## **ORIGINAL ARTICLE**



# Synthesis, characterization of KAIPO<sub>4</sub>F and its application for methyl violet adsorption

R. Bagtache<sup>1</sup> · M. Trari<sup>2</sup>

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## Abstract

KAIPO<sub>4</sub>F was prepared hydrothermally at 453 K, a time-saving method using cheap reagents. The white solid was characterized by different methods such as powder X-ray diffraction, thermal analysis, SEM and UV–Vis diffuse reflectance. The compound was successfully tested for the removal of methyl violet (MV), a hazardous dye. Experiments were carried out as a function of contact time, initial concentration, temperature and pH. The amount of dye uptake was found to vary with increasing initial solution pH and maximum adsorption was observed at pH 10; the equilibrium was attained in 270 min. The amount of dye uptake (mg/g) was found to increase with increase in dye concentration and contact time. The pseudofirst-order, pseudo-second-order, Elovich and intraparticle diffusion models were applied to fit the experimental data to elucidate the kinetic adsorption. The pseudo-second-order model was the best to describe the adsorption process. Different models analyzed the equilibrium isotherms; the applicability for the experimental data follows the order: Freundlich>Langmuir>Temkin. The thermodynamic parameters:  $\Delta H^{\circ}$  (39.034 kJ mol<sup>-1</sup>),  $\Delta S^{\circ}$  (134 J K<sup>-1</sup> mol<sup>-1</sup>) and  $\Delta G^{\circ}$  (-367.01 J mol<sup>-1</sup>) indicated that the adsorption process is endothermic and spontaneous with increasing disorder at the solid–solution interface.

**Keywords** Hydrothermal synthesis  $\cdot$  Methyl Violet  $\cdot$  Adsorption kinetic  $\cdot$  Adsorption isotherm  $\cdot$  Potassium aluminium fluoride phosphate

# Introduction

Industrial discharges containing toxic products of organic nature such as dyes and pesticides or minerals such as heavy metals constitute the first source of the aquatic pollution. Their elimination represents one of the main problems in the treatment processes of liquid discharges. Dyes can be mutagenic and carcinogenic and can have harmful effects on the health such as dysfunction of kidney, reproductive system, liver, brain and central nervous system (Kadirvelu et al. 2003; Wang and You Hu 2007; Benzaquén et al. 2012).

R. Bagtache bagtacheradia@yahoo.fr

M. Trari mtrari@usthb.dz

<sup>1</sup> Laboratory of Electrochemistry-Corrosion, Metallurgy and Inorganic Chemistry, Faculty of Chemistry, (USTHB), BP 32, 16111 Algiers, Algeria

<sup>2</sup> Laboratory of Storage and Valorization of Renewable Energies, Faculty of Chemistry, (USTHB), BP 32, 16111 Algiers, Algeria They can be classified as anionic (direct, acid and reactive dyes), cationic (basic dyes) and non-ionic (disperse dyes) (Mishra and Tripathy 1993). Due to their chemical aromatic structure, they are difficult to degrade biologically. Therefore, numerous physical and/or chemical methods were used for the removal of dyes like the electrochemistry (Giwa et al. 2019), coagulation (Morshedi et al. 2013), chemical oxidation (Nidheesh 2018), membranes (Khumalo et al. 2019), sono-electrochemistry (Radi et al. 2015), microbial (Liu et al. 2019) and Fenton process (Díez et al. 2018) and photocatalysis (Saidi et al. 2020; Fatimah et al. 2019; Chai et al. 2015; Dammala et al. 2019; Das et al. 2021). Among these methods, adsorption has been studied as one of the least expensive alternatives for wastewater treatment. It is therefore necessary to develop low-cost and available materials with high adsorption capacities. Nowadays a wide variety of adsorbents are used such as clay minerals (Park et al. 2019), chitin (Zazycki and Dotto 2019), membranes (Guo et al. 2018), natural phosphates, phosphates (Yan et al. 2019; Zhang et al. 2019), polymers (Yang et al. 2019), carbon (Lawal et al. 2019), nanoparticle (Uddin and Baig 2019).

