



## Adsorptive Removal of Alizarin Red-S from Aqueous Solutions by Using Cobalt and Copper Ferricyanides

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### ABSTRACT

*The adsorption behavior of alizarin red-S (ARS) from aqueous solution on cobalt ferricyanide and copper ferricyanide were studied under various conditions of contact time, different pH and temperature varying initial concentration of ARS using batch technique. Prepared metal ferricyanides were characterized by FTIR, CHN analysis, TGA and XRD. Adsorption capacity of alizarin red-S on cobalt ferricyanide and copper ferricyanide was found maximum at pH 4.15. Results were analyzed by Langmuir and Freundlich models of adsorption. The adsorption capacity of cobalt- and copper ferricyanides were increased gradually with an increase in initial concentration of ARS. Copper ferricyanide was found to be a better adsorbent. Thermodynamic data like free energy ( $\Delta G$ ), enthalpy ( $\Delta H$ ) and entropy ( $\Delta S$ ) of the system suggested that adsorption process was spontaneous and physisorption.*

**Keywords:** Metal ferricyanide, alizarin red-S, adsorption isotherm model, thermodynamic parameters.

### INTRODUCTION

Dyes are common constituents of effluents discharged by various industries, particularly the textile industry. The presence of very small amounts of dyes in water is highly visible and undesirable [1-2]. Dyes may significantly affect photosynthetic activity of aquatic life due to reduced light penetration and may also be toxic to some aquatic life due to its complex aromatic molecular structures which make them more stable and difficult to biodegrade. Dyeing effluent has a serious environmental impact causing damage to aquatic biota or humans by mutagenic and carcinogenic effects [1].

Alizarin red S has been extensively employed since ancient times for dyeing textile materials and widely used in woven fabrics, wool, cotton textiles [3-5]. Alizarin red-S (Fig. 1) is an anionic dye (1, 2-dihydroxy-9, 10-anthra-quinone sulfonic acid sodium salt) is a water soluble, widely used anthraquinone dye. It was synthesized by sulfonation of alizarin which is a natural dye obtained from madder (*Rubia tinctorum*, *L. Rubiaceae*). In clinical practices, it is also used to stain synovial fluid to assess for basic calcium phosphate crystals. ARS is the most hazardous dye, responsible for several hazardous effects like skin and eyes irritation when comes in contact and possible cancer hazard. Due to these severe effects, it is compulsory to remove the dye from waste water, which is generated by the industries.

There are various conventional methods of removing dyes including coagulation and flocculation, oxidation or ozonation, membrane separation and biodegradation [6]. However, these methods are not widely used due to their high cost, economic disadvantage and generation of secondary waste. In contrast, an adsorption technique is by far the most versatile and widely used. It has been reported that many different types of adsorbents are effective in the removal of dyes from polluted water [7-12].

Metal ferricyanides are an important class of compounds and have been used as an adsorbent [13]. Although during last few years, experimental studies on catalytic role of cyano complexes have been carried out in our laboratory [14-19]. Literature on interaction of metal ferricyanide with anionic dyes, alizarin red-S is lacking. Hence present paper describes the adsorption of ARS on the cobalt- and copper ferricyanides. The influences of various operating parameters on adsorption, such as effect of pH, initial dye concentration, contact time and temperature were studied. Metal ferricyanides were characterized by TGA, FTIR, SEM, CHN analysis, XRD. The adsorption capacities were evaluated from equilibrium adsorption isotherms by batch technique and thermodynamic parameters were also determined.

## MATERIALS AND METHODS

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

**Preparation of adsorbents:** Synthesis of metal ferricyanide is not new [13, 20-25], but in the present study, attempt was made to bring fine particles of metal ferricyanides ranging from  $\mu\text{m}$  to  $\text{nm}$  size in order to get maximum surface area. Metal salt solution (cobalt chloride/copper sulfate) of concentration 0.3M, 250 mL were added slowly drop wise (4 drops/min) to a solution of potassium ferricyanide (0.2M, 250 mL) with constant stirring on magnetic stirrer at 50-60°C. The reaction mixture was stirred continuously at 60°C for 24 h and kept as such for 24 h at room temperature. After the completion of the reaction, the solid product was filtered and washed several times with distilled water. The final product was dried in an oven at 60°C for 48 h. The dried product was ground to fine mesh and sieved to 100  $\mu\text{m}$  mesh size through the standard sieves. These products were stored in air tight glass bottles for further use in experiments. No other chemical or physical treatments were used prior to adsorption.

