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Interaction of 2, 4-dinitrophenol (2, 4-DNP) and 2, 4, 6-trinitrophenol (2, 4, 6-TNP) with Metal Hexacyanoferrate (II) Complexes

Abstract -Antimony, cadmium and zirconium ferrocyanides were synthesized and characterized by elemental and spectral studies. Interaction of 2, 4-dinitrophenol (2, 4-DNP) and 2, 4, 6-trinitrophenol (2, 4, 6-TNP) with antimony, cadmium and zirconium ferrocyanides have been studied at neutral pH (7.00 ± 0.01) and temperature (30 ± 1ºC). The progress of adsorption was followed spectrophotometrically by measuring the absorbance of substituted phenols at their corresponding λ_{max}. The nature of adsorption has been interpreted from the shape of adsorption isotherms. The Langmuir type of adsorption is followed in the concentration range of 10^{-3} – 10^{-4} M of 2, 4-DNP and 2, 4, 6-TNP solutions. The 2, 4, 6 -TNP was found to have greater affinity for the antimony, cadmium and zirconium ferrocyanides than 2, 4 – DNP. High adsorption capacity has been observed for cadmium ferrocyanides while it is minimum with zirconium ferrocyanide, which indicate highly porous characteristics of cadmium ferrocyanide in comparison to other metal ferrocyanides studied. Removal of toxic phenol is necessary for the protection of our environment. Phenols react with soil to reduce their fertility therefore its removal from soil is also important for our food security.

Keywords: removal; substituted phenols; adsorption; metal ferrocyanides; adsorption parameters.

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1. INTRODUCTION

Insoluble metal hexacyanoferrate (II) complexes are an important class of compounds and have been widely used as a adsorbents [1, 2] photosensitizers [3] and ion-exchangers [4, 5]. Phenol compounds are the strictly regulated compounds worldwide because of their extreme toxicity. In the receiving bodies themselves both flora and fauna are adversely affected. Phenols react with soil to reduce their fertility. Removal of phenol is important for both agricultural and environmental point of view. Phenol compounds are utilized and also found in the effluents of industries like coke plant, paint and dye formation, automobile manufacturing, explosive manufacturing, chemicals, synthetic fibre and resin manufacture etc.

Lawal et al. [6] reported removal of phenol from water by using carbon adsorbents prepared by pyrolysis of sorghum and millet straws in orthophosphoric acid. Adsorption characteristics of natural zeolites as solid adsorbents for phenol removal from aqueous solutions: kinetics, mechanism and thermodynamics studies investigated by Yousef et al. [7]. Kiran et al. [8] demonstrated simultaneous adsorptive removal of cyanide and phenol from industrial wastewater: optimization of process parameters. Enzyme based process for removal of phenol from wastewater: current status and future challenges is described by Narayan et al. [9]. Ardelean et al. [10] reported adsorption characteristics of some polymeric materials with olefin groups used for removal of phenol and p-nitrophenol from aqueous solutions. Adsorption of phenol from wastewater using locally available adsorbents from agricultural waste materials investigated by Girish et al. [11] .

Various processes such as oxidation, biodegradation, solvent extraction, incineration, reverse osmosis, and adsorption have been proposed to remove phenolic compounds from contaminated

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water, among which adsorption is one of the most effective technique in either laboratory or industrial scale. Literature survey showed adsorptive interaction of phenols with a number of adsorbents viz: potato polyphenol oxidase [12], natural clay [13], activated neem leaf [14], yeast [15] and zeolites [16].

Very little is known about reaction of phenols with metal ferrocyanides and few research articles are available on the interaction of amines, phenols and metal ions with the metal ferrocyanides. In view of this attempt has been made to determine the surface properties of metal ferrocyanides and phenols system. In addition current work describes a removal of 2, 4-DNP and 2, 4, 6-TNP through adsorptive interaction with antimony, cadmium and zirconium ferrocyanides. The 2, 4-DNP and 2, 4, 6-TNP were chosen as representative phenols due to their two and three electron withdrawing groups, respectively.

2. METHODOLOGY

2.1. Chemicals:

Antimony chloride, cadmium chloride, zyrconyl chloride, 2, 4-DNP, 2, 4, 6-TNP and potassium ferrocyanide were obtained from BDH, Poole, United Kingdom. All chemicals used were of Analytical Reagent Grade.

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2.2 Synthesis of Metal Ferrocyanides

Antimony, cadmium and zirconium ferrocyanides were prepared by adding metal chloride (500 ml, 0.1 M) and potassium ferrocyanide (167 ml, 0.1 M) solution with constant stirring [17]. The reaction mixture was heated on a water bath for 3 h and kept as such at room temperature for 24 h. The precipitate was filtered under vacuum, washed several times with distilled water and dried in an air oven at 60º C. The dried product was grounded and sieved to 125 µm particle size.

2.3 Characterization of Metal Ferrocyanides

All three metal ferrocyanides were characterized by elemental and spectral studies. Percentage composition of metals and carbon, hydrogen, nitrogen were determined with the help of IL 751, atomic absorption spectrophotometry and a CEST – 118 CHN Analyzer, respectively. The values are given in Table 1.