In this context, we report the synthesis and its physical characterization (XRD analysis, SEM microscopy, thermal gravimetry and diffuse reflectance) of potassium aluminum fluoride phosphate KAIPO<sub>4</sub>F that was further applied in the removal of methyl violet. It is worth noting that our synthesis differs slightly from those presented elsewhere, which require more time and expensive reagents (Kirkby et al. 1995a). To our knowledge, the literature reported only one article about application of KAIPO<sub>4</sub>F in the luminescence, activated by the rare earth Eu<sup>3+</sup> (Akojwar et al. 2017). Isotherm, kinetic and thermodynamic models were used to fit the experimental adsorption data, in order to determine the adsorption characteristics and mechanisms.

# Experimental

## **Synthesis**

All reagents for the synthesis of our phosphate were obtained from commercial sources and used without any further purification. KAIPO<sub>4</sub>F was prepared by hydrothermal route; a mixture of  $C_9H_{21}AIO_3$  (0.608 g, 97%), KOH (0.980 g); NaF (0.20 g) and distilled water (20 mL), was homogenized under magnetic stirring. The obtained gel was transferred into a Teflon-lined stainless steel autoclave and heated at 180 °C for 3 days under autogenously pressure. The white product was washed several times with distilled water and dried at 60 °C for 24 h.

## Characterization

The X-ray diffraction (XRD) data were collected over the  $2\theta$  range (5–80°) with a Philips X'Pert Pro using Cu K $\alpha$  radiation ( $\lambda = 1.54056$  Å) at a scan rate of 2° ( $2\theta$ ) min<sup>-1</sup>.

Diffuse Reflectance Spectrum was recorded with a Jasco 650 spectrophotometer using  $BaSO_4$  as reference. The SEM image was taken with a JSM-6700F field-emission microscope operating at 5.0 kV. Thermal analysis (TG) was carried out under air flow over the range (20–600 °C) with a heating rate of 5 °C min<sup>-1</sup>. The point of zero charge (pHpzc), an important controlling parameter in adsorption, was determined in NaNO<sub>3</sub> (0.1 M) solutions (25 mL) in which 25 mg of the adsorbent was added; the pH was adjusted in the region (2.0–10.0) using HCl and NaOH (0.01 M) solutions. The mixtures were stirred for 48 h and filtered; the pHs of the solutions were measured before contact (initial pH<sub>i</sub>) and after filtration (final pH<sub>f</sub>).

#### Adsorption

solution (100 ppm) was diluted to the desired concentrations (10–60 ppm). Adsorption tests were performed as follows: The catalyst KAlPO<sub>4</sub>F (10 mg) was suspended in 10 mL of MV solution at room temperature (~20 °C) at natural pH (~7), not adjusted. When the contact the time was over, the mixture was centrifuged at 3000 rpm for 10 min. The remaining MV concentration was evaluated by measuring the absorbance at  $\lambda_{max}$  (=582 nm). The adsorbed amount was calculated from the following expressions:

$$\text{Removal}\% = \frac{(C_o - C_e) \cdot 100}{C_o} \tag{1}$$

$$q_{\rm e} = \left(\frac{V}{m}\right) \cdot \left(C_0 - C_{\rm e}\right) \tag{2}$$

where  $C_0$  and  $C_e$  are the initial and equilibrium concentrations of MV (ppm), respectively, V the volume (L) of the solution, m (g) the adsorbentmass of KAIPO<sub>4</sub>F and  $q_e$  the amount of adsorbed MV (mg/g) at equilibrium.

# Effect of initial pH

To study the pH influence on the adsorption capacity of the synthesized phosphate, experiments were performed at 20 °C with MV concentration of 10 ppm at different initial pHs 3, 5, 7.5 and 10. The pH of each solution was adjusted with HCl or NaOH (0.1 N).

## **Adsorption kinetic**

The adsorption kinetic was studied by testing three theoretical models:

#### The pseudo-first-order

The pseudo-first-order kinetic is given by:

$$\frac{\mathrm{d}q}{\mathrm{d}t} = K_{\mathrm{L}}(q_{\mathrm{e}} - q_{\mathrm{t}}) \tag{3}$$

where  $q_t$  is the adsorbed amount at time *t* (mg/g);  $q_e$  the adsorbed amount at equilibrium (mg/g) and  $K_L$  the rate constant (h<sup>-1</sup>). After integration by applying the initial conditions, one obtains:

$$\ln\left(q_{\rm e} - q_{\rm t}\right) = \ln q_{\rm e} - K_{\rm L}t\tag{4}$$

The plot  $\ln(q_e - q_t)$  against time (t) gives a straight line whose slope and intercept give, respectively, the rate constant  $k_L$  and  $\ln q_e$ .