**Equipment 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  $\text{Cu K}\alpha$  radiation at scanning rate 2 deg/min 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  $\text{cm}^{-1}$ . To examine the morphological characteristics of the metal ferricyanides before and after adsorption sample viewed using a LEO 435 VF (Leo Electron Microscopy Ltd, England) at acceleration voltage of 20 KV. Thermogravimetric 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 adsorbent done by 2400 series II CHNS/O, Perkin Elmer, USA.

**Adsorbate:** The adsorbate used in present study was alizarin red-S (C.I. No. 58005) obtained from CDH, New Delhi was used as received without any purification. The molecular formula of ARS is  $\text{C}_{14}\text{H}_7\text{NaO}_7\text{S}$  with molecular weight 342.26 g/mol and  $\lambda_{\text{max}} = 424$  nm (measured value). The chemical structure of ARS is shown in Fig. (1). It will attain yellow color at pH lower than 7 and dark pink at pH greater than 9.

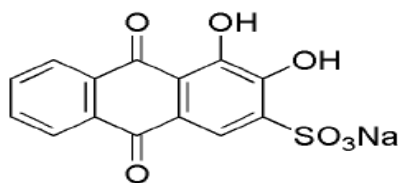


Fig 1. Chemical structure of alizarin red-S

**Adsorption experiments:** The stock solution of ARS was prepared by dissolving the appropriate amount (400 mg) of ARS in a liter of double distilled water. The working solutions were prepared by diluting the stock solution with double distilled water to give the appropriate concentration without adding any buffer to adjust the pH.

The UV-Vis spectrophotometer-119 (Systronic India Ltd.) was used to determine the concentration of ARS dye at maximum absorbance wavelength ( $\lambda_{\max}$ ) of 424 nm. Prior to the analysis a technical calibration curve was plotted between absorbance and concentration of the dye solution and it was very reproducible and linear over the concentration range used in this work.

Adsorption studies were performed by shaking a fixed amount of metal ferricyanide (50 mg) with 10 mL aqueous solution of ARS in 15 mL reaction tubes with stopper. The range of initial concentration of ARS was 18-164 mg L<sup>-1</sup>. The reaction mixture were shaken at constant temperature for 2 h and then allowed to equilibrate with intermittent shaking at fixed time intervals. The equilibrium was attained within 4 h. At the end of equilibrium period, the contents were centrifuged at 3500 rpm for 30 min. The residual concentrations of ARS after adsorption were determined spectrophotometrically at 424 nm.

The amount of adsorbed ARS on metal ferricyanide at equilibrium was calculated based on a mass balance equation as given by equation (1):

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

Where  $q_e$  is the equilibrium capacity per gram dry weight of the adsorbent (mg/g),  $C_o$  and  $C_e$  are the initial and equilibrium concentration of ARS in the solution respectively (mg L<sup>-1</sup>),  $V$  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  $M_3[Fe(CN)_6]_2 \cdot xH_2O$ , where  $M$  represents a exchangeable divalent transition metal ion ( $Co^{2+}$ ,  $Cu^{2+}$ ). The typical XRD patterns of cobalt and copper ferricyanides are shown in fig. 2 and fig. 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  $M(NC)_4(OH_2)_2$  [21]. Crystallite size of CoF and CuF were found to be 8.17 nm and 20.68 nm, respectively from their respective XRD patterns according to Scherrer eqn (2).

$$D = \frac{K\lambda}{b \cos\theta} \dots\dots\dots (2)$$

The equation uses the reference peak width at angle  $\theta$  (deg.), where  $D$  is the crystallite size (Å),  $\lambda$  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).

