

Application of Copper Vanadate Nanoparticles for Removal of Methylene Blue from Aqueous Solution: Kinetics, Equilibrium and Thermodynamic Studies

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ABSTRACT: Copper vanadate nanoparticles were synthesized by a simple coprecipitation method in an aqueous medium and the product were used as adsorbents for eliminating methylene blue (MB) from water. The structure and morphology of the produced nanoparticles were evaluated through X-Ray Diffraction (XRD) and field Emission Scanning Electron Microscopy (FESEM) analysis. The results indicated that the particles were 22-40 nm in diameter. Further, batch adsorption experiments were performed to evaluate the potential capability of the product for the removal of MB and optimizing the adsorption conditions. The effects of pH, quantity of the adsorbent, contact time, dye concentration, and temperature on adsorption were determined. Fitting of the experimental data into the Langmuir and Freundlich adsorption models, revealed a good compliance with the Langmuir model with a maximum adsorption capacity of 151.5 mg/g at pH= 4.0. Evaluation of the kinetic and thermodynamic parameters showed that the adsorption process follows a pseudo-second order kinetic model and reaches equilibrium after 10 min. Desorption of the dye and recycling potential of the adsorbent was also studied.

KEYWORDS: Copper vanadate; Nanoparticles; Removal; Adsorbent; Methylene blue.

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INTRODUCTION

Organic dyes are a major source of environmental contamination and are hence regarded as being dangerous to the environment. Such compounds are unfortunately widely used in different areas, like textile, paper, printing, food, cosmetics industries [1]. As an instance, cationic dyes such as methylene blue are among the important organic compounds with various industrial applications [2, 3], which are suspected to pose dangers to humans and the environment

The majority of such industrial dyes are toxic and mutagenic [4], and are unfortunately rather stable and resistant against light-induced degradation, biodegradation and oxidizing agents [5].

As an effect, water contamination is a common problem in different countries [6, 7], and hence the removal of pollutants such as dyes from water is of critical significance. Many of these compounds also cause health problems such as allergic dermatitis, skin irritation, cancer and mutation in human [8, 9].

A set of physical and/or chemical techniques including adsorption [10-14], and chemical [15, 16], electrochemical [17], and photocatalytic oxidation [18] are currently used for the elimination of such organic pollutants from water samples. Yet many of these compounds are stable against photo and/or bio-degradation and oxidizing [19], and hence adsorption-based procedures constitute economical and highly efficient means for removing dyes from aqueous media. Various efforts have been made to evaluate various sorbents like ion exchange membranes [20], activated carbon [21, 22], clay [23], zeolite [24], and other natural materials [25, 26] for removing low concentrations of such cationic dyes from water. Yet, even through some adsorbent are available in a commercial scale, the need for developing new adsorbents for this purpose still exists.

Nanotechnology, on the other hand, offers powerful approaches which can be used to overcome various problems, and rather recently, nanomaterials have gained a great deal of scientific and industrial attention, in different areas. Some properties of nano-materials are their high surface area/volume ratios, modifiable surfaces, availability in different morphologies, and ease of regeneration. These materials have been proven as being practically applicable in different fields like biosensing, drug delivery, agriculture, waste

management, electronics, and food industry [27-30]. As an instance, nano-structured iron [31], tungsten trioxides [32], and strontium tungstate and molybdate [33] have been reportedly used as adsorbents for hazardous materials like dyes.

As an attractive area of study, the controlled synthesis of salts of different metals needs careful investigation of the effects of various parameters such as the concentration of the reagents on the morphology and size of products [34, 35].

Consequently, the present work was focused on evaluating a facile procedure for preparing nano-sized copper vanadate particles with two different morphologies, and using them as adsorbents for methylene blue from water. The effect of different operating conditions, i.e. solution pH, quantity of the adsorbent, and the adsorption kinetics and thermodynamics were also studied and the adsorption efficiency and mechanism were assessed based on isothermal studies.

EXPERIMENTAL SECTION

Instrumentation

pH readings were performed using a Metrohm 713 pH-meter, and the dye concentrations were determined using a Shimadzo λ 25 double beam spectrophotometer. Scanning Electron Microscopy (SEM) images were acquired on a Philips XL-30 Field-Emission Scanning Electron Microscope (FE-SEM) at 16 kV. Morphology studies were performed using on an XPert MPD advanced XRD instrument with a Cu (K_{α}) radiation (wavelength: 1.5406 Å) under ambient temperature. The 2θ values were scanned from 4 to 120° at a rate of 0.02°/S.