These metal ferrocyanides are found to be insoluble in water and amorphous in nature and give no x-ray pattern. Antimony ferrocyanide Sb_2 [Fe (CN) 6] • 2 H_2O, cadmium ferrocyanide Cd_2 [Fe (CN) 6] • 4 H_2O and zirconium ferrocyanide Zr_2 [Fe (CN) 6] • 8 H_2O were found to have light blue, light green and gray colours, respectively. Antimony, cadmium and zirconium ferrocynaides revealed infrared spectral peaks around 3600 cm^{-1} and 1600 cm^{-1} characteristic of water molecules / OH group and HOH bending, respectively. Two sharp bands at around 2000 cm^{-1} and 580 cm^{-1} are characteristics of cyanide and Fe-C stretching, respectively [18]. Another sharp band at 490 cm^{-1} probable shows the presence of metal – nitrogen band due to polymerization [19]. The infrared spectral data are given in Table 2.

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2.4 Adsorption Studies

The adsorption of 2, 4-DNP and 2, 4, 6-TNP on metal ferrocyanides as a function of phenol concentrations (10^{-3} – 10^{-4} M) was studied at room temperature (30 ± 1 ºC) and different pH. The final adsorption studies of phenols at various concentrations was studied at neutral pH (7.0± 0.01) this is due to physiological significance of neutral pH because most of the reactions in biological systems takes place at neutral pH range. A series of 50-mL test tubes were employed. Each tube was filled with 10 mL of phenol solution of varying concentration and adjusted to desired pH. Metal ferrocyanide (25 mg) was added to each tube and agitated for 24 h. Equilibrium was attained in about 6 h. The equilibrium time and concentration range were however decided after a good deal of preliminary investigations. The concentration of 2, 4-DNP and 2, 4, 6-TNP were measured spectrophotometrically at 360 nm and 382 nm, respectively.

3. RESULTS AND DISCUSSION

The percentage uptake of 2, 4-DNP and 2, 4, 6-TNP as a function of pH and was studied over a pH range of 1.0 – 10.0 (Figures 1 & 2). The percentage uptake was calculated by equation

$$\% \text{ uptake} = \frac{\text{Difference in concentration of substituted phenols before and after adsorption}}{\text{Concentration of substituted phenol before adsorption}} \times 100$$

The values of percentage uptake of 2, 4-DNP and 2, 4, 6-TNP on different metal ferrocyanides are given in Tables 3 &4, respectively.

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The maximum pH value for the uptake of 2, 4-DNP and 2, 4, 6-TNP were found to be 4.0 and 2.0, respectively. It seems that uptake of both 2, 4-DNP (pKa = 3.96) and 2, 4, 6-TNP (pKa = 0.38) are maximum near their respective pKa on all three metal ferrocyanides studied. It is observed from Tables 3 & 4 that 2, 4, 6-TNP is strongly adsorbed on all three metal ferrocyanides in comparison to 2, 4-DNP. Electron density of aromatic ring is strongly influenced by the nature of the substituent's present in it. The nitro group is electron withdrawing and reduces the overall electron density in the pi- system of benzene ring. Since the presence of OH group is common to both 2, 4-DNP and 2, 4, 6-TNP, higher adsorption in case of 2, 4, 6-TNP is due to only to presence of one more withdrawing nitro group.

Adsorption isotherm of 2, 4-DNP and 2, 4, 6-TNP on metal ferrocyanides is shown in Figures 3 & 4 and values of maximum adsorption is given in Table 5. It is observed from Figures 3 & 4 that adsorption is fast in all cases and isotherms are regular positive and concave to the concentration axis. Slow adsorption gradually leading to constancy takes place at higher adsorbate concentration. In general the adsorption curves were characterized by a gradual rise and flattering at higher adsorbate concentration.

The affinity of metal ferrocyanides towards adsorption for both 2, 4-DNP and 2, 4, 6-TNP follows the order:

Cadmium ferrocyanide > antimony ferrocyanide > zirconium ferrocyanide

Present trend of adsorption is justified by specific surface area (SSA) of metal ferrocyanides (CdFc = 101.67; SbFc = 74.30; ZrFc = 47.30) (m^2g^{-1}) was calculated by basic methlyene blue

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dye adsorption. The Langmuir plots for adsorption 2, 4-DNP and 2, 4, 6-TNP on antimony, cadmium and zirconium ferrocyanides are shown in Figures 5 & 6, respectively. The Langmuir constants (b and Q_0) values are given in Table 6.

Sorption data have been correlated with Langmuir adsorption model given by equation [20, 21]

$$1/Q_{eq} = 1/Q_0 + 1/bQ_0 . C_{eq}$$

where C_{eq} is equilibrium conc. of phenol, b is the constant related to the equilibrium constant or binding energy (b α $e^{-\Delta H/RT}$ the parameter b reflects the steepness of the approach to saturation, more precisely to the b values is the reciprocal of concentration at which half saturation of the adsorbent is attained). Q_{eq} is amount (mg) of adsorbate adsorbed per gram of adsorbent and Q_0 is the adsorption maxima, i.e. mg of phenol required per gram of metal ferrocyanide for forming a complete monolayer on the surface.

The liniar nature of Langmuir plots confirm the formation of monolayer of 2, 4, 6-TNP molecules on metal ferrocyanides. The values of Langmuir constants b and Q_0 for all the systems were obtained from the slope and intercept of the plots, respectively. The values of Q_0 have been interpreted as a measure of the accessibility of the adsorption sites and the b may be regarded as a measure of the affinity of the metal ferrocyanides for the adsorbed substituted phenols [22].