#### Pseudo-second-order

The pseudo-second-order kinetic equation can be written in the following form:

$$\frac{\mathrm{d}q_{\mathrm{t}}}{\mathrm{d}t} = K_2 (q_2 - q_{\mathrm{t}})^2 \tag{5}$$

whose integration gives:

$$\frac{t}{q_{\rm t}} = \frac{1}{K_2 q_{\rm e}^2} + \frac{1}{q_{\rm e}} t \tag{6}$$

The second-order rate constant  $K_2$  (g mg<sup>-1</sup> h<sup>-1</sup>) is determined from the intercept of the linearized form of the pseudo-second-order equation.

## **Elovich model**

This model, useful for describing the chemisorption, is expressed as follows:

$$q_{t} = \left(\frac{1}{b}\right)\ln\left(ab\right) + \frac{1}{b}\ln t \tag{7}$$

where *a* is the initial adsorption rate (mg/g min) and *b* the desorption constant related to the extent of surface coverage and activation energy (g/mg). The parameters (1/b) and (1/b) ln (ab) are deducted from Eq. 7.

#### Intraparticle diffusion model

The intraparticle diffusion model with multi-linearity, representing the different stages of adsorption, is given by:

$$q_{\rm t} = K_{\rm p}\sqrt{t+c} \tag{8}$$

where  $K_p$  is the diffusion coefficient and  $q_t$  is adsorbed amount. The plot  $q_t$  versus  $\sqrt{t}$  should be linear, with  $K_p$  as the slope and C as the intercept. Generally, a process is diffusion controlled if its rate depends on the rate at which the components diffuse to each other. A diffusion-controlled reaction should have a small activation energy ( $E_a$ ), if  $E_a$  is large, then the reaction is not controlled by the diffusion rate but rather by the number of molecules whose energy is greater than  $E_a$ . The adsorption mechanism from the solution consists of three stages: (a) diffusion across the particle boundary layer, a process measured by an external device mass transfer coefficient; (b) diffusion within the solid; and (c) adsorption on the sites. Steps (a) and (b) are the major rate-controlling processes, while step (c) is assumed to be fast. It is proposed that two factors, primarily fluid velocity, can distinguish the diffusion-controlled systems from the chemically controlled systems.

### **Thermodynamic parameters**

The standard free enthalpy ( $\Delta G^{\circ}$ ), standard enthalpy ( $\Delta H^{\circ}$ ) and standard entropy ( $\Delta S^{\circ}$ ) for the MV adsorption are also calculated. The knowledge of  $\Delta G^{\circ}$  predicts the spontaneity of the adsorption process, while the entropy  $\Delta S^{\circ}$  describes the degree of disorder or randomness of a system. As for  $\Delta H^{\circ}$ , its determination is useful to know whether the process is exothermic or endothermic.  $\Delta G^{\circ}$  is calculated from the equilibrium constant (*K*):

$$\Delta G^{\circ} = -RT\ln K \tag{9}$$

R is the universal gas constant and T the absolute temperature.

$$K = \frac{C_s}{C_e} \tag{10}$$

where  $C_s$  is the amount of dye adsorbed on the adsorbent (mg/L).

The thermodynamic parameters  $\Delta G^{\circ}$ ,  $\Delta H^{\circ}$  and  $\Delta S^{\circ}$  are determined at different temperatures (293, 303 and 313 K), keeping all other operating parameters constant. The experimental results were used for the determination of thermodynamics:

$$\ln K = -\frac{\Delta G^{\circ}}{RT} = \left(\frac{\Delta S^{\circ}}{R}\right) - \left(\frac{\Delta H^{\circ}}{RT}\right)$$
(11)

 $\Delta H^{\circ}$  and  $\Delta S^{\circ}$  are calculated from the slope and intercept of the plot ln *K* versus 1/T.

#### Adsorption isotherms

The Freundlich, Langmuir, Temkin and Elovich models are commonly used to describe how the adsorbate interacts with the adsorbent and to understand the interaction mechanism. They also provide information on the surface properties of the adsorbent and its affinity with the adsorbate.

