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Kinetic studies for the adsorption of methyl violet by nano potassium zinc ferrocyanide powder from aqueous solution

Sushama Viladkar[a], Ameed Hashmi[b,*]

[a]*Faculty of Science and Technology, Department of Chemistry, ICFAI University, Selaqui, Dehradun 248197, India*
[b]*Faculty of Science and Technology, Department of Biotechnology, ICFAI University, Selaqui, Dehradun 248197, India*
Tel. +91 627 422 2570; email: ameed.haikal@gmail.com

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ABSTRACT

A novel adsorbent; fine particulate sized potassium zinc ferrocyanide powder; $K_2Zn[Fe(CN)_6]$ was synthesized indigenously by a slow co-precipitation method. The adsorbent was characterized by CHN analysis, FT-IR, XRD, and SEM techniques. The powder consists of 50.7 nm grains with good crystalline nature and further supported by XRD sharp diffraction peaks. The surface area and total pore volume of potassium zinc ferrocyanide powder was found with the help of Brunauer-Emmett-Teller. Batch experiments were carried out to test the efficiency of potassium zinc ferrocyanide powder for removing methyl violet. The adsorption studies include contact time, initial dye concentration, pH, and temperature. Freundlich and Langmuir isotherm models were applied to calculate Langmuir and Freundlich adsorption parameters, like X_m, K_L, n, and K_F. Furthermore, ANOVA of the dye concentration data to determine adsorption characteristics was studied and found to have significant effect.

Keywords: Adsorption; Kinetics; Isotherms; Methyl violet; Potassium zinc ferrocyanide; ANOVA

1. Introduction

Effluents from industries have significant quantities of synthetic organic dyes. The discharge of these hazardous dyes in the environment causes considerable nonaesthetic pollution and serious health related risks. Since conventional wastewater treatment plants cannot remove the majority of these pollutants, efficient methods are needed for the decontamination of dyes. The scientific community has been suggesting a number of remedial measures for the exclusion of dyes from waste water, based on: coagulation [1], electro-coagulation [2], electrochemical [3], photocatalytic degradation [4], microbial degradation [5,6], and adsorption. Among the available techniques, degradation of dyes is difficult due to their stability and possibly may even cause secondary pollution problem, hence, adsorption has always been the preferred choice for the removal of toxic dyes from wastewater.

A number of adsorbents have been tried by researchers, such as low-cost bio adsorbent materials like peanut hull [7], orange peel [8], coconut husk [9,10] neem leaf powder [11], egg-shell [12], hen feather [13], and biomass adsorbent like mycelial

*Corresponding author.

Ceriporia lacerate [14], algae [15]. Clay minerals, like betonite [16], montmorilonite [17], press mud [18], sewage sludge [19], bottom ash [20,21], mesoporous hybrid xerogel [22], polymer fibers [23], natural zeolites like aluminosilicates [24] and silica [25].

The present study has been undertaken to study the effectiveness of potassium zinc ferrocyanide powder as an adsorbent for the removal of methyl violet from aqueous solution; this makes it different from the earlier works on the adsorption of methyl violet [26–28]. In this manuscript we report the characterization of potassium zinc ferrocyanide along with the applicability of Langmuir, Freundlich isotherm models for the adsorption of methyl violet.

Methyl violet is a basic cationic dye, belonging to triphenylmethane group and used in dyeing paper or as a component of ball-point pens, ink-jet printers. In addition, it is used in veterinary medicine as a biological stain, for identifying of bloody fingerprints, and in various textile operations. Methyl violet dye is detrimental when inhaled or ingested, and is toxic [29]; it is mutagenic [30] and also causes cancer [31]. It has been reported to cause thrombosis and infarctions in animals [32].

2. Experimental

2.1. Materials and instrumental

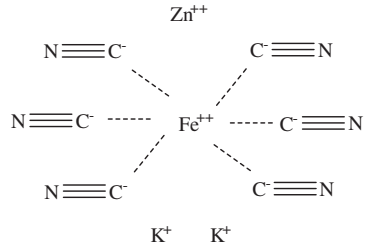
AR grade zinc sulphate, potassium ferrocyanide, and methyl violet were obtained from Sigma and used as such without further purification.

