  $\text{N}_2$  sorption textural results are tabulated in Table 2. The amount of the specific surface area has been increased under thermal treatment. This is due to increase of pore volume after loss of water during of this operation. Calcination and dehydration led to an increase of pore diameter as well as pore expansion [27].

Table 2. The BET analysis results.

Adsorbent	UP	EP	NaOH-UP
surface area ( $\text{m}^2 \cdot \text{g}^{-1}$ ) BET	7.91	109.05	5.51
Average pore diameter (nm)	2.253	2.366	2.255
Pore volume ( $\text{cm}^3 \cdot \text{g}^{-1}$ )	0.045	0.501	0.023

### 3.2. Effect of contact time

Effect of contact time on the MG adsorption is presented in Figure 4. As it is shown, the adsorption

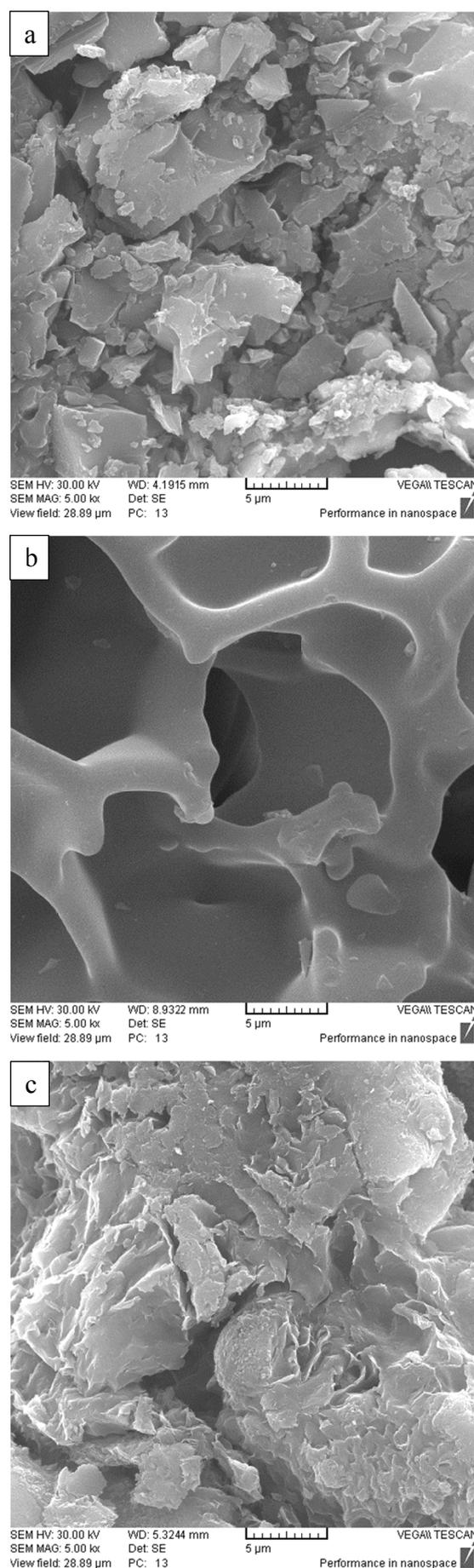


Fig. 3. SEM images of a) UP, b) EP and c) NaOH-UP (magnifications: 5000x).

Effect of contact time on the MG adsorption is presented in Figure 4. As it is shown, the adsorption is very fast at initial contact time and the adsorption capacity increases as the time increases until it reaches equilibrium in about 120 min. Equilibrium adsorption capacities of UP, EP and NaOH-UP were 10.8, 13.6 and 19.27 mg.g<sup>-1</sup>, respectively.

A fast adsorption rate may be attributed to the presence of initial unsaturated sorbing sites and the availability of these sites for dye molecules; the final low adsorption rate (after 120 min) can be attributed to the saturation of the sites with dye molecules. Reasonably, this can promote repulsions between the adsorbed molecules and others molecules present in the interface of the solution bulk [28].

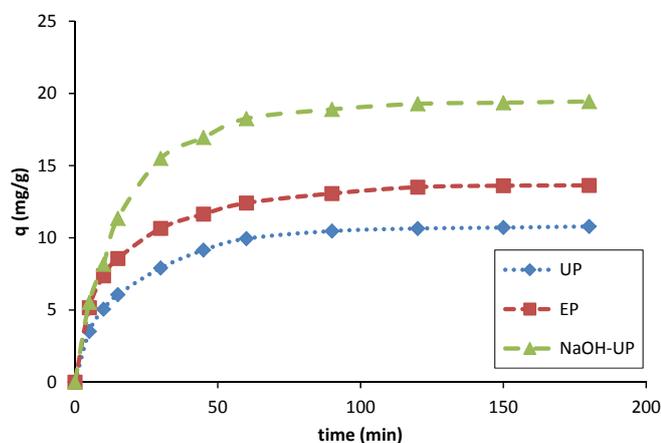


Fig. 4. Effect of contact time on MG adsorption on UP, EP and NaOH-UP.

