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Adsorption Study of Congo red from Aqueous Solution onto Cadmium and Nickel Ferricyanides

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ABSTRACT

The adsorption behavior of Congo red from aqueous solution on cadmium ferricyanide and nickel ferricyanide were studied under various conditions of contact time, different pH and temperature by varying initial concentration of Congo red using batch technique. Prepared metal ferricyanides were characterized by FTIR, SEM, CHN analysis, TGA and XRD. Adsorption capacity of Congo red on cadmium ferricyanide and nickel ferricyanide were decreased with increasing the pH from 2 to 7 of aqueous solution and increased gradually from 7 to 11. Adsorption capacity also increased with increasing concentration of Congo red. Results were analyzed by Langmuir and Freundlich models of adsorption. Cadmium ferricyanide was found to be a better adsorbent than Nickel ferricyanide. Thermodynamic parameters like free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) of the system suggested that adsorption process was spontaneous and physisorption. The positive value of ΔH for Congo red indicated that adsorption was endothermic in nature.

Keywords: Metal ferricyanide, Congo red, Adsorption, Langmuir isotherm, Freundlich isotherm.

INTRODUCTION

Water pollution is the most dangerous pollution in modern world. Industrial development is accompanying with the disposal of a huge number of toxic pollutants that are difficult to degrade by natural means. Color is the first contaminant to be accepted in wastewater. Today many dyes are being used in various industries such as paints, leather, textiles, rubber, cosmetics, food, pharmaceutical, plastics, packaging, pulp and paper etc. to color the goods. The release of colored wastewater from these industries can affect photosynthetic processes of aquatic plants, reducing oxygen levels in water and in severe cases resulting in the suffocation of aquatic flora and fauna **[1-2].** Dyeing effluents are usually released into the environment which can be carcinogenic, mutagenic, allergenic and toxic to the food web and can be resistant to natural biological degradation due to presence of these heats, light, chemical and other exposures stable **[3]**.

Synthetic dyes as congo red (CR) are difficult to biodegrade due to their complex aromatic structures, which provide them physico-chemical, thermal and optical stability **[4]**. Congo red [1-Naphthalenesulfonic acid, 3-3'-(4-4'-biphenylene bis (azo) bis (4-amino) disodium salt] is a benzidine based anionic diazo dye prepared by coupling tetrazotised benzidine with two molecule of napthionic acid **[5]** (Fig. 1). Congo red is commonly used as a pH indicator and histological staining for amyloid. This anionic dye can be metabolized to benzidine, a known human carcinogen **[6]**. It has very irritating and coherent effects on skin, eyes and gastrointestinal tract. Hence, the removal of such colored agents from aqueous effluents becomes significantly environmental, technical and commercial importance **[7]**.

There are several physical, chemical, physico-chemical and biological treatment methods (eg., adsorption, coagulation-flocculation, biodegradation, ion-exchange, chemical oxidation, ozonation, membrane filtration, Fenton's reagent oxidation, reverse osmosis and electrochemical methods) have been applied to remove dye molecules from wastewater **[8, 9]**. Among these methods, adsorption has been found to one of the most popular physico-chemical treatment method for removing dyes with potential applications **[10]**. A number of non-conventional adsorbents such as bentonite **[11-12]**, montmorillonite **[13-14]**, neem leaf **[15-16]**, rice hull ash **[17]**, activated red mud **[18]**, rice husk **[19]**, fungi **[20-21]**, coir pith carbon **[22]**, mesoporus activated carbon **[23]**, chitosan **[24]**, mesoporus Fe_2O_3 **[25]**, have been used for the removal of CR from aqueous solution.

Metal ferricyanides are an important class of compounds and have been used as an adsorbent **[26]**. Literature on interaction of metal ferricyanide with congo red is lacking. Hence, present paper describes the adsorption of CR onto cadmium and nickel ferricyanides. Effect of various parameters on adsorption was also determined. The adsorbent metal ferricyanides were characterized by employing instrumental techniques, viz. Fourier transform infrared spectroscopy (FTIR), Thermogravimetric analysis (TGA), CHN analysis and X-ray diffraction (XRD). The adsorption capacities were evaluated from equilibrium adsorption isotherm by batch technique.

MATERIALS AND METHODS

Chemicals: Potassium ferricyanide, cadmium chloride (Nice Chemical, Cochin, India) and nickel chloride (SD Fine Chem. Ltd., India) were of analytical grade and used as received. Doubly distilled water was used throughout the experiments.