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The values of Langmuir constants indicate favourable conditions for adsorption. The Q_0 values are found to be maximum for CdFc – TNP system while it is a minimum for the ZrFc – DNP system. The b value is found to be a maximum for ZrFc – DNP system and lowerst for CdFc-TNP system.

4. CONCLUDING REMARKS

1. Antimony, cadmium and zirconium ferrocyanides were synthesized, characterized and utilized for the removal of 2, 4-DNP and 2, 4, 6-TNP from the aqueous solution.
2. The most effective pH for the removal of 2, 4-DNP and 2, 4, 6-TNP were found to be 4.0 and 2.0, respectively.
3. Cadmium and zirconium ferrocyanides were found to have maximum and minimum adsorption, respectively for both adsorbents.
4. Adsorbents cheaper than metal ferrocyanides are available for the removal of phenols from the environment but present study indicates feasibility of using metal ferrocyanides for the treatment of phenol bearing wastewater.
5. 2, 4, 6-TNP found to be more adsorbed in comparison to 2, 4-DNP on all three metal ferrocyanides studied.
6. Results in the present study suggest the potential feasibility for the use of metal ferrocyanides in the removal of 2, 4-DNP and 2, 4, 6-TNP from industrial waste, potable water, environment and agricultural soil.

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FIGURE CAPTION

Figure 1 Effect on pH on adsorption of 2, 4-DNP on metal ferrocyanides. (Temperature is 30 ± 1ºC; concentration is 10^{-4} M; amount of metal ferrocyanides is 25 mg)

Figure 2 Effect on pH on adsorption of 2, 4, 6-TNP on metal ferrocyanides.(Temperature is 30 ± 1ºC; concentration is 10^{-4} M; amount of metal ferrocyanides is 25 mg)

Figure 3 Adsorption isotherm of 2, 4-DNP on metal ferrocyanides. (Temperature is 30 ± 1ºC; pH is 7.0 ± 0.01, amount of metal ferrocyanides is 25 mg)

Figure 4 Adsorption isotherm of 2, 4, 6-TNP on metal ferrocyanides. (Temperature is 30 ± 1ºC; pH is 7.0 ± 0.01, amount of metal ferrocyanides is 25 mg)

Figure 5 Langmuir plots of 2, 4-DNP on metal ferrocyanides. (Temperature is 30 ± 1ºC; pH is 7.0 ± 0.01, amount of metal ferrocyanides is 25 mg)

Figure 6 Langmuir plots of 2, 4, 6-TNP on metal ferrocyanides. (Temperature is 30 ± 1ºC; pH is 7.0 ± 0.01, amount of metal ferrocyanides is 25 mg)

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Table 1

Element analysis of antimony, cadmium, and zirconium ferrocyanides

Metal ferrocyanides[a]	Percentage found				
	Metal	Iron	Carbon	Hydrogen	Nitrogen
SbFc	47.50	12.50	15.25	0.89	17.79
CdFc	41.59	11.50	15.13	1.69	17.37
ZrFc	34.66	10.30	12.97	2.90	15.41

[a] SbFc, antimony ferrocyanide; CdFc, cadmium ferrocyanide; ZrFc, zirconium ferrocyanide.

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Table 2

Infrared spectral data of antimony, cadmium, and zirconium ferrocyanides

Metal ferrocyanides[a]	Adsorption frequency (cm^{-1})				
	H_2O molecules/OH groups	HOH bending	νC≡N stretching	νFe-C	Metal-N*
SbFc	3600	1600	2000	580	490
CdFc	3600	1620	2000	600	490
ZrFc	3600	1600	2000	580	500

[a] SbFc, antimony ferrocyanide; CdFc, cadmium ferrocyanide; ZrFc, zirconium ferrocyanide.

* Metal – N bond shows degree of polymerization

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Table 3

Percentage adsorption of 2, 4-dinitrophenol on metal ferrocyanides

(Room temperature: 30 ± 1ºC; λ_{max} 2, 4-DNP = 360 nm; 2, 4-DNP pKa = 3.96)

pH	% adsorption		
	SbFc	CdFc	ZrFc
1.0	49.8	52.7	44.6
2.0	46.7	47.3	40.9
3.0	58.7	62.4	50.3
4.0	76.4	80.5	68.2
5.0	52.6	71.2	55.4
6.0	62.0	66.4	55.4
7.0	57.6	61.0	42.8
8.0	50.3	60.2	47.5
9.0	42.6	48.6	36.2
10.0	38.9	44.7	32.6

2, 4-DNP, 2,4-dinitrophenol

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Table 4

Percentage adsorption of 2, 4, 6-trinitrophenol on metal ferrocyanides

(Room temperature: 30 ± 1ºC; λ_{max} 2, 4, 6-TNP = 382 nm; TNP pKa = 0.38)

pH	% adsorption		
	SbFc	CdFc	ZrFc
1.0	50.7	60.6	46.3
2.0	81.7	87.6	72.2
3.0	72.0	80.2	64.0
4.0	64.3	71.9	64.0
5.0	66.3	68.5	60.9
6.0	60.2	70.6	50.7
7.0	62.7	66.9	56.0
8.0	57.9	70.2	52.3
9.0	52.3	54.8	50.2
10.0	36.0	45.3	34.9