Reagents and solutions

All chemicals were reagent grade and purchased from Fluka and Merck chemical companies and all solutions preparation and washing procedures were performed using Double Distilled Water (DDW). Analytical-grade copper chloridedihydrate and ammonium vanadate as reagents were used as received from the Merck Company (Germany) The commercial Methylene Blue (Fig. 1), a cationic dye with molecular weight 319.85 g/mol, Molecular Formula $C_{16}H_{18}ClN_3S$ and Color Index Number: 52015, was purchased from Sigma Aldrich (Germany). A stock MB solution in DDW was prepared

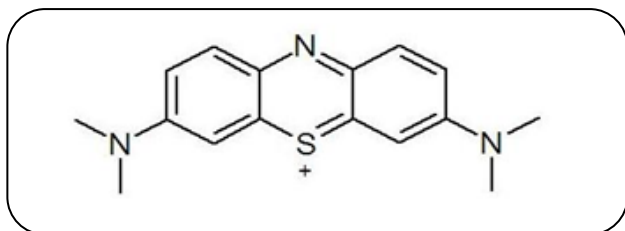


Fig. 1: Molecular structure of Methylene blue.

and the rest of the solutions were prepared through diluting it. The glassware used for trace analysis were stored in dilute nitric acid for a minimum of 1 day, and washed with DDW just before application.

Coprecipitation of the nanoparticles

Analytical-grade copper chloride dihydrate and ammonium vanadate were used as reagents. Copper vanadate particles were prepared by coprecipitation reaction in aqueous media. In a typical synthesis, 0.2339 g of VO_3NH_4 (1 mmol) and 0.1705 g of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (2 mmol) were dissolved in appropriate distilled water separately. Then above copper solution was added directly into the vanadate solution dropwise under vigorous stirring in 35°C in presence of sonication. The pH value of the solution was adjusted to ~ 7 using ammonium hydroxide during coprecipitation. The resulting suspension was stirred for another 10 min. After finishing the precipitation reaction, the resulted copper vanadate was centrifuged and then washed with distilled water three times. Thereafter, the resulted precipitate was washed with absolute ethanol and dried at 80°C during 120 min, followed by natural cooling in air, and then used for further characterization.

Dyes removal experiments

The adsorption properties of the nanoparticles were evaluated through a set of batch experiments, involving the addition of 6 milligrams of the nanoparticles to 5 mL of MB solutions with various concentrations, at $\text{pH}=4.0$. The mixtures were gently shaken for 10 min at room temperature, to adsorb the dye molecules. Next, the solid particles were separated from the mixture through centrifuging for 3 min at 3800 rpm, and the residual amounts of MB in the reaction mixture were determined through spectrophotometry at 665 nm. The percentage of the adsorbed, also known as the removal efficiency, was calculated using the following formula:

$$\%R = \left[\frac{(C_o - C_t)}{C_o} \right] \times 100$$

in which the symbols C_o and C_t are the initial and final (after adsorption) MB concentrations (mg/L).

Optimization of key parameters

The effects of pH, contact time, initial dye concentration and temperature, as the factors influencing the adsorption phenomenon were tested through performing a set of experiments. The kinetics studies were performed through analyzing adsorption capacity at various times. To evaluate the adsorption isotherm, dye solutions of different concentrations, in the range of 10-200 mg/L, were treated using the sorbents under agitation until equilibrium was established and the adsorption isotherms were determined at 298, 323, and 338 K.

The amounts (q) of adsorbed MB were calculated using the formula below:

$$q = \frac{(C_o - C_e)V}{m}$$

in which C_o and C_e represent the initial and equilibrium MB concentrations (mgL^{-1}), and m and V are the mass of the adsorbent (g) and volume of the solution (L).

RESULTS AND DISCUSSION

Adsorbent Characterization

Copper vanadate nanoparticles were synthesized by a simple coprecipitation method using aqueous solutions of copper chloride dihydrate and ammonium vanadate. To assess the quality of the product FE-SEM and XRD analyses were used.

The FE-SEM image of the sample is illustrated in Fig. 2 and results indicated that the particles were 22-40 nm in diameter. The XRD results (Fig. 3) show diffraction peaks and a pattern that could match with the pattern reported for copper vanadate (a mixture of $\text{Cu}_5\text{V}_2\text{O}_{10}$ in JCPDS 027-1135 and CuVO_3 according to JCPDS 024-0383 diffraction software with monoclinic and rhombohedral structures, respectively). This reflects the good crystallinity and purity of the nanoparticles.