Preparation of metal ferricyanides: In the field of chemistry the synthesis of metal ferricyanide is not new **[26-28]**. In present study attempt were made to bring fine particles of metal ferricyanides ranging from µm to nm size in order to get maximum surface area. Metal salt solution of respective metals (0.3M, 250 mL) was mixed drop wise (4 drops min^{-1}) to potassium ferricyanide solution (0.2M, 250 mL) with constant stirring on magnetic stirrer at 50-60˚C. The reaction mixture was stirred for 24 h at 60˚C and then kept as such for 24 h at room temperature. The precipitate was filtered and washed several times with distilled water to remove the water soluble adherent impurities. Then it was dried in oven for 48 hr at 60˚C. The dried product was sieved to 100 µm mesh size through the standard test sieves. These adsorbents were stored in different air tight glass bottles for further experiments. No other chemical or physical treatments were used prior to adsorption.

Equipment used for the characterization of metal ferricyanides: The crystalline nature of the metal ferricyanides were studied on a powder X-ray diffractometer (XRD, Rigaku Miniflex, Japan) with Cu Kα radiation at scanning rate 2 deg min^{-1} from $2\theta = 10$ deg to $2\theta = 85$ deg. Infrared spectra were recorded using KBr discs on a Thermo Nicolet FTIR (Germany) within 4000-400 Cm^{-1}. Scanning electron microscopy LEO 435 VF (Leo Electron Microscopy Ltd, England) is used to examine the morphological characteristics of metal ferricyanides before and after adsorption at acceleration voltage of 20 KV. Thermo gravimetric analysis done by TGA/DSC 1 (Mettler Toledo AG, Analytical CH-8603, Schwerzenbach, Switzerland) at temperature range 25-900˚C. The elemental analysis of the metal ferricyanides recorded on 2400 series II CHNS/O, Perkin Elmer, USA.

Adsorbate: The adsorbate used in present work was congo red obtained from Thomas Baker, Mumbai, was used as received without any purification. The molecular formula of CR is $C_{32}H_{22}N_6Na_2O_6S_2$ with molecular weight 696.67 g mol^{-1} and structure shown in fig. 1. The CR sodium salt is responsible for dying cotton full red and is the first synthetic dye capable of directly dying cotton **[5]**. The color of CR changes from red to blue in the presence of inorganic acids. The change of color is due to the resonance between charged canonical structures **[29]**.

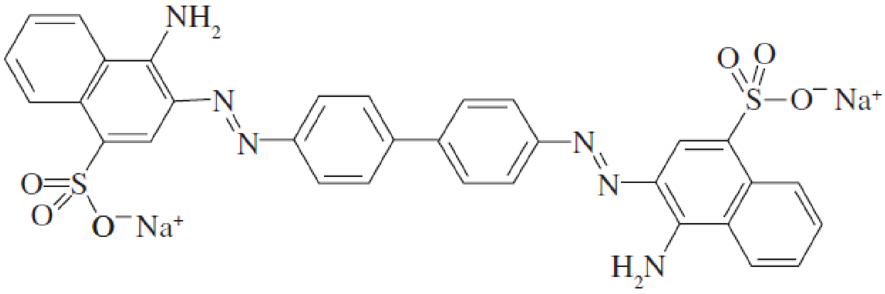


Fig.1. Structure of congo red

Adsorption experiments: The stock solution of CR was prepared by dissolving the appropriate amount (1g) of CR in a liter of double distilled water. The working solutions were prepared by diluting the stock solution to give the appropriate concentration without adding any buffer to control the pH adjustment. The UV-Vis spectrophotometer-119 (Systronic India Ltd.) was used to determine the concentration of CR dye at maximum absorbance wavelength (λ_{max}) of 496 nm. Prior of the analysis a technical calibration curve was plotted between absorbance and concentration of the dye solution.

The adsorption features of CR onto cadmium and nickel ferricyanide were investigated as a function of initial concentration, contact time, initial pH and temperature. Adsorption studies were performed by shaking a fixed amount of metal ferricyanide (50 mg) with 10 ml aqueous solution of CR in 15 ml reaction tubes with stopper. The range of initial concentration of CR was 3-84 mg/L. The reaction mixture were shaken at constant temperature for 2 hrs and then allowed to equilibrate with intermittent shaking at fixed time intervals. The equilibrium was attained within 5 hrs. At the end of equilibrium period, the contents were centrifuged at 3500 rpm for 30 minutes. The residual concentrations of CR after adsorption were determined spectrophotometrically at 496 nm.The amount of adsorbed CR on metal ferricyanide at equilibrium was calculated based on a mass balance equation as given by equation (1):

$$q_e = (C_o - C_e)V/ W \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Where q_e is the equilibrium capacity per gram dry weight of the adsorbent (mg g^{-1}), C_o and C_e are the initial and equilibrium concentration of CR in the solution, respectively (mg L^{-1}), V is the volume of the solution (L) and W is the dry weight of metal ferricyanide (g).