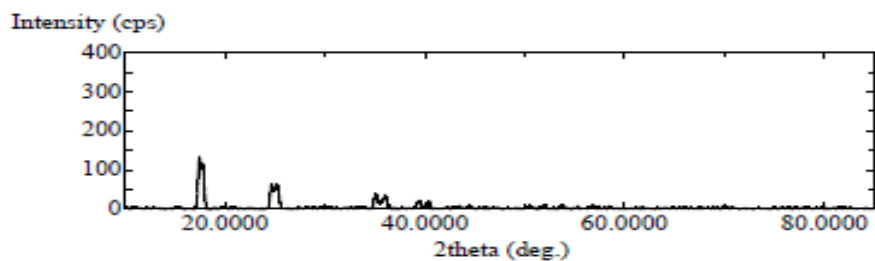


Fig 2. XRD patterns of cobalt ferricyanide

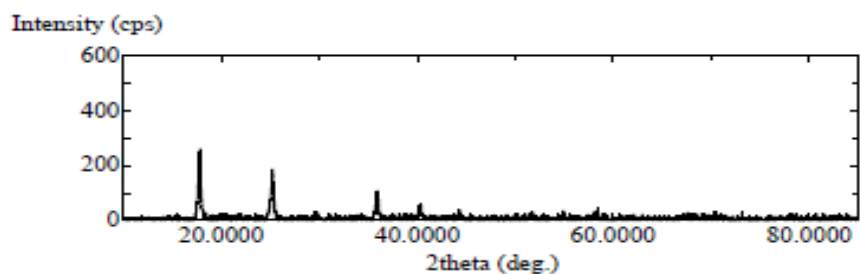


Fig 3. XRD patterns of copper ferricyanide

SEM is one of the most widely used surface diagnostic tools. The SEM micrographs of cobalt and copper ferricyanides before and after adsorption shown in fig 4. Figures show that ARS molecule adsorbed on the surface of the adsorbent.

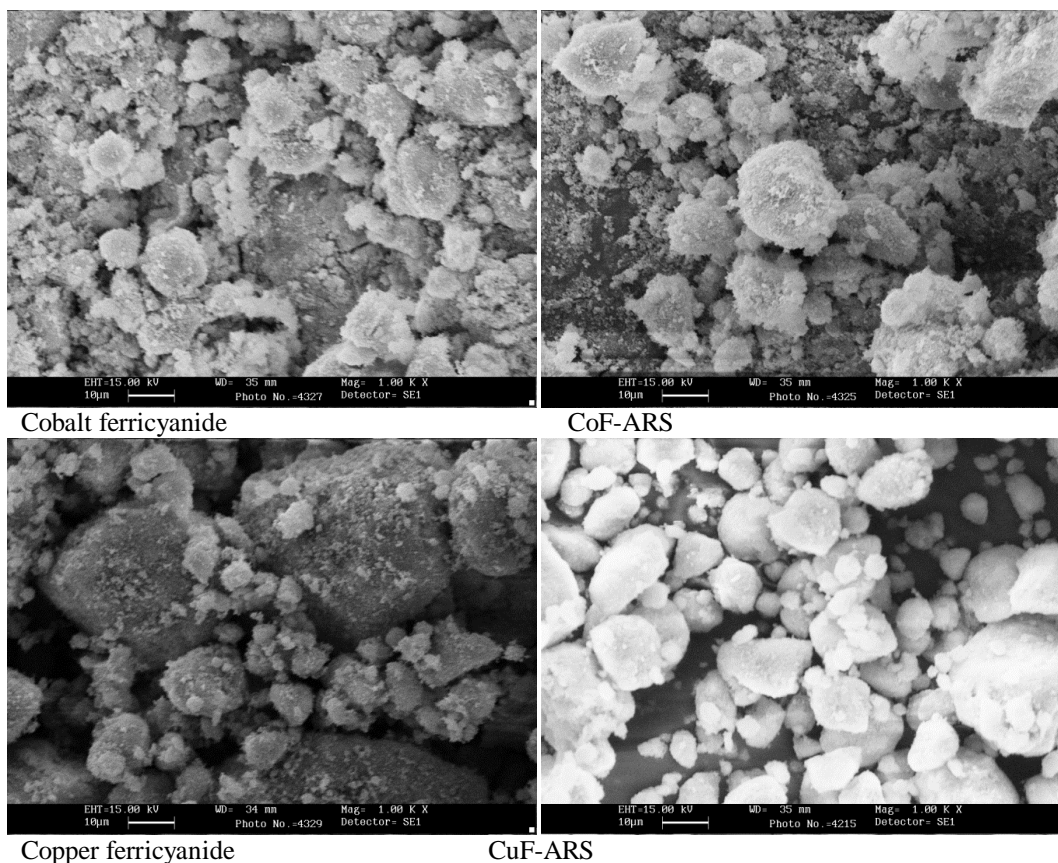


Fig 4. SEM images of cobalt and copper ferricyanides before and after adsorption.