#### **Freundlich model**

In this model, the adsorption takes place on a heterogeneous surface, through a multilayer adsorption mechanism. The adsorbed amount at equilibrium  $(q_e)$  is related to the concentration  $(C_e)$  by the relation:

$$q_{\rm e} = K_F \cdot C_{\rm e}^{1/n} \tag{12}$$

where  $K_F$  is a constant related to the adsorption capacity of the adsorbent and 1/n its intensity. The linear form of the model is expressed as follows:

$$\ln q_{\rm e} = \ln K_F + \frac{1}{n} \ln C_{\rm e} \tag{13}$$

The values of  $K_F$  and 1/n are calculated from the intercept and slope of the straight-line plot of ln  $q_e$  versus ln  $C_e$ , respectively.

#### Langmuir model

Initially, this model described the adsorption of gas molecules onto metal surfaces and has been extended later to the sorption of various molecules and /or ions in liquid phase, onto different adsorbents. It is based on the assumption that the adsorption occurs on specific homogeneous sites on the adsorbent surface. Once a molecule occupies a site, no further adsorption can take place, leading to a monolayer adsorption:

$$q_{\rm e} = \frac{q_{\rm m} K_L C_{\rm e}}{1 + K_L C_{\rm e}} \tag{14}$$

where  $q_{\rm m}$  is the maximum adsorption capacity (mg/g) and  $K_L$  a constant related to the adsorption energy (L/mg). The linearized form is as follows:

$$\frac{1}{q_{\rm e}} = \left(\frac{1}{q_{\rm m}}\right) + \left(\frac{1}{K_L \cdot C_{\rm e} \cdot q_{\rm m}}\right) \tag{15}$$

The essential characteristics of a Langmuir isotherm can be expressed in terms of a dimensionless separation factor or equilibrium parameter  $R_I$ , defined by Guiza (2017):

$$R_L = 1/(1 + K_L C_o) \tag{16}$$

The values of  $q_{\rm m}$  and  $K_L$  were determined from the slope and intercept of the linear plot of  $1/q_{\rm e}$  versus  $1/C_{\rm e}$ .

#### **Elovich model**

This relation differs from the previous model in the evolution of the adsorption site overlap: The number of available sites varies exponentially during adsorption, which implies adsorption in several layers:

$$\ln\left(\frac{q_{\rm e}}{C_{\rm e}}\right) = \ln\left(K_{\rm E} \cdot q_{\rm max}\right) - \left(\frac{q_{\rm e}}{q_{\rm max}}\right) \tag{17}$$

where  $C_{\rm e}$  is the equilibrium concentration (mg/L),  $q_{\rm e}$  the amount of product adsorbed per mass unit of the adsorbent (mg/g),  $q_{\rm max}$  the theoretical maximum adsorption capacity (mg/g) and  $K_{\rm E}$  the Elovich thermodynamic equilibrium constant (L/mg).

#### **Temkin model**

The isotherm is described by the following equation:

$$q_{\rm e} = B {\rm Ln} \, A_T + B {\rm Ln} C_e \tag{18}$$

where  $B = RT/b_T$  and B is a constant related to the heat of adsorption (J/mol),  $b_T$  and  $A_T$  are the isotherm constants (L/g).

# **Results and discussion**

## Characterization of the adsorbent

The XRD pattern of KAlPO<sub>4</sub>F prepared by hydrothermal route is shown in Fig. 1. The narrow peaks indicate a good crystallization, and they are indexed in an orthorhombic system with the space group Pnna. The lattice parameters: a = 12.612(5), b = 10.172(3), c = 6.205 Å are in a good agreement with those reported elsewhere (Kirkby et al. 1995b).

The SEM micrograph, illustrated in Fig. 2a, shows crystals with hexagonal sections. The structure is made up of  $AlF_2O_4$  octahedra and  $PO_4$  tetrahedra where the K<sup>+</sup> ions are disordered (Fig. 2b); a detailed description of the structure was previously reported (Kirkby et al. 1995b).

Thermal analysis shows that our phosphate is thermally stable up to 300 °C (Fig. 3). With raising temperature, a progressive weight loss occurs, accompanied by an exothermic peak, due to the decomposition of KAIPO<sub>4</sub>F.