RESULTS AND DISCUSSION

Characterization of the adsorbent: The general formula of metal ferricyanide as $M_3[Fe(CN)_6]_2 . xH_2O$, where M represents a exchangeable divalent transition metal ion (Cd^{2+}, Ni^{2+}). The typical XRD patterns of cadmium and nickel ferricyanides are shown in Fig. 2,3, respectively. These compounds were found to be simple cubic and the cell edge corresponds to the Fe-C≡N-M-N≡C-Fe chain length. In these structures, both metal centers have octahedral coordination. The iron atom in linked to the C ends of six CN ligands. The outer metal, M has mixed coordination sphere formed by four N ends from the CN group plus two coordinated water molecule $M(NC)_4(OH_2)_2$ **[29]**. We calculated the crystallite size measurement of CdF and NiF were 39.55 nm and 12.99 nm, respectively from their respective XRD patterns according to Scherrer equation (2).

$$D = \frac{K\lambda}{b\,\mathrm{Cos}\theta} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots. (2)$$

The equation uses the reference peak width at angle θ (deg.), where D is the crystallite size (Å), λ is the wavelength of incident X-ray (1.54Å), b is the width of the XRD peak at half height (radian) and K is the shape factor (0.91).

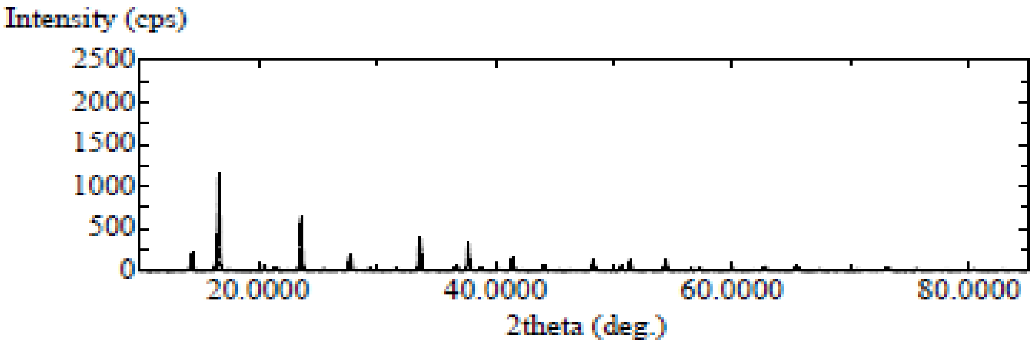


Fig. 2. XRD patterns of cadmium ferricyanide

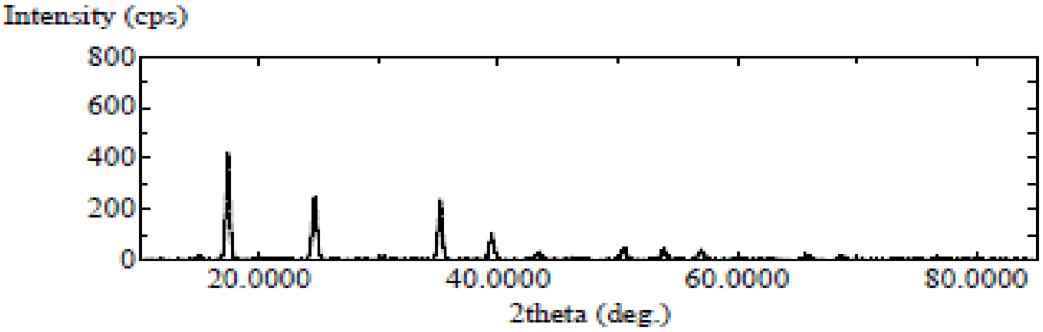
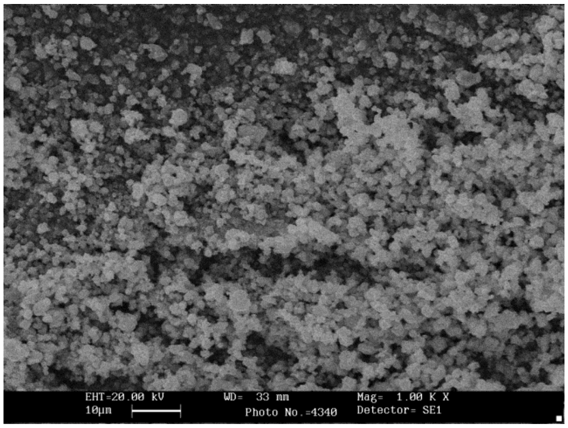
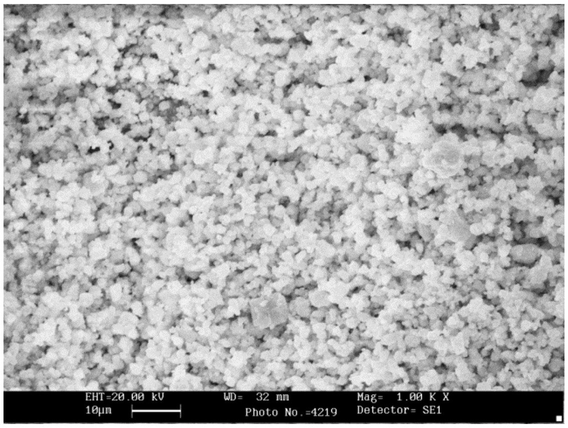