2, 4, 6 –TPN, 2,4,6-trinitrophenol

297 Table 5

298

299 Maximum uptake of 2, 4-dinitrophenol and 2, 4, 6-trinitrophenol on metal ferrocyanides

300 (Room temperature 30 ± 1ºC; pH = 7.0 ± 0.01)

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302

Substituted phenols	Metal ferrocyanides	Particle size (µm)	Maximum uptake (mg/g)
2, 4 – DNP	SbFc	125	30.7
(pka = 3.96)	CdFc	125	37.0
λ_{max} = 360 nm	ZrFc	125	25.0
2, 4, 6 – TNP	SbFc	125	33.3
(pka = 0.38)	CdFc	125	39.0
λ_{max} = 382 nm	ZrFc	125	26.2

303

304 2, 4-DNP, 2, 4- dinitrophenol

305 2, 4, 6-TNP, 2,4,6- trinitrophenol

Table 6

Langmuir constants for adsorption of 2, 4-dinitrophenol and 2, 4, 6-trinitrophenol on metal ferrocyanides

(Room temperature = 30 ± 1ºC; pH = 7.0 ± 0.01)

Substituted phenols	Metal ferrocyanides	Particle size (μm)	Langmuir constants	
			b x 10^2 ($l\ mol^{-1}$)	Q_0 ($mg\ g^{-1}$)
2, 4 – DNP	SbFc	125	16.69	45.45
(pka = 3.96)	CdFc	125	11.39	100.00
λ_{max} = 360 nm	ZrFc	125	20.02	32.26
2, 4, 6 – TNP	SbFc	125	12.46	58.82
(pka = 0.38)	CdFc	125	4.80	166.67
λ_{max} = 382 nm	ZrFc	125	17.91	38.46

2, 4-DNP, 2, 4- dinitrophenol

2,4,6-TNP, 2,4,6- trinitrophenol

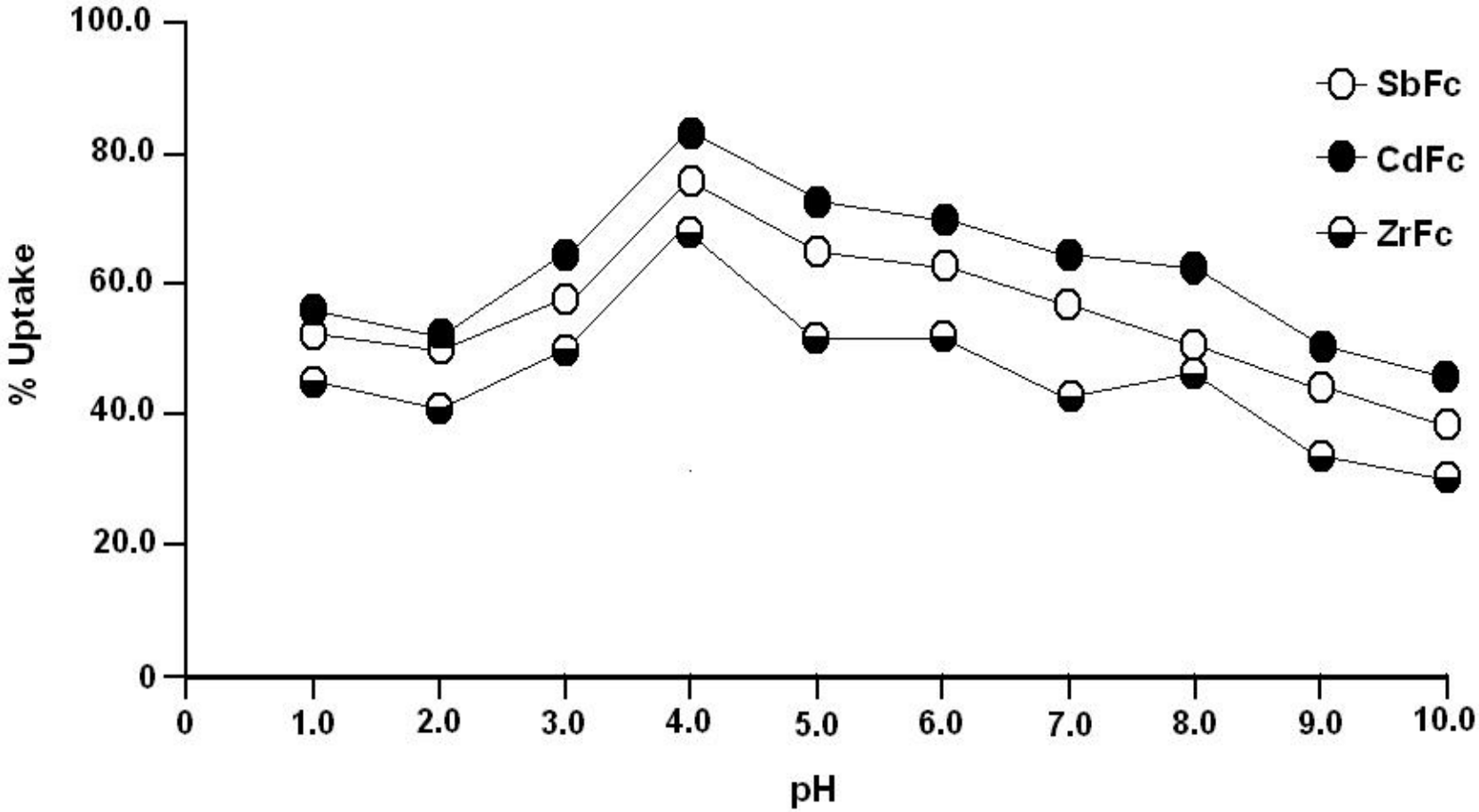

Figure 1 Effect on pH on adsorption of 2, 4-DNP on metal ferrocyanides. (Temperature is 30 ± 1ºC; concentration is 10^{-4} M; amount of metal ferrocyanides is 25 mg)