UV–vis spectra and absorbance measurements were carried on Perkin Elmer Lambda 25 spectrophotometer. FT-IR spectra were obtained using Perkin Elmer Spectrum RX. X-ray diffractograms were obtained using Bruker AXS D8 powder diffractometer. The CHN analysis was done using Elementar Analysen Systeme GmbH Vario EL III elemental analyzer. Micromeritics International Corp Flow Sorb 2300 was used for the surface area and total pore volume calculations. Morphological features of samples were obtained with field emission electron microscope (FE-SEM) using a FEI Quanta 200F microscope operating at an accelerating voltage of 20 kV.

2.2. Preparation of $K_2Zn[Fe(CN)_6]$ nano-powder

In order to reduce the particle size and increase the surface area, metal complex was synthesized with little modification to the earlier reported co-precipitation method in order to reduce the particle size and increase the surface area [33].

$$ZnSO_4 + K_4[Fe(CN)_6] \longrightarrow K_2Zn[Fe(CN)_6] + K_2SO_4$$



Potassium zinc ferrocyanide was prepared by adding zinc sulphate (500 ml; 0.1 M) drop wise to potassium ferrocyanide (250 ml; 0.1 M) with constant stirring for up to 36 h. Reaction mixture was further stirred for another 12 h. The precipitate was washed several times with double distilled water and then oven dried at 60°C. The dried potassium zinc ferrocyanide was grinded and then sieved in 150 μm BSS mesh size.

2.3. Adsorption method

Preparation of Standard Solution: structure, λ_{max}, standard curve equation of methyl violet is given in table 1. Stock solution of methyl violet [0.001 M] was prepared by dissolving appropriate amount in 10 ml absolute alcohol and distilled water was added to make 50 ml of the solution. For adsorption studies, additional dilutions were done with double distilled water.

3. Result and discussion

3.1. Characterization of $K_2Zn[Fe(CN)_6]$ nanocrystals

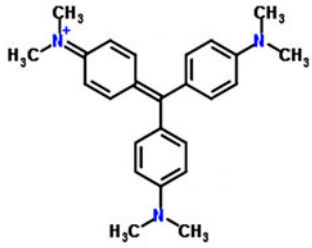
3.1.1. CHN elemental analysis

Solid sample was weighed and packed in tin boats. WO_3 was added to the potassium zinc ferrocyanide sample in a ratio 1:1 in order to bind earth alkaline ions. The daily factor was determined using sulfanilic acid. Elemental analysis of potassium zinc ferrocyanide powder showed C = 20.11% and N = 28.01%.

3.1.2. BET analysis

Surface area and total pore volume are critical quality attributes of materials and have a major impact on adsorption properties. Specific surface area was measured by single point nitrogen adsorption isotherm using the Brunauer-Emmett-Teller (BET) method. The surface area and total pore volume of potassium zinc ferrocyanide is 22.8443 m^2/g and 0.0115 m^3/g, respectively.

Table 1
Details of the dye used

Dye	Structure	λ_{max}	Standard curve
Methyl violet		579 nm	$y = 0.1039 \times R^2 = 0.9639$

3.1.3. FT-IR analysis

IR spectroscopy is an ideal technique for differentiating the various coordination modes of cyanide groups in metal complexes and can help in the identification of the functional groups. The FT-IR spectrum of potassium zinc ferrocyanide powder was recorded in KBr in the range 4,000–600 cm^{-1} as shown in Fig. 1.

The free cyanide ion has ν(C≡N) at 2,080 cm^{-1}, whereas $K_4[Fe(CN)_6]$ shows an intense peak at 2,046 cm^{-1} due to ν(C≡N), which shifted to 2,093 cm^{-1} for the potassium zinc ferrocyanide. Previous studies on metal ferrocyanides [34,35] also noted a similar shift for ν(C≡N) band which is higher with respect to free CN^-. In general, CN^- is a good σ-donor and a poor π-acceptor.