Fig. 3. XRD patterns of nickel ferricyanide

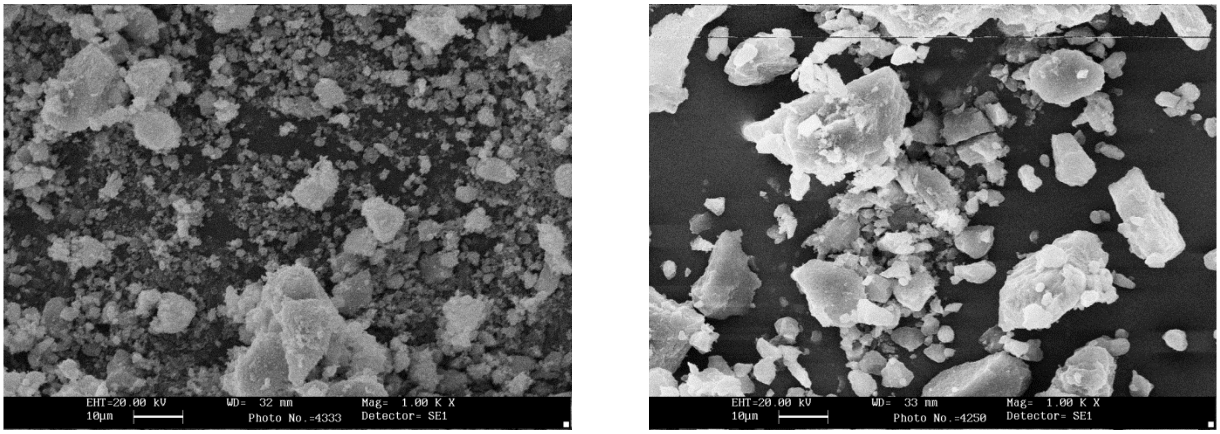
SEM is one of the most widely used surface diagnostic tools. The SEM images of the cadmium and nickel ferricyanides before and after adsorption shown in fig. 4. Figures show that CR molecule adsorbed on the surface of the adsorbent.



Cadmium ferricyanide



CdF-CR



Nickel ferricyanide NiF-CR

Fig. 4. SEM images of cadmium and nickel ferricyanides before and after adsorption

Elemental analysis showed the results: C-15.71%, H-1.35%, N-18.00% in cadmium ferricyanide and C-17.16%, H-2.12%, N-20.14% in nickel ferricyanide, which were in good agreement with cadmium- and nickel ferricyanides formulae.

Thermogravimetric data showed that metal ferricyanide have both coordinated and zeolitic water molecules. Under the material heating the crystal waters evolves below 200˚C (Fig. 5). The mass loss in case of CdF was 16% at below 150˚C , while it was 20% for NiF at below 160˚C of the sample weight, which shows the presence of 8 water molecule per formula unit.

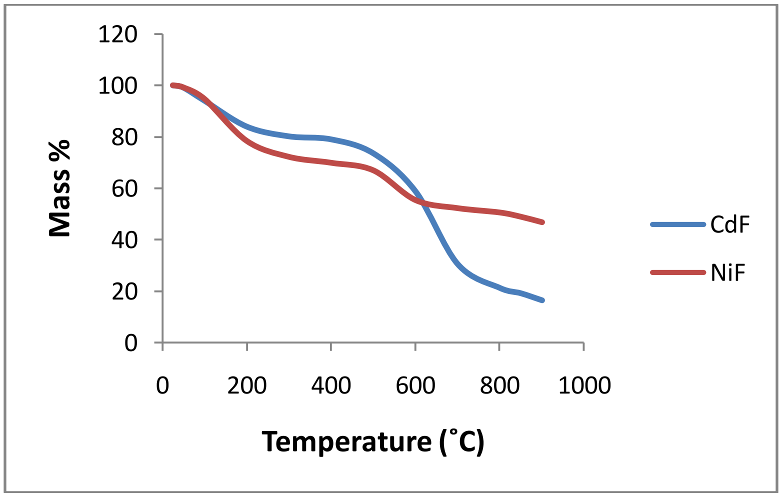


Fig. 5. TGA curve of cadmium and nickel ferricyanides

Metal ferricyanides-CR adducts were washed with distilled water and dried. The infrared spectra for all of the metal ferricyanides before and after adsorption were recorded and analyzed. Results are shown in table 1 and Figs. 6,7. Characteristic bands of metal ferricyanide (ν C≡N, δ Fe-CN and ν Fe-C) do not show any remarkable change after adsorption. This indicates that adsorption of CR on metal ferricyanides were occurred through divalent metal ions (Cd^{2+}, Ni^{2+}) of respective ferricyanides. The hetero atom of the amino group in CR can provide a lone pair of electron for interaction with metal ions.