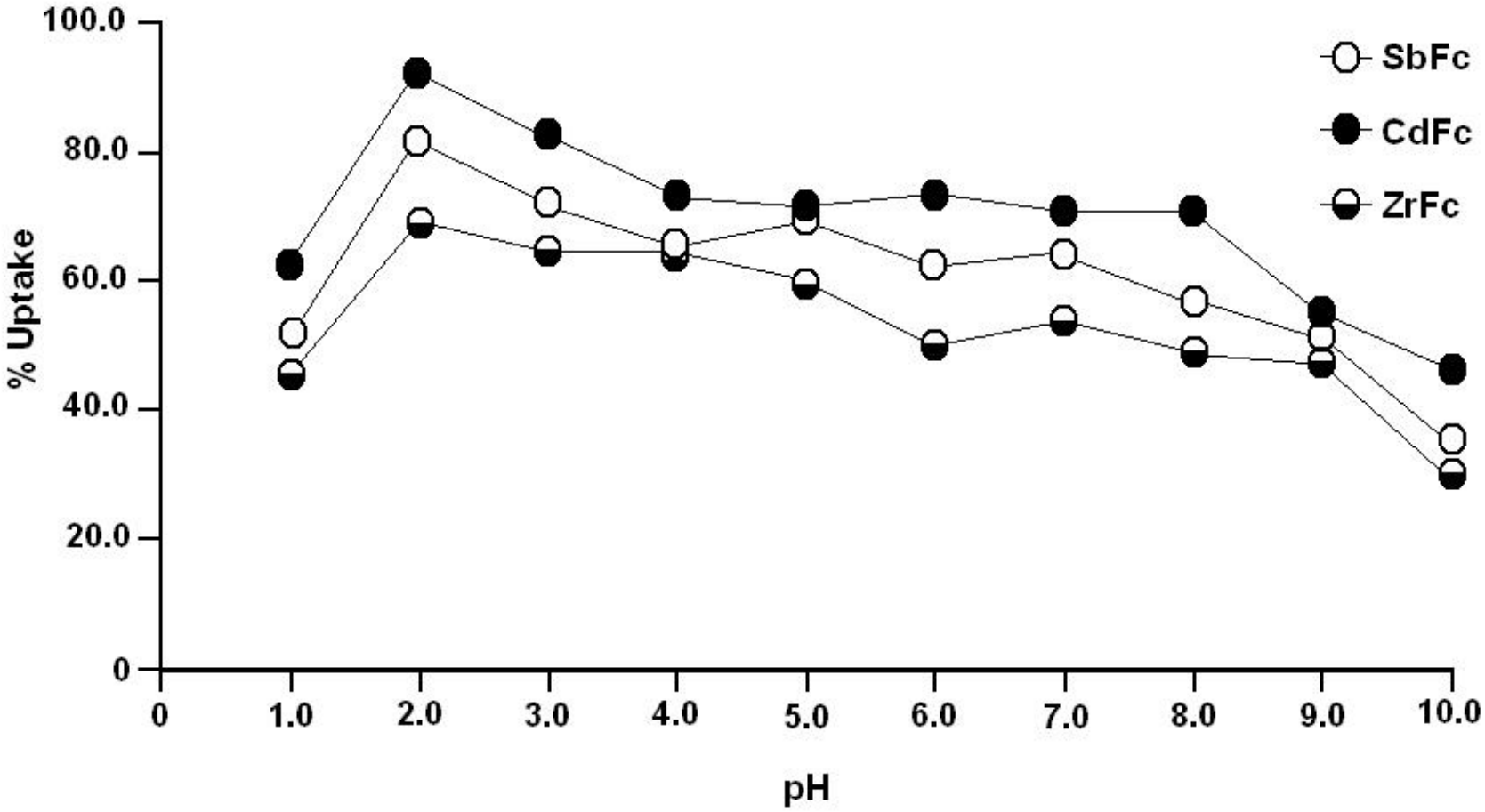

Figure 2 Effect on PH on adsorption of 2, 4, 6-TNP on metal ferrocyanides. (Temperature is 30 ± 1ºC; concentration is 10^{-4} M; amount of metal ferrocyanides is 25 mg)