### 3.3. Effect of solution pH

The effect of solution pH on the adsorption of MG on the UP, EP and NaOH-UP have been investigated at fixed initial dye concentration, adsorbent dosage, and temperature of 100 mg.l<sup>-1</sup>, 0.5 g and 23°C, respectively. Adsorption tests under alkaline conditions were not conducted due to the intrinsic structure alteration of the dye molecules (a chemical decolourization) at higher pH values [29]. Figure 5 shows the MG adsorption at different pH values (in the range of 2 and 6). It was found that the removal rate of MG increased as the pH increased, a similar trend was reported for the adsorption of MG on cellulose modified with maleic and phthalic anhydride [30]. As pH of the system increased, the number of negatively charged adsorption sites increased. Therefore, the electrostatic repulsions between the adsorbent site and the positively charged

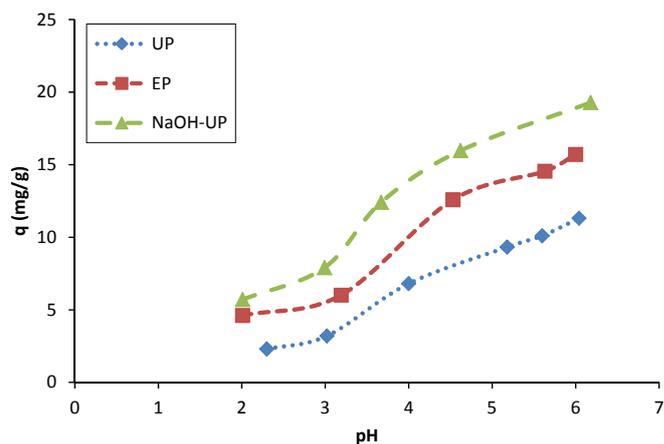


Fig. 5. Effect of solution pH on the adsorption of MG on UP, EP and NaOH-UP.

dye ions may result in an increase of the adsorption capacity [31,32].

### 3.4. Effect of adsorbent dosage

Adsorbent dosage is an important parameter because of its impact on the adsorption capacity. The effect of adsorbent dosage was studied in the removal of MG at a pH of 6, temperature of 23 °C and initial concentration of 100 mg.l<sup>-1</sup>. The plots of adsorption capacity and dye removal percentage are shown in Figure 6. When the adsorbent dosage increases the removal efficiency also increases based on the increase of the active sorbing sites [33].

### 3.5. Adsorption kinetics

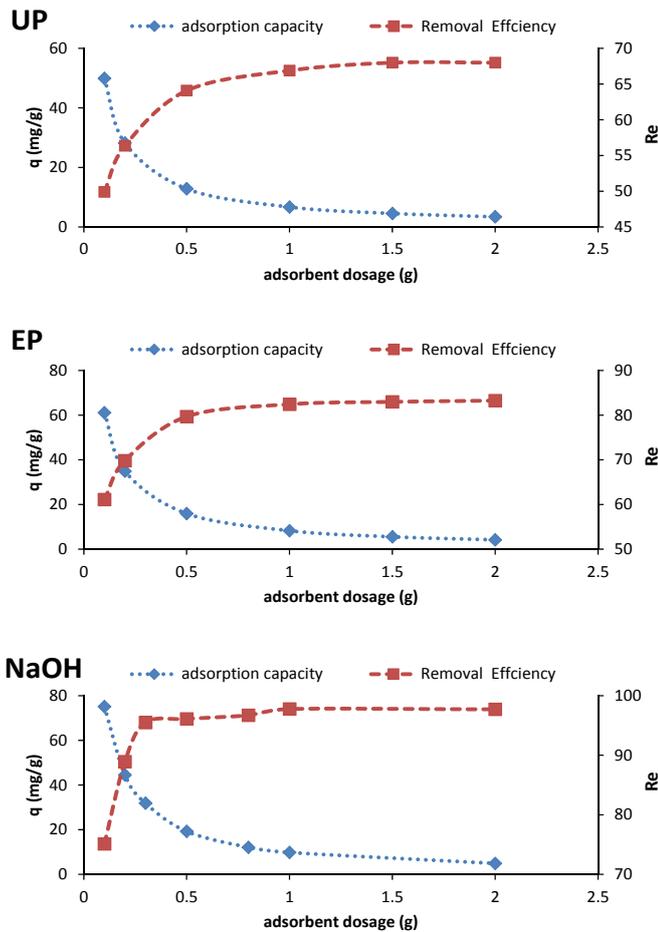
To study the process of MG adsorption two kinetic models of pseudo-first-order and pseudo-second-order were used to describe the adsorption mechanism. The pseudo-first-order equation can be expressed as Eq. (3) [34,35].