3.1.4. X-ray diffraction studies

Potassium zinc ferrocyanide was analyzed by X-ray diffraction (XRD) using a powder diffractometer, in the 2θ range from 5 to 60° with an interpolated step of 0.080 using Cu-K_α ray. The XRD spectrograms were used to calculate relative intensities and value of θ for prominent peaks.

The XRD values have been compared with the standard joint committee on powder diffraction standards data and are found to be similar to those of reported values confirming the crystalline nature of the sample. The (d) values thus obtained are in close agreement with the reported values of potassium zinc ferrocyanide but the exact PDF file of $K_2Zn[Fe(CN)_6]$ is not available. As evident from the crystallogram shown in Fig. 2 the potassium zinc ferrocyanide formed is in crystalline state. The calculated particle size is 50.7 nm using Sherrer's equation.

3.1.5. Field emission electron microscopy

FE-SEM is widely adopted with other methods to characterize the size, shape, structure, and composition of the material. In order to observe external morphology and surface structure of the potassium zinc ferrocyanide, the FE-SEM image as shown in Fig. 3 was

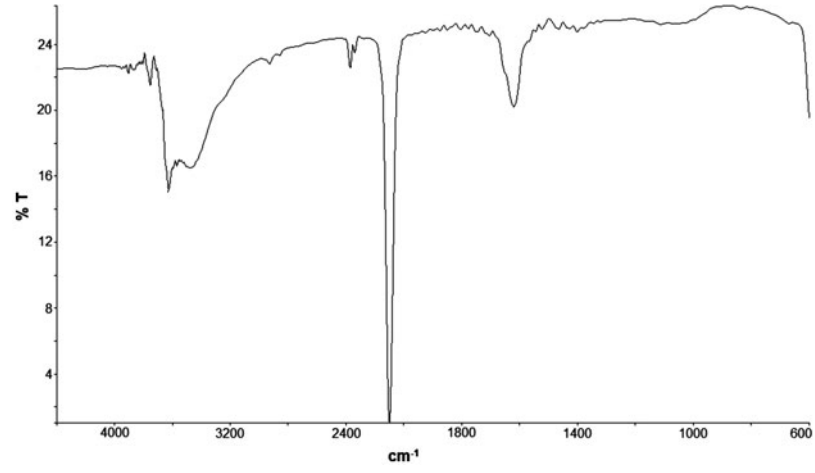


Fig. 1. FT-IR of potassium zinc ferrocyanide powder.

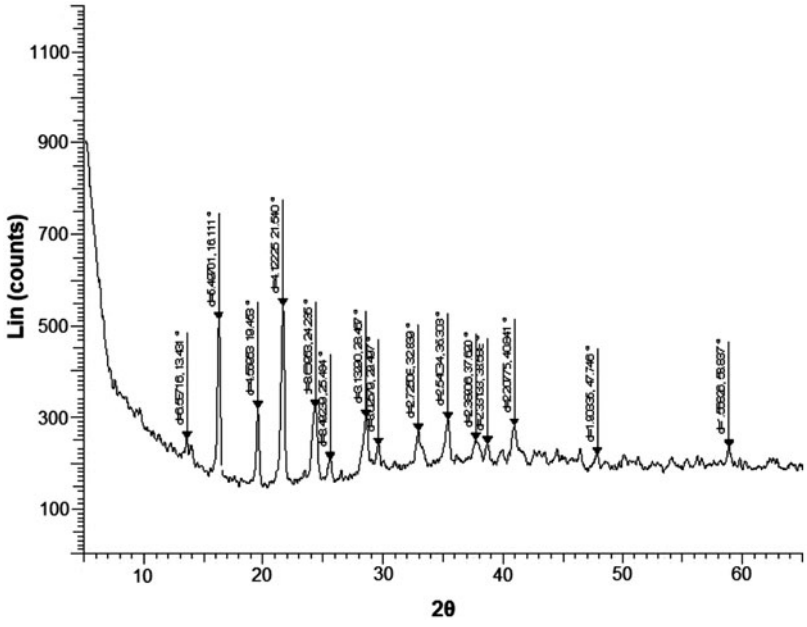


Fig. 2. XRD of potassium zinc ferrocyanide powder.