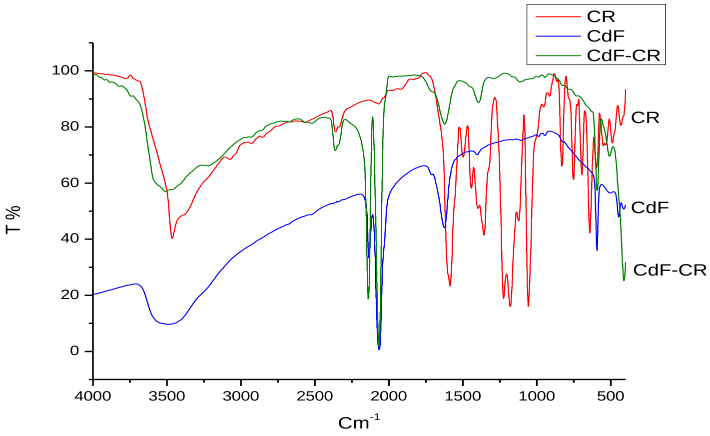


Fig. 6 Infrared spectra of congo red, cadmium ferricyanide and adsorption adduct of CdF-CR

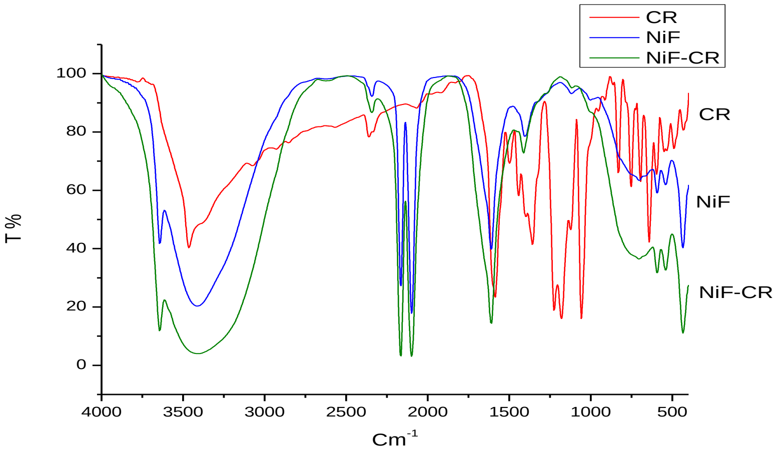


Fig. 7 Infrared spectra of congo red, nickel ferricyanide and adsorption adduct of NiF-CR

Table 1. Infrared spectral frequencies (Cm^{-1}) of metal ferricyanides before and after adsorption

Metal ferricyanide	Metal ferricyanide characteristics Frequency		
	ν C≡N	δ Fe-CN	ν Fe-C
Cadmium ferricyanide	2134, 2065 (2138, 2066)	592 (594)	432 (423)
Nickel ferricyanide	2165, 2098 (2165, 2098)	594, 541 (594, 541)	435 (434)

Note: Values in bracket show the frequencies after adsorption.

Effect of contact time: The effect of contact time on adsorption amount of CR onto metal ferricyanide was examined, taking initial concentration 68.3 mg L^{-1} of CR with 5 g L^{-1} of CdF and NiF at pH 6.9 keeping room temperature. Study was carried out at room temperature. The results are shown in fig. 8. The rate of removal of CR was found to be very rapid during the initial 60 min. onto NiF and 120 min. for CdF, but it declines gradually and reaches equilibrium at around 300 min. No significant change observed after

300 min. The initial rapid phase may be due to the availability of more adsorption vacant sites. As a result, there exists an increased concentration gradient of adsorbate between solution and adsorbent. This can be explained by strong attractive forces between CR and ferricyanide molecule **[30]**.

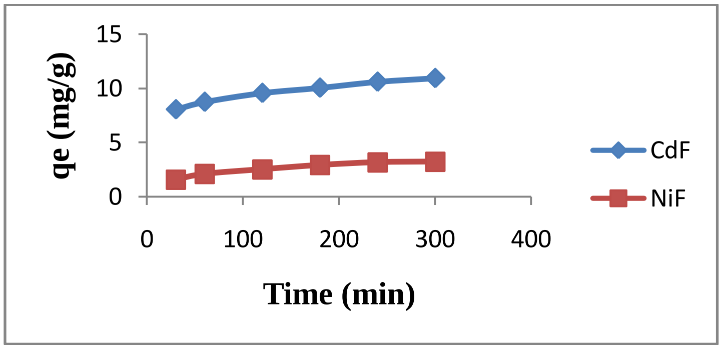


Fig. 8. Effect of contact time on the adsorption of CR on cadmium and nickel ferricyanides

Effect of initial dye concentration: The effect of initial dye concentration was studied under equilibrium conditions varying the initial concentration from 3 to 84 mg L^{-1} at room temperature. Results showed that the adsorption capacity of CR on CdF increased from 0.61 to 13.10 mg g^{-1} (Fig. 9), while in case of NiF, it was increased from 0.35 to 3.4 mg g^{-1} (Fig. 10). This may be due to the fact that an increase in the initial dye concentration leads to an increase in mass gradient between the solution and adsorbent, and thus acts as a driving force for the transfer of dye molecules from bulk solution to the particles surface, which ultimately leads to the higher adsorption.

