Studies in Adsorption: Determination of Specific Surface Area of Aluminum, Stannous and Vanadium Ferrocyanides by a Cationic Organic Dye Adsorption

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Abstract: The present paper deal with the determination of specific surface area of aluminum, stannous and vanadium ferrocyanides by solution adsorption of methylene blue a cationic organic dyestuff at room temperature (30 ± 1ºC). The adsorption of methylene blue solution was studied in pH range (2.0 - 10.0) and at concentration of 10^{-5} - 10^{-6} M. The process was very fast initially and maximum adsorption was attained within 6 h of contact time. The experimental data are fitted to the Langmuir isotherm equation and value of corresponding constant was determined from the slope and intercept of the plot. Methylene Blue Dye (MBD) appears to be adsorbed flatwise from water with an effective molecular area of 130Å^2. The Specific Surface Area (SSA) has been calculated. The SSA of particle size 125 µm was found to be 46.36 ± 0.05, 69.00 ± 0.11 and 81.42 ± 0.07 m^2g^{-1} for aluminum, stannous and vanadium ferrocyanides , respectively.

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Keywords: Methylene blue dye; adsorption; metal ferrocyanides; Langmuir constants; specific surface area.

1. Introduction

Dye adsorption data have been largely used for determination of specific surface area of solids (Brina, 1987) [1]. Dye adsorption, preferentially the uptake of methylene blue, has been often used as a substitute for BET measurement for determining the total surface of such compounds (Potgieter, 1991; Pekarek, 1972) [2, 3]. The measurement of SSA of finally divided solids becomes increasingly important in laboratory and technical processes. The determination of SSA of solids by solution adsorption is simple and has been shown to give reliable results with a wide variety of solids. Due to ease of formation of cyanide under prebiotic conditions (Beck, 1978) [4]. It is thought that insoluble double - metal ferrocyanides were produced on the primitive earth due to interaction of cyanides with metal ions readily available in the environment. These double - metal ferrocyanides have acted as adsorbents (Tewari, 1993; Tewari, 1998; Ali, 2006) [5-7], ion-exchangers (Kourin, 1964; Malik, 1976; Bastian, 1967) [8-10] and Photosensitizers (Tewari, 1996; Tewari, 1996) [11, 12].

A search of literature indicated that several report available on removal, kinetic, thermodynamic, equilibrium studies of adsorption of MBD on various adsorbents (Chen, 2011; Chaari, 2011; Ferrero, 2010; Wanchanthuek, 2011; Hashemian, 2011; Yadav, 2011; Altaher, 2011; Wang, 2010; Annadurai, 2002; Froba, 2006) [13-22], Some report available on determination of SSA of various solids by MBD adsorption (Yukselen, 2006; Avena, 2001; Itodo, 2010; Santamarina, 2002; Tsai, 2011; Rubin, 2010; Inel, 2000; Shangareeva, 2006; Hang, 1970; Kaewprasit, 1998; Kipling, 1960) [23-33], but no report available on determination of SSA of aluminum, stannous and vanadium ferrocyanides by MBD adsorption. In view of this attempt has been made to determine the SSA of these metal ferrocyanides. In addition, present paper describes an MBD adsorption method for the determination of SSA of aluminum, stannous and vanadium ferrocyanides.

2. Experimental Section

2.1 Materials

Potassium ferrocyanide, aluminum chloride, stannous chloride and sodium vanadate were obtained from BDH, Poole, UK. Methylene blue dye was obtained from E. Merck, Darmstadt, Germany. All chemicals used were of AnalaR grade. Doubly distilled water was used for the preparation of solutions.

2.2 Synthesis of Metal Ferrocyanides

Aluminum ferrocyanide was prepared by Kourim's method (Kourim, 1964) [34] by adding slowly a potassium ferrocyanide (167 ml: 0.1 M) solution to a solution of aluminum (III) chloride (50 ml: 0.1 M) with constant stirring. Reaction mixture was heated onto a boiling waterbath for 2-3 h and then cured for 24 h. The precipitate was filtered, washed with distilled water and dried in a oven at 60ºC.

Stannous ferrocyanide was prepared by mixing solution of 0.25 M potassium ferrocyanide and stannous chloride in ratio (2:1) (Tewari, 1995) [35]. The precipitate was cured at room temperature for 24h, filtered, washed and dried at 40ºC.

Vanadium ferrocyanide complex was isolated (Baetsle, 1966; Huys, 1964) [36, 37] by adding (10 ml: 1.0 M) HCl to a mixture containing sodium vanadate (500 ml: 0.3 M) and potassium ferrocyanide (500 ml: 0.1 M) solution with constant stirring. Reaction mixture to be heated on a boiling water bath for 3 h to 4 h and then allowed to cool at room temperature overnight. The precipitate formed was formed was filtered and dried at 50 ºC. The dried products were ground and sieved to 125 µm mesh size.