The elemental analysis indicates C-17.48%, H-1.94%, N-21.22% for CoF and C-14.22%, H-1.75%, N-21.09% in case of CuF.

Thermogravimetric data showed that metal ferricyanide have both coordinated and zeolitic water molecules which are weakly bonded and under the material heating the crystal waters evolves below 200°C (fig. 5). The mass loss corresponds to 20% of the sample weight which indicates 8 water molecules per formula unit. Such dehydration process is also related to the porous framework of these materials.

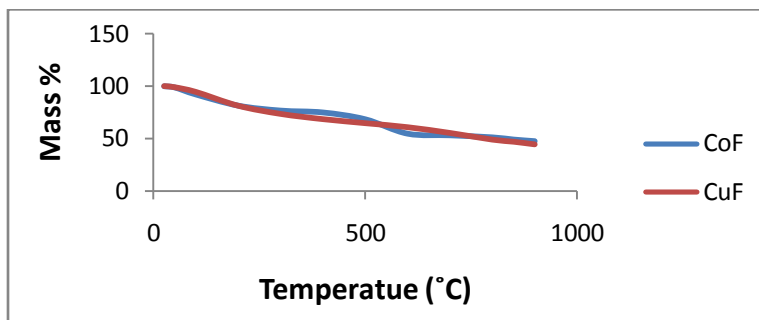


Fig 5. TGA curves of cobalt and copper ferricyanides.

Metal ferricyanides-ARS 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 fig. 6 and fig. 7. Characteristic bands of metal ferricyanide ( $\nu$  C $\equiv$ N,  $\delta$  Fe-CN and  $\nu$  Fe-C) do not show any remarkable change after adsorption. This indicates that adsorption of ARS on metal ferricyanides were occurred through divalent metal ions (Co<sup>2+</sup>, Cu<sup>2+</sup>) of respective metal ferricyanides.

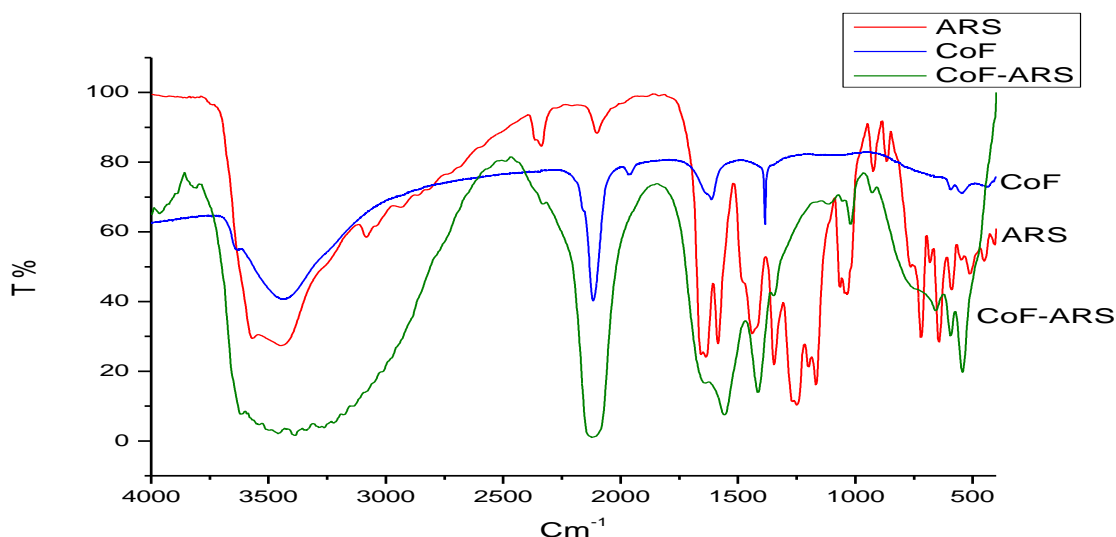


Fig 6. Infrared spectra of alizarin red-S, CoF and adsorption adduct of CoF-ARS.