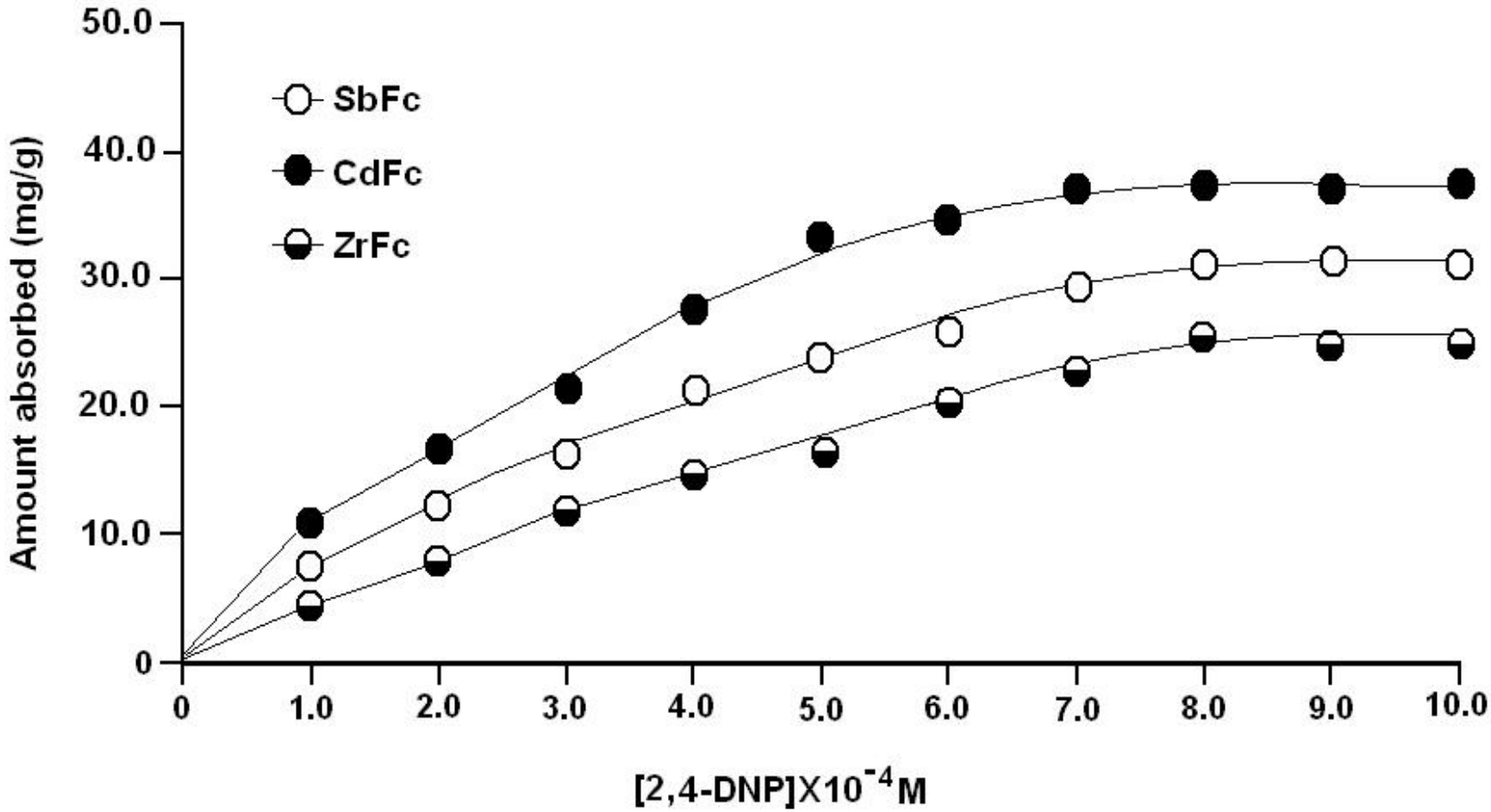

Figure 3 Adsorption isotherm of 2, 4-DNP on metal ferrocyanides. (Temperature is 30 ± 1ºC; pH is 7.0 ± 0.01, amount of metal ferrocyanides is 25 mg)