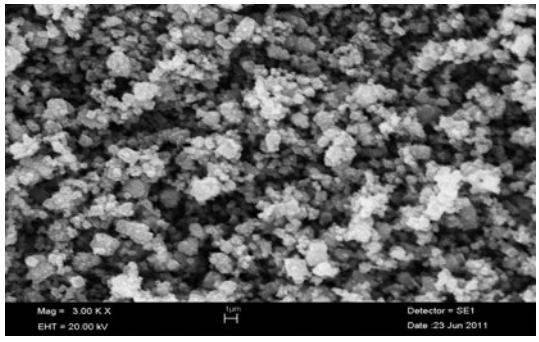


Fig. 3. SEM image of potassium zinc ferrocyanide powder.

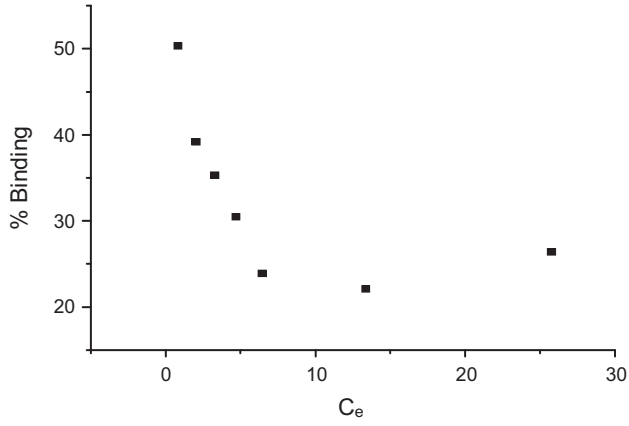


Fig. 4. % Binding of methyl violet on potassium zinc ferrocyanide powder.

recorded at an accelerating voltage of 20 kV. The powder consists of 1–2 μm facet grains due to agglomeration with good crystalline shape which is supported by sharp peaks observed in the XRD pattern.

3.2. Adsorption studies

3.2.1. Batch equilibration method

Batch adsorption experiments were carried out by using 0.05 g of metal ferrocyanide with 5 ml of dye solution with different initial concentrations (1.0×10^{-6}–2.0×10^{-5} M). Sample solutions was centrifuged after intermittent shaking for 24 h and the absorbance in the supernatant dye solution was measured spectrophotometrically, and the final concentration was determined from the standard curves, used for the determination of the percentage adsorption.

The percentage binding of methyl violet on potassium zinc ferrocyanide powder can be seen in Fig. 4. It shows that the % binding ranges up to 50% for methyl violet.

3.2.2. Effect of contact time

The effect of contact time on the adsorption of dye was estimated by keeping initial concentration, pH,

Table 2
Linear fit summary of the Langmuir and Freundlich plots

Dye	Summary		$1/X_e$	Log X_e
Methyl violet	No. of points		7	7
	Degree of freedom		5	5
	Residual sum of squares		6.64172	0.046
	Adj. R^2		0.89058	0.91821
	Intercept	Value	2.58596	−1.09114
		Standard error	0.60048	0.06469
	Slope	Value	8.26493	0.65019
		Standard error	1.1708	0.07864

and temperature constant. It was found that adsorption equilibrium is rapidly established within 30–40 min and gradually increases from 80–90% within 4 h with the maximum adsorption taking place in 24 h. Adsorption of phenol entity takes place very fast with high concentration.