Also, the Debye-Scherrer equation was used for calculating the average crystallite size of the particles:

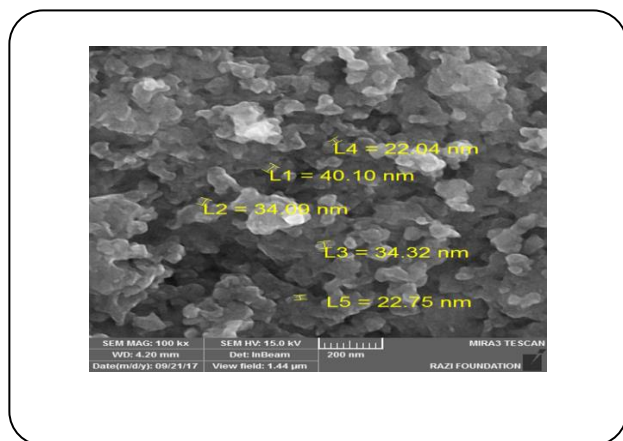


Fig. 2: FESEM image of as-prepared copper vanadate nanoparticles.

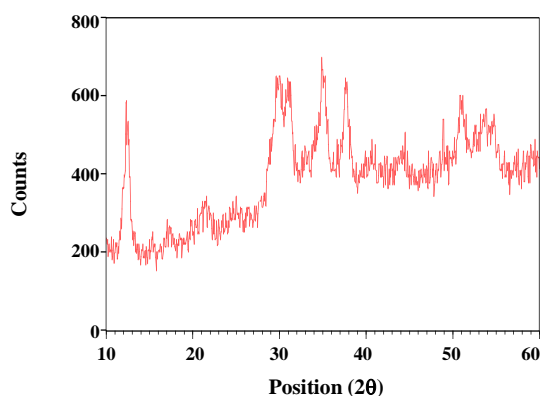


Fig. 3: XRD pattern of as-prepared copper vanadate nanoparticles

$$D=0.9\lambda/(\beta \cos\theta)$$

In this equation λ (X-ray radiation wavelength) is 0.154059 nm, β represents the corrected band broadening, and θ is Bragg's angle [36-39]. Based on the calculations, the average crystal size of the particles was determined to be about 16 nm.

Effect of pH

The studies were performed in the pH range of 3.0 to 10.0 and the results are given in Fig. 4. The pH adjustments were induced using HCl and NaOH solutions and the measurements were performed using a digital pH meter. The pH of the sample plays a key role in the adsorption process and it has a significant effect on electrostatic charges that are imparted by ionized dye molecules between adsorbent and dyes. MB is known

to exist in cationic forms in water [32] and is hence expected to have a natural tendency to be adsorbed on negatively charged surfaces.

According to the results, adsorption increased upon increasing the solution pH from 3 to 4, and then decreased by increasing the pH. This was attributed to the fact that in alkaline condition the aqueous OH^- may simultaneously adsorbed by the MB cations and the resulting electrostatic repulsion can negatively influence the adsorption and hence considerably decrease the MB adsorption. Also at pH values below 4, the H^+ ions can compete with MB in adsorption onto copper vanadate nanoparticles, which lowers the adsorption of MB at pH=3.0. A maximum adsorption efficiency of 95% was observed at pH= 4, and this pH was used in all experiments.

Quantity of the adsorbent

Studies focused on determining the optimal amount of the adsorbent were performed in the optimal pH, using 0.003 to 0.015 g of the adsorbent in 5 mL of a 100 mg/L solution of MB in water. Based on the results (Fig. 5), the adsorption efficiency linearly increased with the amount of the adsorbent up to 0.01 g of the nanoparticles. In more details, using 0.006 g of the adsorbent 97% efficiency, and using 0.010 g of the nanoparticles, the maximum removal efficiency of 99% were observed and above this value the efficiency stayed constant.

Adsorption kinetics

Using a 100 mg L^{-1} solution (pH=4.0), under ambient conditions, the effect of contact time on the adsorption efficiency was investigated. The concentration of the solution at different times (after 4, 5, 10, 15 and 20 min) was determined through spectrophotometry. According to the results (Fig. 6) the adsorption capacity rapidly increases at first and is then gradually increases at a lower speed until equilibrium is reached after 10 min. So, 10 min was applied as the optimal separation period in later studies.