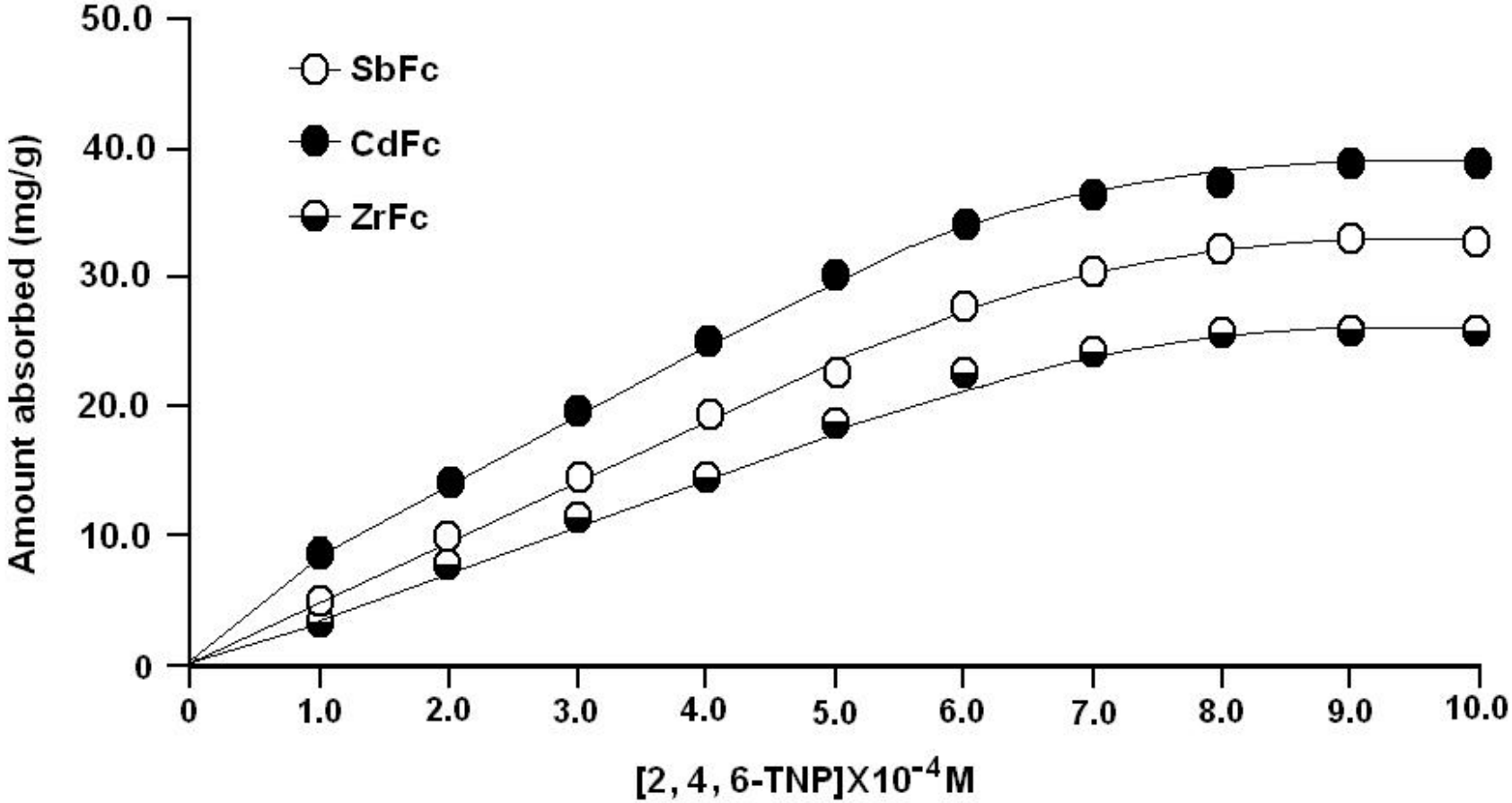

Figure 4 Adsorption isotherm of 2, 4, 6-TNP on metal ferrocyanides. (Temp. 30 ± 1ºC; pH = 7.0 + 0.01; amount of metal ferrocyanides is 25 mg)