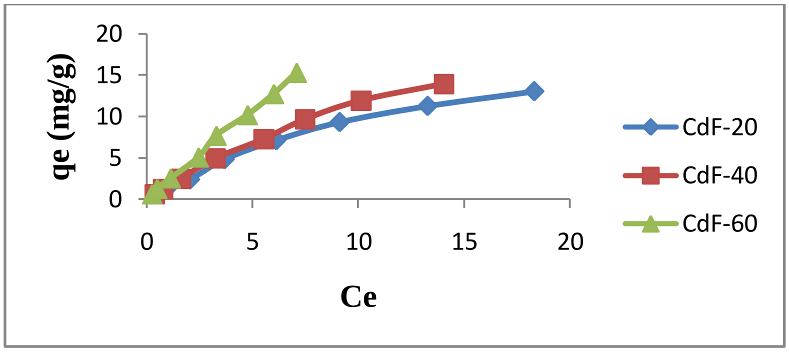


Fig. 9. Adsorption isotherm of CR on CdF at three different temperatures (20˚C, 40˚C and 60˚C)

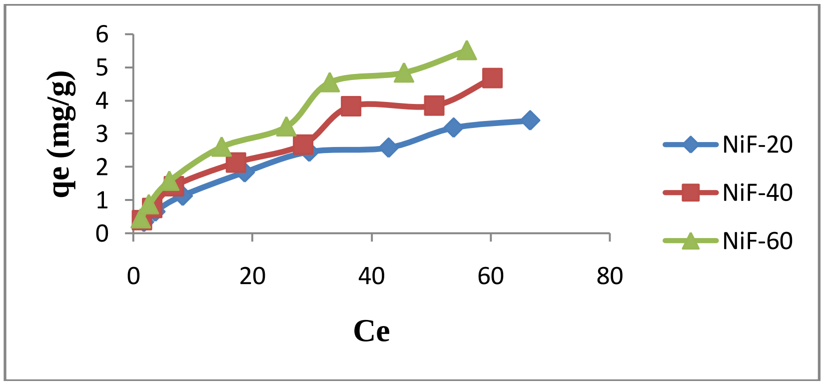


Fig. 10. Adsorption isotherm of CR on NiF at three different temperatures (20˚C, 40˚C and 60˚C)

Effect of temperature: Effect of temperature on adsorption capacity was also studied at three different temperatures (20, 40, 60 ˚C). Results are shown in fig. 9 and 10. Adsorption capacity of CR on both ferricyanides increases with increase in temperature, which indicated endothermic nature of adsorption. This may be due to the fact that increasing the temperature, the rate of diffusion of the CR molecule across the internal pores of the adsorbent particle also increase, owing to the decrease in the viscosity of the solution. Thus the adsorption of dyes is leading to an increase in the residual forces on the surface and hence causing an increase in the surface energy of the adsorbent **[31]**.

Effect of pH: The initial pH of adsorption medium is one of the most important parameters affecting the adsorption process; it controls the electrostatic interactions between the adsorbent and adsorbate. The effect of pH was studied under equilibrium conditions. The pH of the solution was adjusted with either dilute HCl or NaOH before experiment. The initial concentration of CR was 70.4 mg L^{-1} under studied pH range. Fig. 11 shows that, in both the cases, the uptake of CR ions was minimum at pH 7.0 and observed maximum at pH 11.0. However, when the pH of the solution was increase or decrease from pH 7.0, the uptake of CR ions was increased on both metal ferricyanides. This is due to the fact that, a change in pH of the solution results in the formation of different ionic species and different charges on the surface of adsorbents. It was observed that basic solution had given better adsorption results than acidic solution.

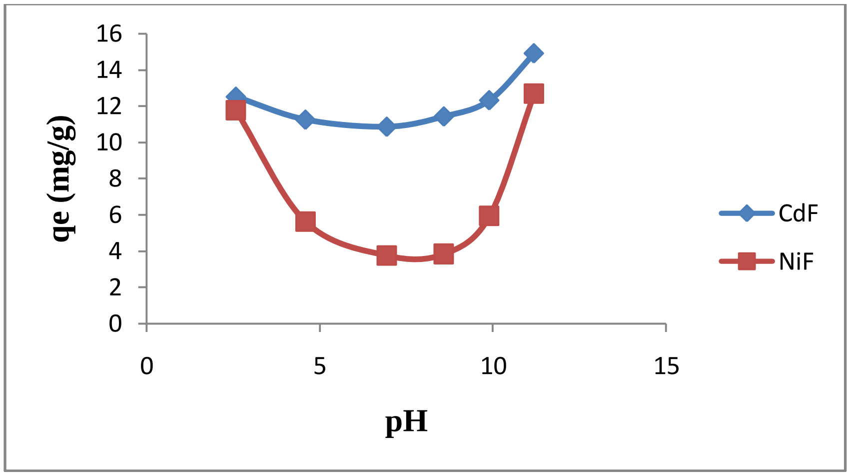


Fig. 11. Effect of pH on the adsorption of CR on Cadmium and nickel ferricyanides