$$\ln (q_e - q_t) = \ln q_e - k_1 t \quad (3)$$

Where  $q_e$  (mg.g<sup>-1</sup>) and  $q_t$  (mg.g<sup>-1</sup>) are the amounts of the adsorbed dye at equilibrium state and at any time of  $t$  (min), respectively.  $k_1$  (min<sup>-1</sup>) is the rate constant of the pseudo-first-order model.

The pseudo-second-order kinetic equation can be expressed by Eq. 4 [36].

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (4)$$



**Fig. 6.** Effect of adsorbent dosage on MG adsorption onto UP, EP and NaOH-UP.

where  $K_2$  ( $\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$ ) is the rate constant of the model. It is necessary to introduce the correlation coefficient ( $R^2$ ) to estimate the suitability of different models. The equation which has a  $R^2$  value closer to unity describes the adsorption kinetics better and can be accepted as the describing model [29].

The kinetic parameters presented in Table 3 were calculated from plots of  $\log(q_e - q_t)$  versus  $t$  and the  $t/q_t$  versus  $t$ . For the first-order kinetic model, the obtained  $R^2$  value was relatively low and the calculated  $q_e$  (cal.) was very different from the experimental  $q_e$  (exp.) value. For the second-order kinetic model, the computed  $R^2$  was higher than 0.99. The  $R^2$  values of the pseudo-second-order model are higher than those calculated from pseudo-first-order equation, implying that the kinetics of MG adsorption can be better described by the pseudo-second-order model.

### 3.6. Adsorption isotherms

The adsorption isotherms reveal the specific relationship between the concentration of adsorbate

**Table 3.** Parameters of the first-order and second-order kinetics models for MG adsorption onto the studied adsorbents.

First order model	$q_e$ (exp.) ( $\text{mg} \cdot \text{g}^{-1}$ )	$k_1$ ( $\text{min}^{-1}$ )	$q_e$ (cal.) ( $\text{mg} \cdot \text{g}^{-1}$ )	$R^2$
UP	10.78	0.033	7.97	0.9875
EP	13.62	0.038	11.05	0.9839
NaOH-UP	19.44	0.036	14.50	0.9871
Second order model	$k_2 \times 10^3$ ( $\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$ )		$q_e$ (cal.) ( $\text{mg} \cdot \text{g}^{-1}$ )	$R^2$
UP	6.70		11.63	0.9994
EP	6.96		14.47	0.9998
NaOH-UP	3.88		21.05	0.9988

and its sorption degree onto the adsorbent surface at constant temperature under equilibrium condition [37]. Adsorption isotherm models are used to describe the adsorption progress and to investigate the equilibrium state of the adsorption operation [32]. Thus, several experiments were carried out to investigate the adsorption isotherm of MG at a solution pH of 6 and adsorbent dosage of 0.5 g. In these tests the initial concentrations of dye were changed in the range of 10 and 200  $\text{mg} \cdot \text{l}^{-1}$ .

Several theoretical and empirical correlations have been reported in the literature for modelling the adsorption isotherm. Two common isotherm models, Langmuir and Freundlich, are usually studied to describe the equilibrium data of MG sorption by various adsorbents.

The Langmuir assumed that the energy of adsorption is the same for all active surface sites and since a monolayer of adsorbate would ultimately build up on the surface of the sorbent, it does not depend on the degree of coverage. The adsorption process can be assumed a reversible one [38]. The linear form of the Langmuir isotherm equation is given by Eq. (5) [32].

$$\frac{1}{q_e} = \frac{1}{q_m K_L} \frac{1}{C_e} + \frac{1}{q_m} \quad (5)$$

where  $C_e$  is the equilibrium concentration of the adsorbate ( $\text{mg} \cdot \text{l}^{-1}$ ),  $q_e$  is the amount of the solute adsorbed per unit mass of the adsorbent ( $\text{mg} \cdot \text{g}^{-1}$ ),  $K_L$  is the Langmuir adsorption constant ( $\text{l} \cdot \text{mg}^{-1}$ ), and  $q_m$  is the theoretical maximum monolayer adsorption capacity ( $\text{mg} \cdot \text{g}^{-1}$ ).