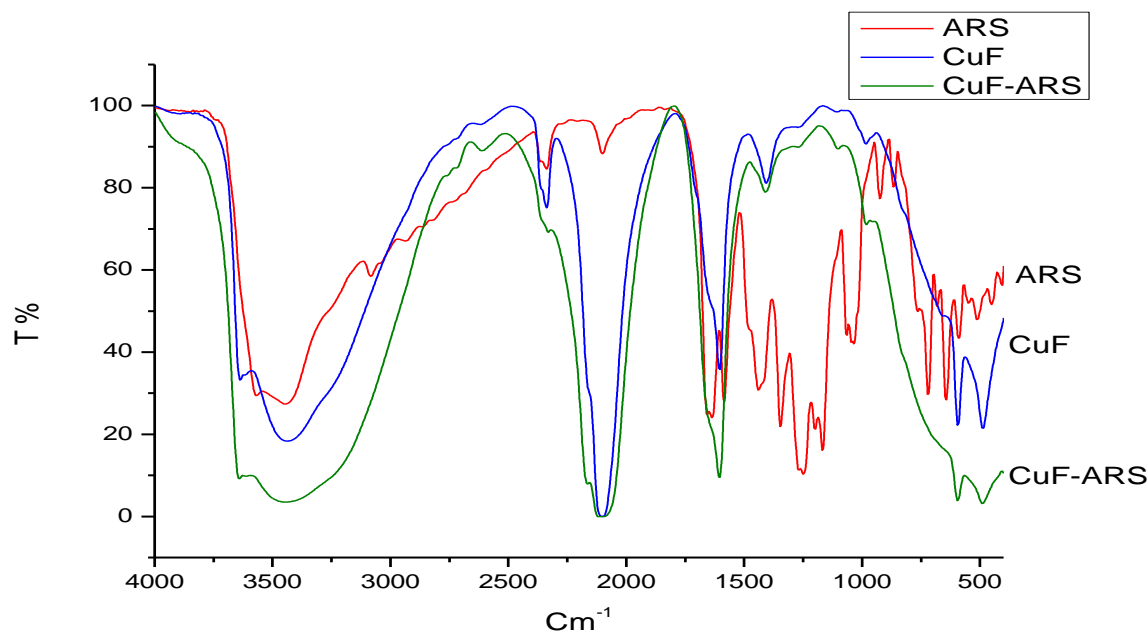


Fig 7. Infrared spectra of alizarin red-S, CuF and adsorption adduct of CuF-ARS.

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

Metal ferricyanide	Metal ferricyanide	characteristics	Frequency
	$\nu \text{C}\equiv\text{N}$	$\delta \text{Fe-CN}$	$\nu \text{Fe-C}$
Cobalt ferricyanide	2114 (2119)	596 (594)	546 (544)
Copper ferricyanide	2100 (2106)	594 (594)	488 (488)

Note: Values in bracket show the frequencies after adsorption.

**Effect of contact time:** The effect of contact time on uptake of anionic dye, ARS onto metal ferricyanide was examined taking initial concentration  $114.5 \text{ mg L}^{-1}$  with  $5 \text{ g L}^{-1}$  CoF and CuF at pH 5.58 keeping room temperature. The results are shown in fig. 8. The adsorption of ARS dye increased with increasing contact time and found rapid increase during the initial 100 min after that slightly increase observed. No significant change observed in the removal of ARS after about 240 min. The initial rapid phase may be due to the availability of more adsorption vacant sites at the initial stage. As a result, there exists an increased concentration gradient of adsorbate between solution and adsorbent. This can be explained by strong attractive forces between ARS molecules and adsorbent and also by the fast diffusion into the interparticle matrix to attain rapid equilibrium [26].