The UV–Vis adsorption spectrum of as-prepared material is shown in Fig. 4 (https://www.sciencedirect.com/ science/article/abs/pii/S0277538717300736#f0030). The



Fig.1 X-ray diffraction pattern of  $KAIPO_4F$  prepared by hydrothermal route



Fig. 3 Thermal analysis of

KAlPO<sub>4</sub>F carried out under air flow at a heating rate of

5 °C min<sup>-1</sup>





Fig.4 UV–Visible diffuse reflectance of KAlPO<sub>4</sub>F synthetized hydrothermally at 180  $^\circ C$ 

absorbance peaks 232 nm and decreases progressively to  $\sim$  400 nm with a saturation up the near infrared. The bands at 218 and 232 nm correspond to oxygen to metal charge transfer transitions (Li et al. 2010).

The pHpzc was found to be 6.9 and corresponds to the point where the curve  $pH_f$  versus  $pH_i$  intersects the line

 $pH_f = pH_i$  (SM 1). This indicates a negative surface charge of the adsorbent at pH > 6.9, which becomes positive above pH 6.9. In our study, the pH of our solutions is ~7, close to the natural environment without any adjustment, so the surface of the compound is near neutrality. As expected, below pHpzc the surface inhibits the adsorption of MV, a cationic dye due to repulsive interactions of positive charges.

# **Adsorption studies**

#### Effect of contact time

The effect of contact time on the MV adsorption was studied at 20 °C, in 10 mL MV solution (10 ppm) and adsorbent mass of 10 mg. The amount of adsorbed MV increases and slows down as the adsorption proceeds with increasing contact time and reaches equilibrium (Fig. 5a). The deceleration of the adsorption rate is reflected by a low increase in the uptake capacity of KAIPO<sub>4</sub>F due to the decrease in the MV amount in solution and the number of available binding sites





for adsorption; this stage lasts approximately  $\sim 50$  min. The observed saturation up to 270 min is due to the almost total occupation of the adsorption sites.

#### Effect of initial dye concentration

The dyes in the real effluents reach concentrations as high as 40 ppm, and it is interesting to study the influence of this parameter on the MV adsorption. The initial dye concentration  $(C_0)$  is a critical parameter affecting the adsorption in wastewater treatment; its effect is shown in Fig. 5b (https:// www.sciencedirect.com/science/article/abs/pii/S027753871 7300736#f0060). The adsorption amount increases from 7 mg/g (at the lower MV initial concentration of 10 ppm) to 25 mg/g for concentration of  $C_0$  of 60 ppm. The increased adsorbed amount at equilibrium (mg/g) augments with the initial concentration  $C_0$  due to the increase of the driving force. The latter comes from the concentration gradient for the mass transfer with increasing  $C_0$ . In addition, it has been observed that the adsorption was rapid at the beginning due to the large number of vacant sites and gradually decreases as the adsorption proceeds until equilibrium. Over time, the remaining binding sites become difficult to reach because of the repulsive interactions between the MV species and the bulk phase.



# Effect of initial pH

The pH effect on the MV removal was studied at different pHs (3, 5, 7.5 and 10) as shown in Fig. 6a under the working conditions ( $C_0 = 10$  ppm, T = 20 °C, catalyst dose 1 mg/mL). The results revealed an optimal adsorption at pH ~ 10 where the adsorption increases significantly due to attractive interactions between the cationic dye MV and the catalyst surface charged negatively. The high ionic strength leading to the attachment of MV molecules also accounts for the uptake performance on the vacant sites.

## Effect of temperature

The adsorption studies were carried out at three different temperatures, namely 293, 303 and 313 K. The results showed that the adsorption percentage increased with increasing temperature, highlighting the endothermic nature of the removal process (Fig. 6b). This shows the affinity of binding sites for the MV molecules, which increases at high temperatures.



#### Kinetic modeling of MV adsorption

In the aim to elucidate the adsorption mechanism and ratelimiting steps, the pseudo-first-order, pseudo-second-order, Elovich and intraparticle models were used to fit the experimental data (Figs. 7a, b and 8a). The best kinetic model may be checked by the linear regression coefficient ( $R^2$ ).