Adsorption isotherm studies: The Langmuir isotherm assumes monolayer adsorption on a uniform surface with a finite number of adsorption sites. Once a site filled, no further adsorption can take place at that site. As such, the surface will eventually reach a saturation point where the maximum adsorption of the surface will be achieved. The Langmuir equation may be written as

$$q_e = q_m K_L C_e / 1+ K_L C_e \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

Or $$1/q_e = (1/ K_L q_m)*(1/ C_e) + 1/ q_m \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$

Where C_e is the equilibrium concentration of the CR in the solution (mg L^{-1}), q_e is the amount of CR adsorbed per unit weight of adsorbent (mg L^{-1}), q_m signifies the maximum adsorption capacity corresponding to complete monolayer coverage on the surface (mg g^{-1}), K_L is the Langmuir constant related to the free energy of adsorption (L/mg). The values of q_m and K_L of linear expression of Langmuir adsorption isotherm were calculated from the intercept and slope of the linear plot of $1/q_e$ versus $1/ C_e$ (Fig. 12), respectively, by using equation (4) with the correlation R^2 are listed in table 2.

The essential features of the Langmuir isotherm can be expressed in terms of a dimensionless constant called separation factor (R_L, also called equilibrium parameter) that is given by the following equation (5).

$$R_L = 1/ (1+ K_L C_o) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5)$$

Where C_o (mg L^{-1}) is the highest initial dye concentration, K_L (L/mg) is Langmuir constant. The value of R_L indicates the shape of isotherms to be either unfavorable ($R_L>1$), linear ($R_L=1$), favorable ($0<R_L<1$) or irreversible (R_L=0). The R_L value for the adsorption of CR onto both CdF and NiF (Table 2) are observed to be in range 0-1, indicating that the adsorption was favorable process.

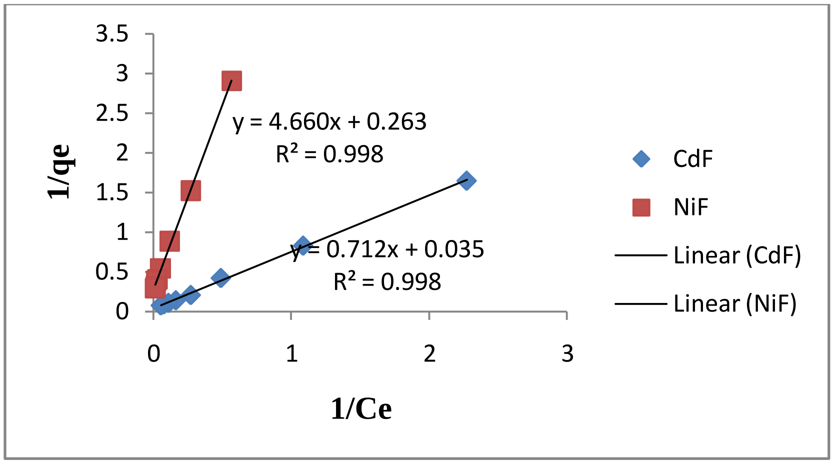


Fig. 12. Langmuir adsorption isotherm for CR with cadmium and nickel ferricyanide

The Freundlich isotherm model can be applied to non-ideal and reversible multilayer adsorption system on heterogeneous surfaces, accompanied by interaction between adsorbed molecules **[4]**. This model is represented by equation (6).

$$q_e = K_F\, C_e^{\ 1/n} \quad \text{...(6)}$$

Where K_F ($mg^{1-1/n}$ $L^{1/n}$ g^{-1}) is the Freundlich constant related to adsorption capacity and n is related to adsorption energy distribution. The linearized form of the Freundlich adsorption isotherm is given by equation (7), obtained by taking logarithms of equation (6).

$$\ln q_e = \ln K_F + 1/n \ln C_e \quad \text{.. (7)}$$

The value of K_F and 1/n were calculated from the intercept and slope of the linear plot of ln q_e versus ln Ce (Fig. 10), respectively and listed with correlation coefficient, R^2 in Table 2. The favorable adsorption of this model can be characterized such that if a value for n (CdF: n=1.179; NiF: n=1.626) is greater than 1, indicating that the adsorption is favorable and physical process **[32]**.