3.2.3. Effect of pH

By keeping other parameter constant, effect of pH on adsorption of dye was studied by maintaining pH of the dye solution at 4, 5, 6, 7, 8, and 9. The acidic and alkaline pH of the solution was maintained by adding the required amounts of dilute hydrochloric acid and sodium hydroxide solutions. It was observed that on potassium zinc ferrocyanide powder, the adsorption capacity significantly increases with increase in the pH and maximum adsorption was observed at pH 7.0 for methyl violet. At acidic pH, the protonated dyes are difficult to adsorb due to the electrostatic repulsion between the protonated dyes and positively charged adsorbent sites.

3.2.4. Effect of temperature

Adsorption ability of potassium zinc ferrocyanide powder was found out by batch technique at 25, 45, 55, and 65°C temperatures in neutral pH. The maximum adsorption was found to occur at 25°C.

4. Adsorption isotherms

Adsorption is the accumulation of adsorbate at an adsorbent and adsorption isotherms correlate the relationship between the amount of dye adsorbed at constant temperature and its concentration in the equilibrium state. In the present study Langmuir and Freundlich isotherms are used. The Linear Fit and the ANOVA summary of the isotherm models are included in Tables 2 and 3, respectively.

4.1. Langmuir isotherm

The Langmuir adsorption isotherm has been commonly used to predict the adsorption space. The underlying assumption of the Langmuir theory is that sorption takes place at specific homogeneous sites within the adsorbent. Once an adsorbate molecule occupies a site, subsequently, no further adsorption can take place at that site representing saturation limit or monolayer formation and that the coverage is independent of binding energy. Further, there is no interaction between adsorbate molecules. The saturated monolayer can be represented by the linear form of Langmuir isotherm using Eq. (1):

$$1/X_e = 1/X_m + (1/X_m K_L)(1/C_e) \quad (1)$$

where C_e is the equilibrium concentration; X_e is the amount of dye adsorbed onto per unit mass of metal ferrocyanide; X_m is a constant for complete monolayer capacity or maximum adsorption capacity, a constant related to sorption, K_L is a constant related to the affinity of the binding sites and energy of adsorption ($mg\,L^{-1}$). The linear Langmuir plots of $1/C_e$ vs. $1/X_e$ are shown in Fig. 5. The Langmuir parameters estimated are summarized in Table 4.

4.2. Freundlich isotherm

Freundlich isotherm is an empirical equation describing heterogeneity of adsorption sites. The Freundlich isotherm is commonly presented using Eq. (2):

$$\log X_e = \log K_F + (1/n) \log C_e \quad (2)$$

Table 3
ANOVA summary of the Langmuir and Freundlich plots

Dye	Parameter		*D F*	Sum of squares	Mean square	*F* value	Prob > *F*
Methyl violet	$1/X_e$	Model	1	66.19506	66.19506	49.83276	8.81857E−4
		Error	5	6.64172	1.32834		
		Total	6	72.83678			
	Log X_e	Model	1	0.62888	0.62888	68.35742	4.2225E−4
		Error	5	0.046	0.0092		
		Total	6	0.67488			

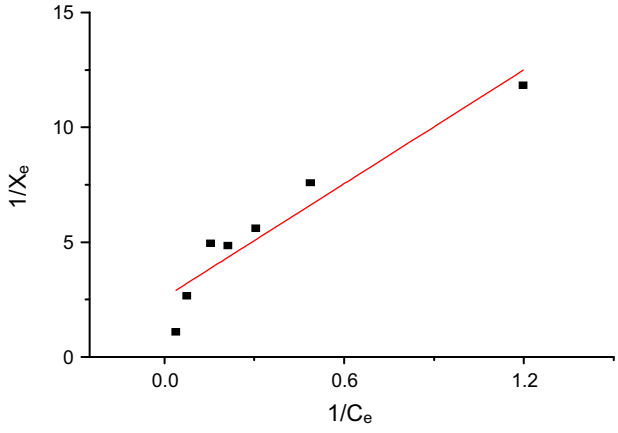


Fig. 5. Langmuir isotherm plot of methyl violet on potassium zinc ferrocyanide powder.