2.3 Characterization of Metal Ferrocyanides

Aluminum, stannous and vanadium ferrocyanides are found to have light blue, dark blue and green colour, respectively. These complexes are amorphous solid and show no X-ray pattern. All three metal ferrocyanides were characterized on the basis of elemental analysis and spectral studies. Aluminum, stannous, vanadium and iron were estimated by atomic adsorption IL-751 spectrophotometer - carbon, hydrogen and nitrogen analysis was performed on CEST-118, CHN analyzer.

Table 1. Elemental analysis of aluminum, stannous and vanadium ferrocyanides

Metal ferrocyanides[a]	Percentage Found				
	Metal	Iron	Carbon	Hydrogen	Nitrogen
AlFc	9.90	11.10	13.20	4.90	16.60
SnFc	38.75	10.90	14.25	1.75	18.10
VaFc	24.10	13.90	18.10	2.00	19.73

AlFc = aluminum ferrocyanide;
SnFc = Stannous ferrocyanide;
VaFc = Vanadium ferrocyanide.

The values are given in Table 1. All three metal ferrocyanides show a broad peak at around 3650 cm^{-1}, characteristic of water molecule and OH group. Also, a peak at around 1600 cm^{-1} due to HOH bending appeared in all the metal ferrocyanides studied. Two sharp bands at 2100 cm^{-1} and 600 cm^{-1} are characteristics of cyanide and Fe-C stretching, respectively. Another sharp band at around 500 cm^{-1} probable show the presence of metal - nitrogen band due to polymerization. The infrared spectral data are given in Table 2. Metal ferrocyanides are found to be stable in acids (HCl, HNO_3, H_2SO_4) and bases (NaOH , KOH, NH_4OH) solutions in the concentration range 0.1 - 2.0 M.

Table 2. Infrared spectral data of aluminum, stannous and vanadium ferrocyanides

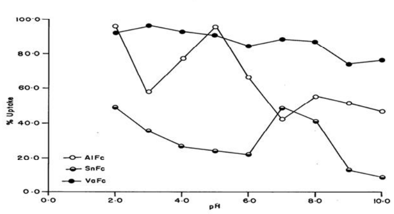
Metal ferrocyanides[a]	Adsorption frequencies (cm^{-1})				
	H_2O molecules / OH group	HOH bending	C ≡ N Stretching	Fe-C	Metal - N[b]
AlFc	3600	1660	2000	600	490
SnFc	3600	1600	2000	600	500
VaFc	3600	1600	2040	600	490

[b] Metal - N band shows degree of polymerization

2.4 Adsorption Studies

The adsorption of MBD on metal ferrocyanides as a function of MBD concentration [10^{-5} - 10^{-6} M] was studied at room temperature (30 ± 1ºC) and pH 7.01 ± 0.01. A series of 50 ml test tubes were employed. Each tube was filled with 10 ml of MBD solution of varying concentration and adjusted to desired pH appropriate buffer. Metal ferrocyanide (50 mg) was added to each tube and agitated for 24 h. Equilibrium was attained in about 6 h. The equilibrium time and concentration ranges were however decided after a good deal of preliminary investigations. The concentration of MBD solution before and after adsorption was measured spectrophotometrically at λ_{max} 665 nm.

Figure 1. Effect of pH on adsorption of methylene blue dye on metal ferrocyanides.



Temperature = 30 ± 1ºC; amount of MFc = 50 mg; particle size = 125 µm; λ_{max} MBD = 665 nm.

3. Results and Discussion

The variation of adsorption of MBD on aluminum, stannous and vanadium ferrocyanides with varying hydrogen ion concentration is given in Figure 1. The percentage adsorption was calculated by the general formula

$$\% \text{ Adsorption} = \frac{\text{difference in concentration of MBD before and after adsorption}}{\text{concentration of MBD before adsorption}} \times 100$$

Aluminum and stannous ferrocyanide showed maximum adsorption at pH 2.0, while vanadium ferrocyanide has maximum adsorption at pH 3.0. The percentage uptake of MBD on aluminum, stannous and vanadium ferrocyanides is given in Table 3.

Table 3. Percentage adsorption of methylene blue on metal ferrocyanides

pH	Percentage adsorption		
	AlFc	SnFc	VaFc
2.0	98.08	49.25	93.25
3.0	58.68	35.80	96.46
4.0	77.75	27.15	92.60
5.0	95.83	24.35	91.85
6.0	66.46	22.30	85.27
7.0	42.32	48.65	89.10
8.0	55.72	40.50	87.43
9.0	52.57	12.86	74.55
10.0	47.25	9.00	77.10

Room temperature = 30±1ºC; amount of MFc's = 50mg; λ_{max} methylene blue dye = 665 nm; particle size = 125 µm.

A neutral pH was chosen to run the adsorption isotherms of the methylene blue dye in a wide range of concentration because most biological redox reactions takes place in neutral medium. Adsorption isotherm as C_{eq} (equilibrium adsorbate concentration versus q (amount mg of adsorbate adsorbed per gram of adsorbent) for the adsorption of MBD on aluminum, stannous and vanadium ferrocyanides is shown in Figure 2.