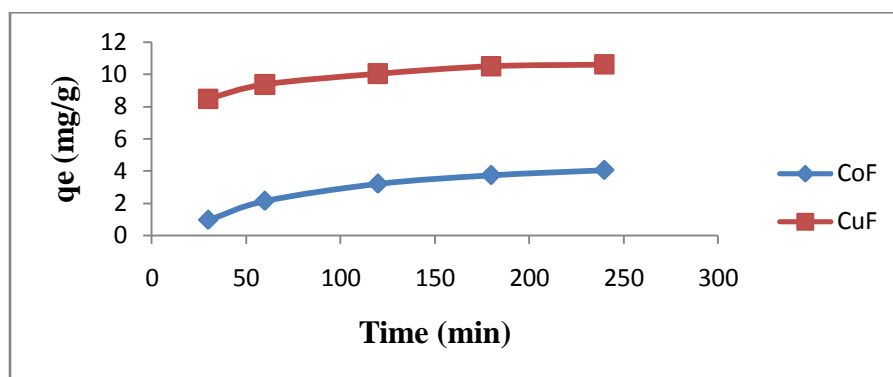


Fig 8. Effect of contact time on the adsorption of ARS on cobalt and copper ferricyanides.

**Effect of initial dye concentration:** The effect of initial dye concentration was investigated under equilibrium conditions at different initial concentration ranging from 18 to 164 mg L<sup>-1</sup>. Results show that the adsorption capacity of ARS on CoF increased from 1.26 to 4.55 mg g<sup>-1</sup> (fig. 9) and adsorption capacity on CuF increased from 1.79 to 14.85 mg g<sup>-1</sup> (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 leads to the higher adsorption.

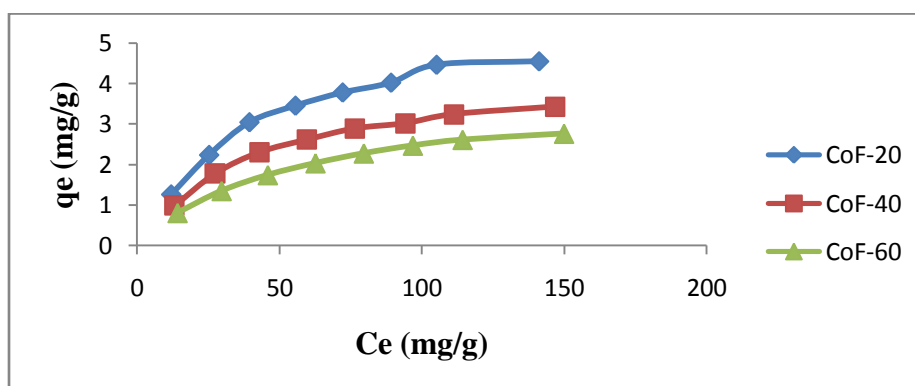


Fig 9. Adsorption isotherm of ARS on CoF at three different temperature (20°C, 40°C and 60°C).

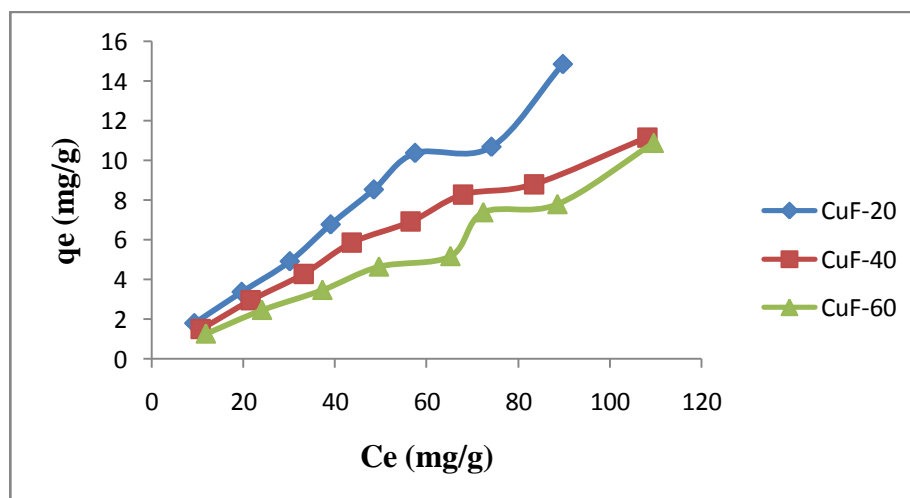


Fig 10. Adsorption isotherm of ARS on CuF at three different temperatures (20°C, 40°C and 60°C).

**Effect of temperature:** To observe the effect of temperature on adsorption capacity, experiments are carried out at three different temperatures (20, 40, 60 °C). The results are shown in fig. 9 and fig. 10. It has been observed that with increase in temperature, adsorption capacity of ARS on CoF and CuF decreases respectively. Since adsorption is an exothermic process. Thus the adsorption of dyes is leading to a decrease in the residual forces on the surface of adsorbent and hence causing a decrease in the surface energy of the adsorbent [27].