A pseudo first-order and a pseudo-second-order kinetic model were used for fitting the data and determining the adsorption mechanism. The pseudo-first-order (Lagergren) equation is described by [40]:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303}$$

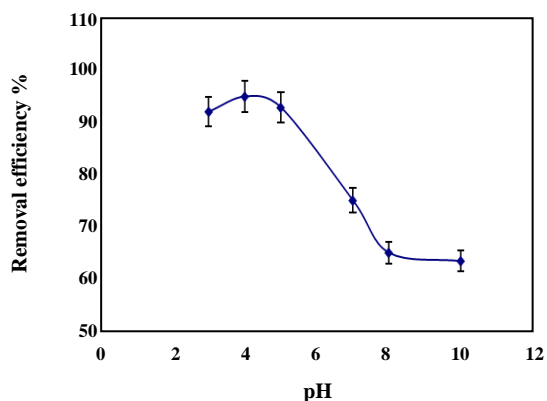


Fig. 4: The effect of pH on the adsorption of MB onto the copper vanadate nanoparticles.

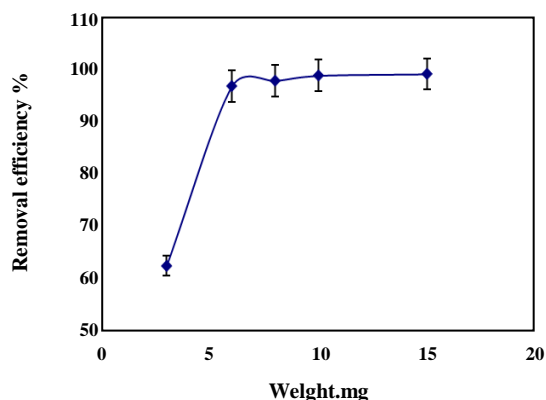


Fig. 5: The percentage of dye removal using different amount of copper vanadate nanoparticles for MB.

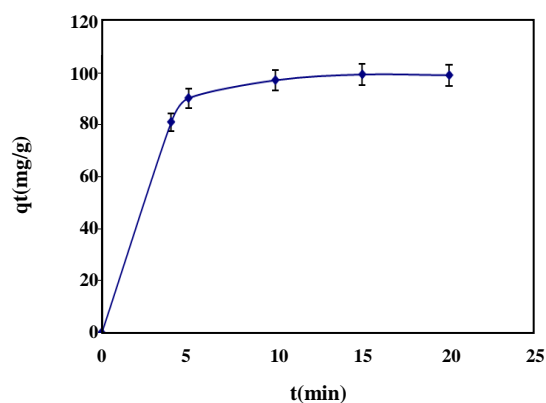


Fig. 6: The effect of contact time on the adsorption of MB on copper vanadate nanoparticles.

in which k_1 is the pseudo-first-order rate constant (min^{-1}), q_e and q_t express the amounts of the adsorbed MB (mg/g) after equilibrium and also at time t (min).

The pseudo-second-order model followed the following equation [41]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$

where, k_2 ($\text{g/mg}\cdot\text{min}$) is the pseudo-second-order rate constant and the rest of the variables are according to the Lagergren equation.

The kinetic constants for both models, which were determined through the linear regression, are given in Fig. 7 and the results are presented in Table 1. The R^2 (correlation coefficient) for the pseudo-first-order model was rather low and the calculated q_e values ($q_{e,\text{cal}}$) did not show a good agreement with the experimental results ($q_{e,\text{exp}}$). This naturally indicates that this model cannot be applied to the adsorption process. In case of the second model, however, the R^2 value (i.e. 0.9992) and the good agreement between the $q_{e,\text{cal}}$ and $q_{e,\text{exp}}$ values reflected the applicability of the second-order model for describing the adsorption mechanism.

Adsorption isotherms

The Effect of MB concentration, was studied while other parameters were kept constant. Among the various isotherm equations available, two important models (i.e. Langmuir and Freundlich models) were used. The adsorption capacities were independently measured at $\text{pH}=4.0$ while the MB concentration was changed in the range of 10–200 mg/L . The equilibrium MB contents of the solutions were determined and the results are presented in Fig. 8.