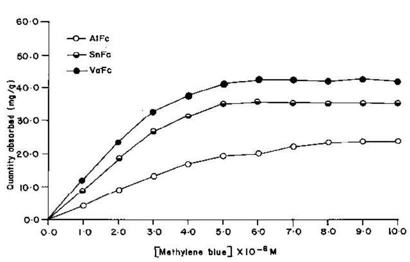


Figure 2. Adsorption isotherm of methlyene blue dye on metal ferrocyanides.
Temperature = 30 ± 1ºC; pH = 7.0 ± 0.01; amount of MFc = 50 mg; particle size = 125 µm; λ_{max} MBD = 665 nm.

The isotherms are positive and concave to the concentration axis. At low concentration adsorption is rapid, then slows down at higher concentration until adsorption becomes constant and the graph levels off. This leveling off or 'plateau' indicates the saturation point (point at which maximum uptake of dye). The order of maximum uptake of MBD on metal ferrocyanides at neutral pH is as follows:

Vanadium ferrocyanide > stannous ferrocyanide > aluminum ferrocyanide

Adsorption isotherm data have been analyzed in terms of the Langmuir isothermal adsorption equation (Langmuir, 1918) [38].

$$\frac{C_{eq}}{Q_{eq}} = \frac{1}{bQ_o} + \frac{C_{eq}}{Q_o}$$

$$\frac{1}{Q_{eq}} = \frac{1}{C_{eq}} \cdot \frac{1}{bQ_o} + \frac{1}{Q_o}$$

Where C_{eq} is the equilibrium concentration of MBD; b, a constant related to enthalpy (ΔH) of adsorption (b α $e^{-\Delta H I RT}$); q_{eq}, the amount (mg) of solute adsorbed per gram weight of adsorbent and Q_0 is the amount (mg) of solute required per gram weight of metal ferrocyanides. Langmuir plots for adsorption of MBD on metal ferrocyanides are shown in Figure 3.

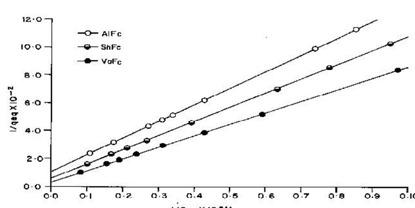


Figure 3. Langmuir plots of methylene blue dye on metal ferrocyanides.
Temperature = 30 ± 1ºC; pH = 7.0 ± 0.01; amount of MFc = 50 mg; particle size = 125 µm; λ_{max} MBD = 665 nm.

All three Langmuir plots are liniar in behavior. The values of Q_0 and b were determined from intercept and slope of Langmuir plot and are presented in Table 4.

The approximate specific surface area of aluminum, stannous and vanadium ferrocyanides has been obtained with the help of following equation (Giles, 1970; Giles, 1964; Giles, 1962) [39-41]

Specific Surface Area(SSA)= $6.02 \times 10^{-2}\ M_f\ A_m$ (m^2g^{-1})

Where M_f = m Mole of MBD adsorbed per 100 gram metal ferrocyanides, when the surface is covered with monolayer, A_m = area per molecule in $Å^2$ on the surface. Under the condition of optimum flocculation, the area per adsorbed molecule of MBD is taken as $130Å^2$, which corresponds to the molecule lying flat on the adsorbent surface. The calculated SSA values of metal ferrocyanides are given in Table 4. It is observed from Table 4 that vanadium ferrocyanide and aluminum ferrocyanide have maximum and minimum surface area, respectively.

Table 4. Langmuir constants for adsorption of methylene blue dye on metal ferrocyanides

Metal ferrocyanides	Particle size (µm)	Specific surface area ($m^2\ g^{-1}$)	Langmuir constants	
			b x 10^5 (liters / mol)	Q_0 x 10^2 (mg/g)
AlFc	125	46.36 ± 0.05	1.00 ± 0.02	0.83 ± 0.06
SuFc	125	69.00 ± 0.11	0.72 ± 0.09	1.39 ± 0.01
VaFc	125	81.42 ± 0.07	0.49 ± 0.03	2.50 ± 0.11

Room temperature = 30 ± 1°C; pH = 7.0 ± 0.01; amount of metal ferrocyanide = 50 mg; λ_{max} methylene blue = 665 nm.

It is also observed from Table 4 that vanadium ferrocyanide have highest Q_o and lowest b value, while aluminum ferrocyanide have lowest Q_0 and highest b values among all three metal ferrocyanides studied.

4. Concluding Remarks

a) All three metal ferrocyanides showed maximum percentage uptake at very low pH level.
b) Vanadium ferrocyanide is considered to be more porous in comparison to aluminum and stannous ferrocyanide.
c) Present study conclude that adsorption of MBD on metal ferrocyanides is quite satisfactory.
d) Results of present study suggest the potential use of MBD in the determination of SSA of metal ferrocyanides.
e) The use of basic MBD for the determination of SSA is more useful, because it is highly pure and suitable for immediate use, as this dye is easily analyzed spectrophotometrically.
f) Determination of SSA by MBD adsorption is simple, rapid and reliable, therefore the present method has significant advantages over other methods reported in chemical literature for the determination of SSA of solids.

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