In order to determine the adsorption favourability, a dimensionless constant called the separation factor or equilibrium parameter,  $R_L$ , is defined according to Eq. (6) [39].

$$R_L = \frac{1}{1 + bC_0} \quad (6)$$

The  $R_L$  value indicates the type of isotherm to be either favourable ( $0 < R_L < 1$ ), unfavourable ( $R_L > 1$ ), linear ( $R_L=1$ ) or irreversible ( $R_L=0$ ).

The Freundlich isotherm is used for non-ideal adsorption on a heterogeneous surface. The heterogeneity arises from the presence of different functional groups on the surface and various adsorbent–adsorbate interactions [40,41]. The linear form of the Freundlich isotherm is given by Eq. (7).

$$\log q_e = \log K_F + \left(\frac{1}{n}\right) \log C_e \quad (7)$$

$K_F$  is a constant related to the adsorption capacity and  $1/n$  is an empirical parameter related to the adsorption intensity. The  $1/n$  parameter varies with the heterogeneity property of the sorbent surface [42]. The constants calculated from the linear forms of the isotherms are given in Table 4.

**Table 4.** Isotherm models and constants for adsorption of MG onto the studied adsorbents.

Langmuir isotherm model	$q_m$ (mg.g <sup>-1</sup> )	$K_L$ (min <sup>-1</sup> )	$R^2$	$R_L$
UP	23.81	0.066	0.9974	0.37-0.93
EP	29.41	0.010	0.9934	0.27-0.90
NaOH-UP	39.68	0.209	0.9978	0.02-0.32
Freundlich isotherm model	$n$ (g.L <sup>-1</sup> )	$K_F$ (mg <sup>1-1/n</sup> .L <sup>1/n</sup> .g <sup>-1</sup> )	$R^2$	
UP	1.092	0.14	0.9829	
EP	1.010	0.35	0.9745	
NaOH-UP	3.380	12.08	0.7928	

The correlation coefficients ( $R^2$ ) reported in Table 4 for both Langmuir and Freundlich isotherm models show that both models are able to describe the relationship between  $q_e$  and  $C_e$  values. However, comparing the computed values demonstrates that the Langmuir model fits the examined equilibrium data better than the other. The values of  $R_L$  for UP, EP and NaOH-UP are in the ranges of 0.37-0.93, 0.27-0.90 and 0.02-0.32 respectively. Hence, the adsorption of MG onto UP and EP can be considered favourable.

Adsorption uptakes of the applied adsorbents are compared with some reported data. Adsorption capacities are listed in Table 5. The data given in Table 5 show that NaOH-UP has a slightly higher ability to remove MG from aqueous solutions compared to some of the other examined low cost adsorbents.

**Table 5.** Adsorption uptakes of some low cost adsorbents for MG removal.

Adsorbent	$q_{max}$ (mg.g <sup>-1</sup> )	Reference
Rice husks	6.5	[43]
Cadmium hydroxide nanowires loaded on activated carbon	19.0	[44]
Bentonite	178.6	[15]
Zea mays cob	16.72	[45]
Citrus limetta peel	8.73	[45]
Unexpanded perlite	23.81	This study
Expanded perlite	29.41	This study
NaOH-modified unexpanded perlite	39.68	This study

#### 4. Conclusion

In this study unexpanded (UP), expanded (EP) and NaOH modified unexpanded perlite (NaOH-UP) were used as adsorbents for the removal of malachite green (MG) from aqueous solutions.

NaOH can change and modify some surface functional groups of the adsorbent. It was found that the equilibrium state of adsorption can be achieved after about 2 hours. The adsorbed amount of MG slightly decreased with increasing adsorbent dosage and it increased with increasing pH in the acidic solutions. Adsorption capacity of EP is more than that of UP because of the morphology changes of EP in thermal treatment. The maximum adsorption capacity of EP was 29.41 mg.g<sup>-1</sup>. Modification of UP with NaOH increased the maximum adsorption capacity of the sorbent from 23.81 to 39.68 mg.g<sup>-1</sup>. The kinetics data can be fitted well to second order for all experiments. The experimental data were well correlated by the Langmuir isotherm for EP, UP and NaOH-UP.

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