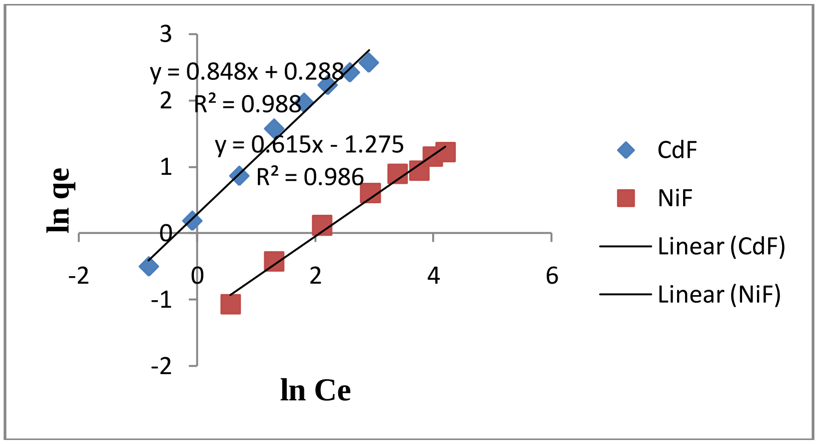


Fig. 12. Freundlich adsorption isotherm for CR with cadmium and nickel ferricyanides

Table 2. Langmuir and Freundlich parameters for the adsorption of CR on metal ferricyanides

Adsorbent	Langmuir isotherm				Freundlich isotherm		
	q_m (mg/g)	K_L (L/mg)	R_L	R^2	K_F ($mg^{1-1/n} L^{1/n} g^{-1}$)	n	R^2
Cadmium ferricyanide	27.93	0.050253	0.192	0.99	1.335	1.179	0.98
Nickel ferricyanide	3.79	0.05648	0.175	0.99	0.2793	1.626	0.98

Thermodynamics study: The value of thermodynamic parameters like free energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS) of the adsorption process at three different temperatures (20, 40, 60˚C) were calculated by using the following equation:

$$\ln K = -\frac{\Delta H}{R}\left(\frac{1}{T}\right) + \frac{\Delta S}{R} \quad \text{-- (8)}$$

$$\Delta G = \Delta H - T\Delta S \quad \text{-- (9)}$$

The values of ΔH (KJ mol^{-1}) and ΔS (J mol^{-1}) can be obtained from the slope and intercept of a linear plot between ln K and 1/T and are listed in Table 3. Where K is the Langmuir constant (L mol^{-1}), T is temperature of the solutions (K) and R is the gas constant (8.314 J mol^{-1} K).

Table 3. Thermodynamic parameters of CR on metal ferricyanides

Adsorbent	Temperature (K)	ΔG (KJ/mol)	ΔH (KJ/mol)	ΔS (J/mol)
Cadmium ferricyanide	293 313 333	-25.57 -27.93 -30.29	9.00	117.62
Nickel ferricyanide	293 313 333	-25.77 -27.79 -29.81	3.87	101.17

Negative values of ΔG indicating the feasibility and spontaneity of the adsorption process. The positive value of ΔS reveals the increased randomness at solid-solution interface during the fixation of the active sites of the ferricyanide. The positive value of ΔH (CdF: ΔH= 9.00; NiF: ΔH= 3.87) indicated the adsorption was endothermic and physical in nature. Physical adsorption and Chemisorption can be classified to certain extent by the magnitude of enthalpy change. It is accepted that bonding strengths of < 80 KJ mol^{-1} are those of physisorption type bonds. Chemisorption bond strength can range from 80 to 400 KJ mol^{-1} **[33]**.

APPLICATIONS

Cadmium and nickel ferricyanides are effective adsorbent for the removal of congo red from aqueous solution at its optimized conditions. It may be also applied for the removal of other dyes which are finding in industrial effluents and these wastewaters may be further used in the industrial process after the purification.

CONCLUSIONS

An effective adsorbent, metal ferricyanide (CdF and NiF) synthesized in the form of fine particles and successfully applied for the removal of CR from aqueous solution. Factors affecting adsorption, such as initial dye concentration, contact time, initial pH and temperature were evaluated. Under the batch conditions equilibrium was attained in 5 hrs and maximum removal of CR was obtained at basic pH, depends upon the formation of different ionic species and different surface charges on the adsorbents during the change in pH. The Langmuir and Freundlich adsorption isotherm model were used for the mathematically description of the adsorption data but the correlation coefficient values showed that the adsorption data better fitted the Langmuir model. Maximum adsorption capacity of CdF and NiF were found to be 27.93 and 3.79 mg/g, respectively. The obtained thermodynamic parameters indicated that the adsorption was spontaneous, feasible and endothermic in nature. The study also proved that the increased randomness at the solid/solution interface. Result show that CdF is better adsorbent than NiF.

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