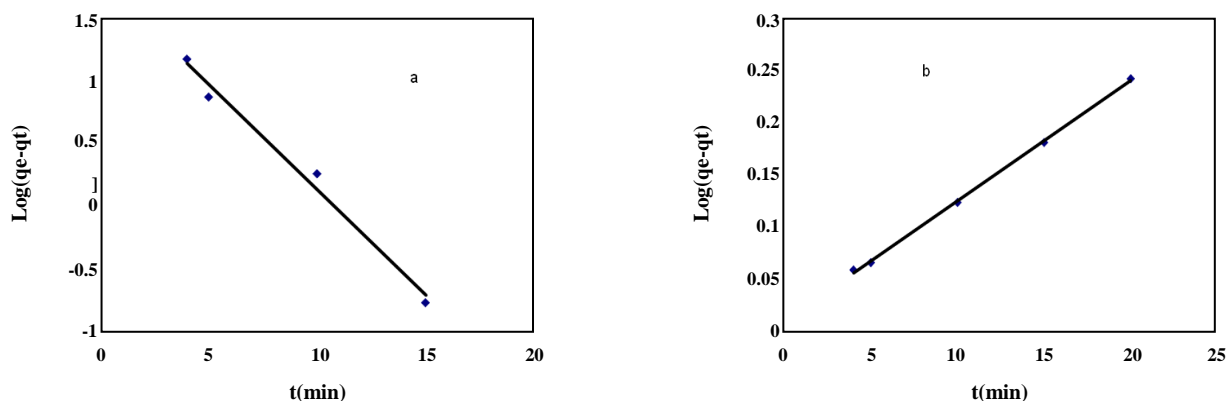
The linearized form of the Langmuir isotherm model is expressed as below [42]:

$$\frac{C_e}{q_e} = \frac{1}{b q_m} + \frac{C_e}{q_m}$$

(q_m =the maximum adsorption capacity for a complete monolayer coverage, and b =the equilibrium constant (L/mg)). The data was found to fit well to this model, resulting in a respective R^2 and maximum adsorption capacity of 0.9978 and 151.5 mg/g for the concentration range applied in the studies.

Table 1: Adsorption kinetic parameters of MB adsorption onto the copper vanadate.

Pseudo-first order			Pseudo-second order			Experimental data
K_1 (min^{-1})	$q_{e,\text{cal}}$ ($\text{mgg}^{-1}\text{min}^{-1}$)	R^2	K_2 ($\text{mgg}^{-1}\text{min}^{-1}$)	$q_{e,\text{cal}}$ (mgg^{-1})	R^2	$q_{e,\text{exp}}$ (mgg^{-1})
0.386	65.75	0.986	13.23×10^{-3}	86.95	0.999	82.75

**Fig. 7: The pseudo-first-order kinetics (a) and the pseudo-second-order kinetics (b) of adsorption MB on the copper vanadate nanoparticles.**

Further the linearized form of the Freundlich model [43] was used:

$$\log q_e = \log k_f + \frac{1}{n_f} \log C_e$$

In this equation K_f and $1/n_f$ are a rough indicator of the adsorption capacity, and the adsorption intensity. $1/n_f$ ranges between 0 and 1 and reflects the adsorption intensity or surface heterogeneity [44]. The constants presented in in Table 2, which were determined through the linear regression analysis, indicate the Freundlich model as being not suitable, while the Langmuir isotherm model, with a higher R^2 led to a better fit.

Effect of temperature and adsorption thermodynamics

Thermodynamic factors like the change in the Gibbs free energy (ΔG° , kJ/mol), enthalpy (ΔH° , kJ/mol) and entropy (ΔS° , J/mol.K) can be used as indicators for practical applications. The thermodynamic results expressed in Fig. 9, were obtained at 298, 323 and 338 K. To determine these parameters of dyes adsorption, the K_d values were calculated using the Van't Hoff equation [45]:

$$\Delta G^\circ = -RT \ln K_d \quad K_d = \frac{q_e}{C_e} \quad \ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}$$

(K_d =the distribution coefficient, T =temperature(K), R =the gas constant (8.3145 J/mol.K), C_e = equilibrium concentration of MB in water (mg/L), q_e =the amount of the adsorbed MB per unit mass of the adsorbent (mg/g)).

The results (Table 3) indicate negative ΔG° values reflecting the process as being spontaneous. The negative enthalpy changes, on the other hand, indicate the exothermic nature of the process, which could be attributed to the formation of physical bonds between MB molecules and the active sites present on the nanoparticles. These bonds are naturally weakened by increasing the temperature, while the solubility of MB increased. Hence the solute/solvent interactions become stronger than the solute/adsorbent interactions. The positive ΔS° values indicate increased disorder at the adsorbent/solution interfaces during the adsorption process [2].

Desorption and recycling study

Given the importance of the reusability of an adsorbent, the potential of regenerating and reusing the nanoparticles were further studied through washing the dye-loaded adsorbent with 10.0 ml of ethanol and DDW, and it was found that the adsorbent could be reused after this procedure. Desorption equilibrium could be reached only after about 10 min, as in the case of the adsorption. The results showed that the adsorbent could be used at least 3 times without significant losses in its capacity.