**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 experimentation. The pH of the samples were measured by using a digital pH meter (perfit) and calibrated with 4.0 and 9.2 buffers. The initial concentration of ARS 123.12 mg L<sup>-1</sup> and under studied pH range from 2 to 12. Fig. 11 shows that, in both cases, the maximum amount of the dye was adsorbed at a pH of 4.15 and it decreased before and after this pH. This can be explained on the basis of zero point of charge on 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. At higher pH, the metal ferricyanides would have a net negative charge, leading to electrostatic repulsion of dye anions, leads to the lower adsorption.

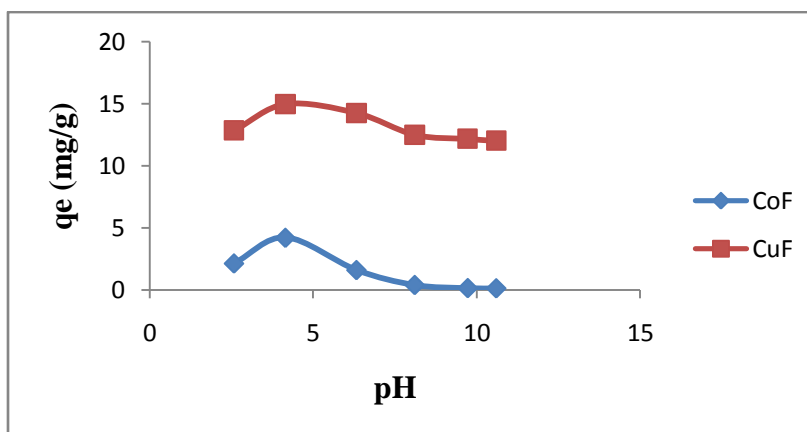


Fig 11. Effect of pH on the adsorption of ARS on cobalt and copper ferricyanides.

**Adsorption isotherm studies:** An adsorption isotherm describes the relationship between the amount of adsorbate that is adsorbed on the adsorbent at constant temperature and its concentration in the equilibrium solution. Equilibrium isotherm studies were carried out with different initial concentration of ARS (18-164 mgL<sup>-1</sup>) at room temperature and pH 5.58. The equilibrium isotherms in this study were analyzed using the Langmuir and Freundlich isotherms.

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

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

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

Where  $C_e$  is the equilibrium concentration of the ARS in the solution (mg L<sup>-1</sup>),  $q_e$  is the amount of ARS adsorbed per unit weight of adsorbed (mg L<sup>-1</sup>),  $q_m$  signifies the maximum adsorption capacity corresponding to complete monolayer coverage on the surface (mg/g),  $K_L$  is the Langmuir constant related to the free energy of adsorption (L mg<sup>-1</sup>). 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 coefficient  $R^2$  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).

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

Where  $C_o$  (mg/L) 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 ARS onto both CoF and CuF (Table 2) are observed to be in range 0-1, indicating that the adsorption was favorable process.

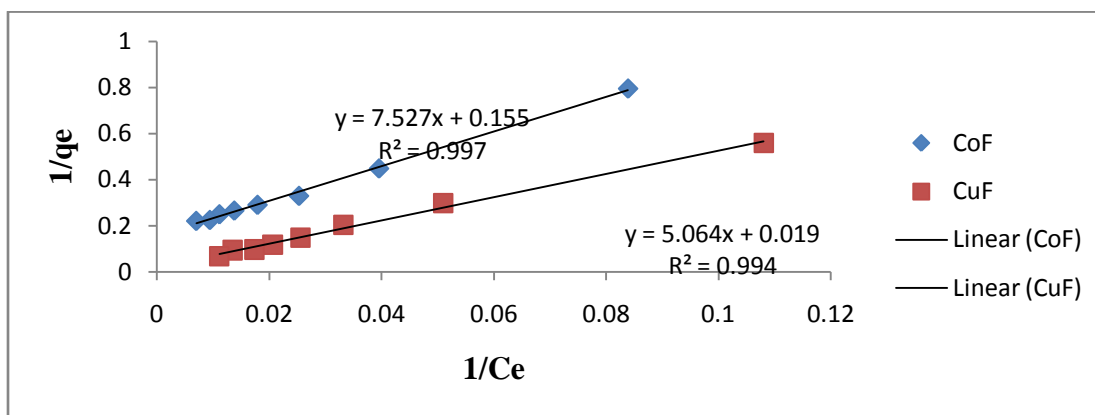


Fig 12. Langmuir adsorption isotherm for ARS with cobalt and copper ferricyanide.