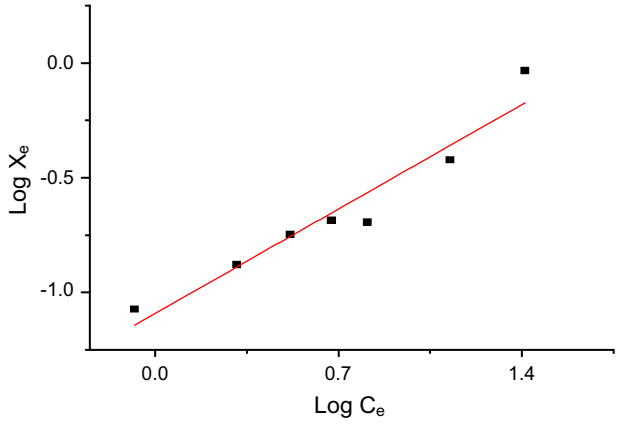


Fig. 6. Freundlich isotherm plot of methyl violet on potassium zinc ferrocyanide powder.

Table 4
Kinetic and thermodynamic parameters of the adsorption of dye on potassium zinc ferrocyanide powder

Parameters	Methyl violet
K_L	3.19607
X_m	0.38670
R_L	6.80909×10^{-3}
K_F	0.08106
n	1.53801
ΔG°	−2.87805

where K_F and n are the Freundlich constants; K_F is related to the adsorption capacity and n is a dimensionless heterogeneity parameter linked to adsorption intensity of the sorbent; smaller the value of n greater the heterogeneity. The linear Freundlich plots of log X_e against log C_e are shown in Fig. 6. The values of K_F and n are calculated from intercept and slope, respectively, and listed in Table 4.

5. Thermodynamic parameters

The thermodynamic parameters: Gibb's free energy change (ΔG°) was calculated using Eq. (3):

$$\Delta G^\circ = -RT \ln K_L \quad (3)$$

Gibb's free energy change is the fundamental criterion of spontaneity. Reactions occur spontaneously at a given temperature if ΔG° is a negative value. The Gibb's energy of adsorption of methyl violet at 25°C was $-2.87\,\mathrm{kJ\,mol^{-1}}$ implying that adsorption is spontaneous and favorable.

6. Desorption studies

Regeneration of used adsorbent is the obvious requirement of adsorption studies; desorption studies illustrate the nature of adsorption and possibility of recycling of the spent adsorbent and dyes. When the adsorbed dyes can be desorbed using neutral pH water, then the attachment of the dyes on the adsorbent is weak. When sulfuric acid or alkaline water desorps the dyes, then the adsorption takes place by ion exchange. When organic acids, like acetic acid desorp the dyes, then the dye is attached to the adsorbent through chemisorptions. The effect of various reagents used for desorption studies shows that neutral pH

water is a good reagent for desorption, and ~70–80% dye is desorbed, once again confirming possibility of physical adsorption. Yet, better desorption is obtained in 50% ethanol.

Adsorption reaction may lead to change in molecular and crystalline structure of the adsorbent and hence an understanding of the molecular structure and crystalline structure of the adsorbent and the resulting changes thereof would provide valuable information regarding adsorption reaction. Adsorbent after desorption with distilled water and drying, subjected to XRD, SEM, and FT-IR studies indicate no significant changes in the molecular and crystalline structure of adsorbent.

7. Conclusion

The results of the investigation on adsorption of methyl violet reveal potassium zinc ferrocyanide powder is a fairly good adsorbent. Gibbs free energy at 25°C is negative implying spontaneous adsorption process. Desorption studies show possibility of weak interactive forces and possibility of physical adsorption of dyes. XRD, IR, and SEM studies did not show any remarkable change after adsorption/desorption, which confirms weak forces are involved in adsorption. The F > Prob in ANOVA shows that the dye concentration is a significant factor that governs adsorption.

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