The  $R^2$  value for the pseudo-second-order model is higher than that of the other models (Table 1), which indicates a better fitness. Moreover, the  $q_e$  value was found to be 8. 17 mg/g which is close to the experimental value. Generally, the bulk diffusion is assumed rapid and is not rate determining since the pseudo-second-order cannot elucidate the diffusion mechanism and the film diffusion is not negligible. In the intraparticle model, the plot does not pass by the origin (Fig. 8b) and this indicates that the intraparticle diffusion is not the only rate-limiting step; other processes may be involved in the MV adsorption on KAlPO<sub>4</sub>F.

The adsorption tends to be divided into two stages. The initial phase is generally referred to external mass transport and the next to the penetration of the adsorbate into the pores until equilibrium is reached; all parameters are listed in Table 2.

The intercept gives an idea about the thickness of the boundary layer, i.e., the larger intercept the greater is the boundary layer effect. The  $k_p$  values were calculated by using correlation analysis. The  $R^2$  coefficients suggest that the MV uptake varies almost linearly with  $t^{1/2}$ . This



Table 1 Adsorption kinetic parameters for the MV adsorption on  $KAlPO_4F$  for the pseudo-first-order, pseudo-second-order and Elovich models at 293 K

Pseudo-first-order model $K_1 (\min^{-1})$	Pseudo-second-order model					Elovich 1	Elovich model	
	$\overline{R^2}$	$q_{\rm e} ({\rm mg/g})$	$K_2$ (g/mg min)	$R^2$	$q_{\rm e} ({\rm mg/g})$	$\overline{R^2}$	b	а
0.005	0.90	5.51	0.002	0.95	8.17	0.86	0.68	0.36

Table 2 Kinetic parameters for intraparticle diffusion model for the MV adsorption (10 mg/L) on KAIPO<sub>4</sub>F, at 293 K

Fig. 9 a Langmuir model, b

Freundlich models for the MV adsorption onto KAlPO<sub>4</sub>F







Model	Parameters			
Langmuir	$R^2 0.98$	$K_I$ (L mg <sup>-1</sup> ) 0.09	$q_{\rm m} ({\rm mg \ g^{-1}})  29.41$	$R_{I}$ (L mg <sup>-1</sup> ) 0.52
Freundlich	$R^2 0.99$	$K_F (\text{L g}^{-1}) 3.84$	$n_F 1.87$	
Elovich	$R^2 0.97$	$K_E$ (L mol <sup>-1</sup> ) 0.19	$q_{\rm m} ({\rm mg \ g}^{-1}) 16.47$	
Temkin	$R^2 0.97$	$A_T (\text{L g}^{-1}) \ 1.43$	B (J mol <sup>-1</sup> ) 7.47	<i>b</i> <sub>T</sub> 326.13

4.0

-0.80

functional relationship corresponds to the characteristic of the intraparticle diffusion.

0 + 1.0

2.0

3.0

Ln Ce

(a)

# **Adsorption isotherms**

The various isotherm models are presented in Figs. 9a, b and 10a, b, and the constants values are summarized in Table 3. According to the regression coefficients  $R^2$ , the Freundlich isotherm seems to be the best to describe the adsorption

data, suggesting that MV molecules are adsorbed on several binding sites. The value of *n* is higher than 1 (n = 1.87), and this indicates a favorable adsorption of MV onto KAIPO<sub>4</sub>F.

# Adsorption thermodynamics

The thermodynamic functions give in-depth information of energetic exchanges association the adsorption process and are reliably determined. The adsorption capacity of

 $q_e (mg/g)$ 

(b)

 $C \,(\text{mmol/g})$ 

MV onto KAIPO<sub>4</sub>F increases with raising temperature in the range (293–313 K), beyond which the loss by vaporization becomes problematic. The insights of the adsorption mechanism are determined from the thermodynamic standard parameters, namely the enthalpy ( $\Delta H^{\circ}$ ), entropy ( $\Delta S^{\circ}$ ) and free enthalpy ( $\Delta G^{\circ}$ ).

The positive enthalpy  $\Delta H^{\circ}$  and negative free enthalpy  $\Delta G^{\circ}$  show an endothermic and spontaneous MV adsorption (Table 4) (https://www.sciencedirect.com/science/article/pii/S221237171400016X#t0040). The low  $\Delta H^{\circ}$  value (<40 kJ/mol) suggested that the uptake mechanism is typically considered to be that of physisorption bonds (Kirkby et al. 1995a, 1995b; Akojwar et al. 2017; Guiza 2017; Li et al. 2010; Bello et al. 2012); the chemisorption interactions are between 80 and 420 kJ/mol. In other words, the positive enthalpy  $\Delta H^{\circ}$  indicates that the adsorption of MV molecules onto KAIPO<sub>4</sub>F is endothermic corroborated by the increased adsorbed amount as temperature increases.