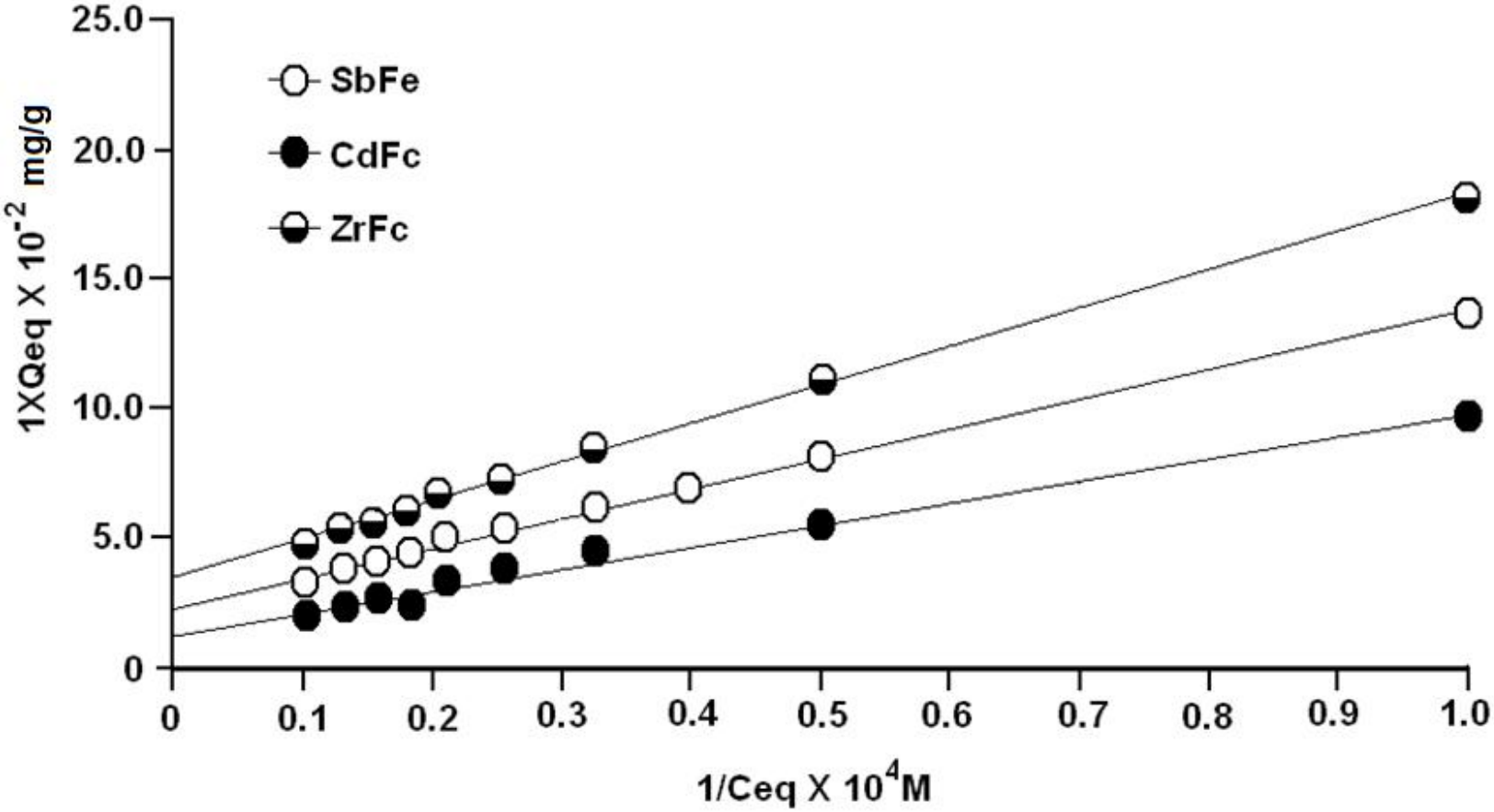

Figure 5 Langmuir plots of 2, 4-DNP on metal ferrocyanides. (Temperature is 30 ± 1ºC; pH is 7.0 ± 0.01, amount of metal ferrocyanides is 25 mg)

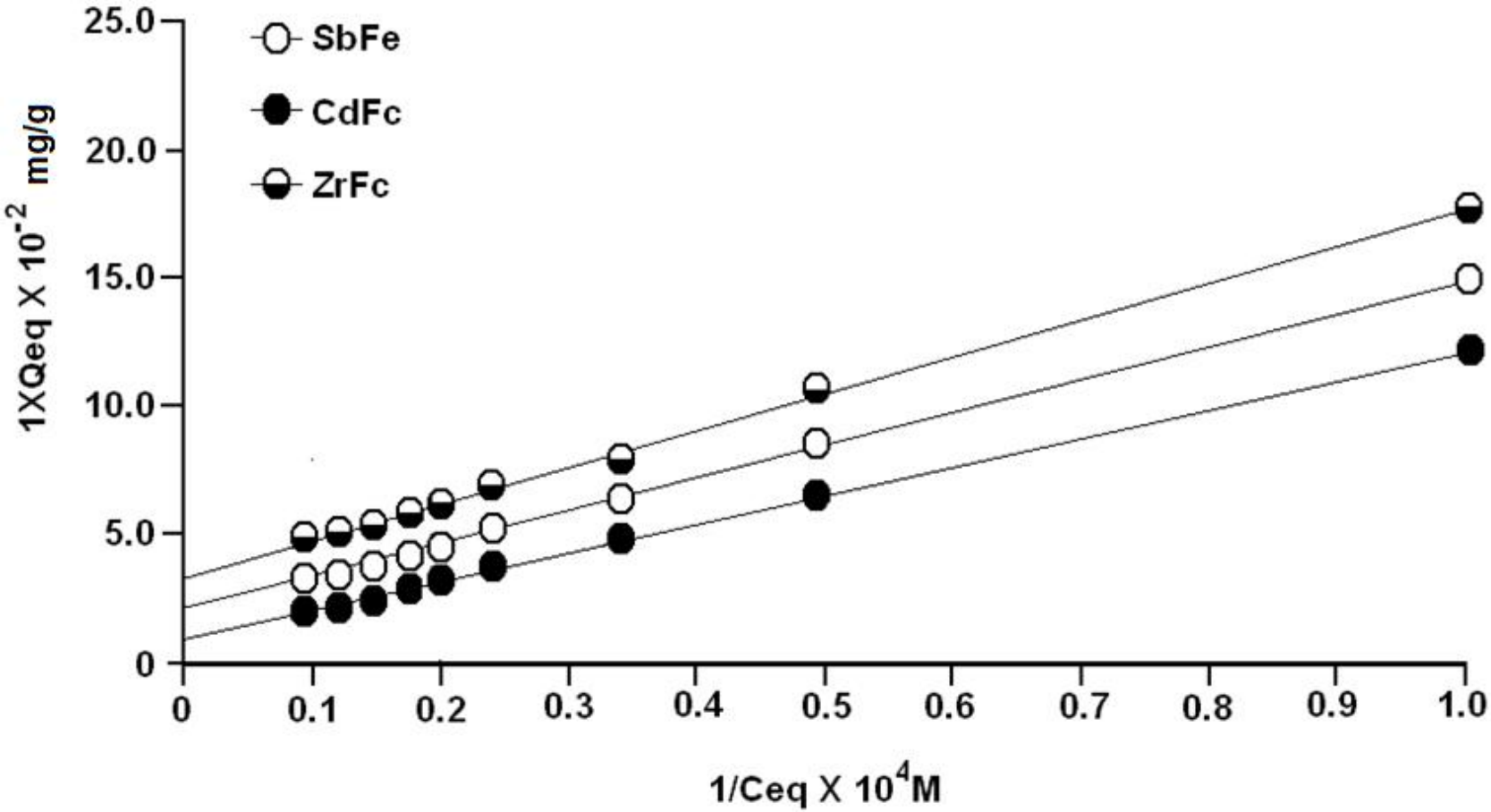

Figure 6 Langmuir plots of 2, 4, 6-TNP on metal ferrocyanides. (Temperature is 30 ± 1ºC; pH is 7.0 ± 0.01, amount of metal ferrocyanides is 25 mg)