Table 2: Isotherm parameters for adsorption of MB on copper vanadate nanoparticle.

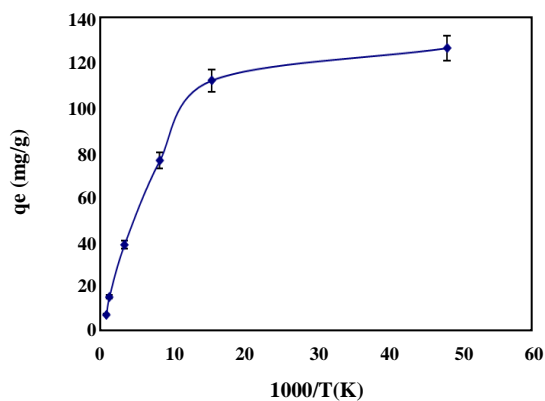
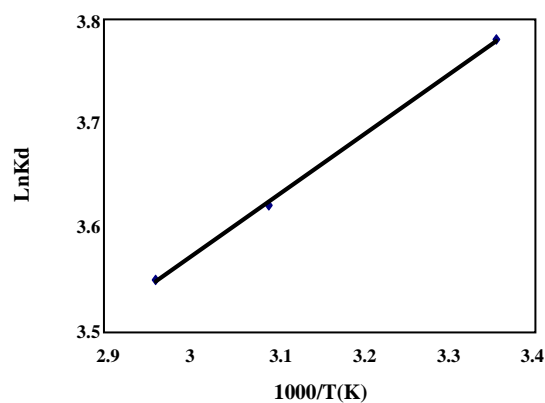
Dye	Langmuir			Freundlich		
	$q_m(\text{mg/g})$	$b(\text{L/mg})$	R^2	$K_f(\text{mg/g})$	$1/n$	R^2
MB	151.51	0.108	0.9978	17.84	0.5847	0.9129

Table 3: Values of thermodynamic parameters of adsorption of MB adsorption onto the copper vanadate nanoparticles

$\Delta H^\circ(\text{kJ/mol})$	$\Delta S^\circ(\text{J/mol.K})$	$\Delta G^\circ(\text{kJ/mol})$		
		298	323	328
-4.84	15.17	-9.36	-9.72	-9.97

Table 4: Comparison of the maximum capacity factor of MB onto various adsorbents

Adsorbents	Capacity Factor(mg/g^{-1})	References
Copper vanadate	151.5	Proposed work
tungsten trioxides (WO_3)	35.9	[32]
Magnetic Magnesium Silicate Hollow Nanotubes	175.1	[46]
Fe_3O_4 -TAN	90.9	[12]
carboxymethyl cellulose/k-carrageenan/activated montmorillonite	10.75	[11]
Fe_3O_4 @C	44.4	[47]
Mantomorillonite/ CoFe_2O_4 composite	97.7	[2]
Mn@ CuS/ZnS-NC-AC	126.4	[48]
Magnetic graphene-carbon nanotube composite	65.8	[49]
Fe(III)/Cr(III) hydroxide	22.8	[3]

**Fig. 8: Adsorption isotherm of MB for copper vanadate nanoparticles.****Fig. 9: The Van't Hoff plot of $\ln K_d$ versus $1/T$.**

CONCLUSIONS

Copper vanadate nanoparticles were prepared through coprecipitation of solution of copper chloride dihydrate and ammonium vanadate solutions in water. The nanoparticles could be dispersed in water and also easily separate from the mixtures through centrifugation. The adsorbent was found to effectively remove methylene blue as a model dye. The adsorption process happened quickly,

and agreed with the Langmuir adsorption model. The maximum adsorption capacity was found to be 151.5 mg/g at pH=4. Adsorption kinetics of MB on the prepared adsorbent followed the pseudo-second-order kinetic model and reaches equilibrium after 10 min. Table 4 compares the adsorption capacity of the copper vanadate nanoparticles with different adsorbents previously used for removal of MB [2, 3, 12, 32] [46- 49]. It can be seen that the adsorption

capacity of the copper vanadate nanoparticles is promising and higher than that of many other previously reported adsorbents. Also the preparation of copper vanadate nanoparticles is easy and inexpensive and the process of purifying water pollution is clean and safe. Hence, this methodology can be suitable for the large-scale removal of the pollutant dyes from water.

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