The positive entropy  $\Delta S^{\circ}$  shows that the degree of freedom increases at the solid–liquid junction during the MV adsorption.

The equilibrium constant (*K*) was calculated from the amount of dye adsorbed on the adsorbent (mg/L).  $\Delta H^{\circ}$  and  $\Delta S^{\circ}$  are deduced from the slope and intercept of the linear plot ln *K* versus 1/*T* (Fig. 11). A more negative  $\Delta G^{\circ}$  signifies a great driving force of adsorption, resulting in increased adsorption capacity.

Table 5 gives the adsorption capacity of our material compared with those reported in the literature (Mall et al. 2006; Ofomaja and Ho 2008; Ahmad 2009; Rahchamani et al. 2011; Sama Al-Jubouri et al. 2023; Ali Nisreen et al. 2022; Kashif Uddin et al. 2021; Hadj-Otmane et al. 2020; Kua et al. 2020; Xiang et al. 2024) and shows that our synthetized KAIPO<sub>4</sub>F possesses relatively a good adsorption.

The hydrothermally developed KAlPO<sub>4</sub>F adsorbent has proven to be suitable for the removal of dyes from aqueous solutions, due to its availability, low-cost preparation and good adsorption capacity.

Table 4 Thermodynamic parameters for MV dye adsorption onto  $\mathrm{KAIPO}_4\mathrm{F}$ 

$T(^{\circ}C)$	$\Delta S^{\circ} (\mathrm{J} \mathrm{K}^{-1} \mathrm{mol}^{-1})$	$\Delta H^{\circ} (\mathrm{J} \mathrm{mol}^{-1})$	$R^2$	$\Delta G^{\circ} (\mathrm{J} \mathrm{mol}^{-1})$
Parame	ters			
20	134	39034	0.99	- 367.01
30				- 1632.52
40				-2971.83



Fig. 11 Ln K versus 1/T for the MV adsorption on KAlPO<sub>4</sub>F

## Conclusion

KAIPO<sub>4</sub>F was synthesized hydrothermally at 453 K, a timeconsuming method using inexpensive reagents. The present study showed that KAlPO<sub>4</sub>F is relatively a potential adsorbent for the removal of crystal violet dye from aqueous solutions. The results indicated that the experimental kinetic data fitted best the pseudo-second-order model with a multi-step diffusion. The adsorption process was well described by the Freundlich model, and the equilibrium time was reached within 270 min at 20 °C. The thermodynamic parameters were also calculated, and the positive enthalpy  $\Delta H^{\circ}$  indicates that the MV adsorption was endothermic and spontaneous. The effect of the initial concentration of the solute on the rate of reaction was significant. The uptake rate of methyl violet increased with increasing the initial concentration, temperature and pH. Moreover, the best result was observed at pH 10 and the equilibrium was reached within 270 min.

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s13201-024-02116-3.

 Table 5
 Comparison of reported adsorption capacities of MV for adsorbents

Adsorbent	$Q_{\rm max}$ (mg/g)	References
Bagasse fly ash	26.25	Mall et al. (2006)
Mansonia wood sawdust	24.6	Ofomaja and Ho (2008)
CPBP	32.78	Ahmad (2009)
PAA	1136	Rahchamani et al. (2011)
Zeolite nanocrystals composite (NYC)	108.7	Sama Al-Jubouri et al. (2023)
Date seeds	59.9	Ali Nisreen et al. (2022)
M-MoS <sub>2</sub> @bentoniteNC	384.61	Kashif Uddin et al. (2021)
DPP-biochar	18.8	Hadj-Otmane et al. (2020)
Ipomoea aquatica (IA)	267.9	Kua et al. (2020)
Bio-MOF-2Me	157.1	Xiang et al. (2024)
KAlPO <sub>4</sub> F	29.41	This work

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#### Declarations

**Conflict of interest** The authors attest that there are not conflict of interest financial, personal or other relationships with other people, laboratories or organizations worldwide.

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