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

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

Where  $K_F$  ( $\text{mg}^{1-1/n} \text{L}^{1/n} \text{g}^{-1}$ ) 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).

$$\ln q_e = \ln K_F + 1/n \ln C_e \quad \dots\dots\dots (7)$$

The value of  $K_F$  and  $1/n$  were calculated from the intercept and slope of the linear plot of  $\ln q_e$  versus  $\ln C_e$  (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  $n$  (CoF:  $n=1.927$ ; CuF:  $n=1.078$ ) is greater than 1, indicating that the adsorption is favorable.

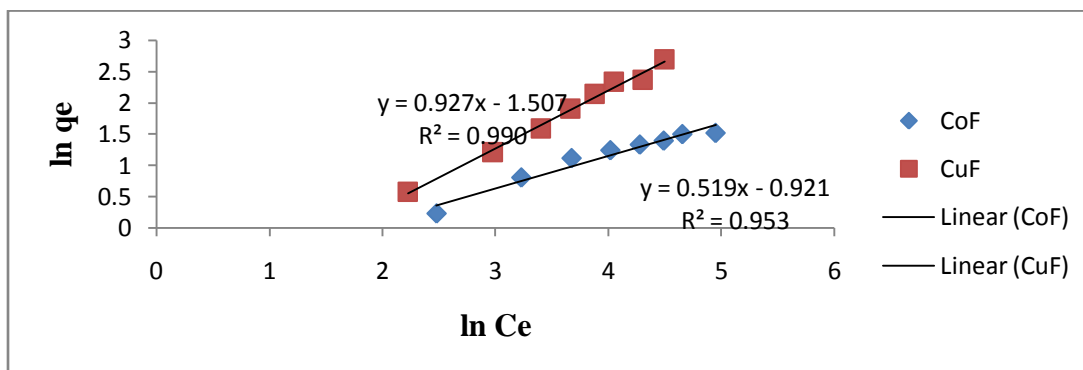


Fig 13. Freundlich adsorption isotherm for ARS with cobalt and copper ferricyanides.

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

Adsorbent	Langmuir isotherm				Freundlich Isotherm		
	q <sub>m</sub> (mg/g)	K <sub>L</sub> (L/mg)	R <sub>L</sub>	R <sup>2</sup>	K <sub>F</sub> (mg <sup>1-1/n</sup> L <sup>1/n</sup> g <sup>-1</sup> )	N	R <sup>2</sup>
Cobalt ferricyanide	50.51	0.00391	0.609	0.99	0.3979	1.927	0.95
Copper ferricyanide	84.75	0.05517	0.218	0.99	0.2215	1.078	0.99

**Thermodynamics study:** The value of thermodynamic parameters like free energy change ( $\Delta G$ ), enthalpy changes ( $\Delta H$ ) and entropy changes ( $\Delta S$ ) 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  $\Delta H$  (KJ/mol) and  $\Delta S$  (J/mol) 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 ( $L \text{ mol}^{-1}$ ),  $T$  is temperature of the solutions (K) and  $R$  is the gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}$ ).

**Table 3.** Thermodynamic parameters of ARS on metal ferricyanides

Adsorbent	Temperature (K)	$\Delta G$ (KJ/mol)	$\Delta H$ (KJ/mol)	$\Delta S$ (J/mol)
Cobalt ferricyanide	293	-21.75	-1.24	69.99
	313	-23.15		
	333	-24.55		
Copper ferricyanide	293	-17.70	-3.49	48.51
	313	-18.67		
	333	-19.64		

As shown in table 3 the negative values of  $\Delta G$  at different temperature indicate the feasibility and the spontaneous nature of the adsorption. The negative value of  $\Delta G$  is increasing with the increase in temperature from 20 to 60°C. Generally, the change in adsorption enthalpy for physisorption is  $< 80 \text{ KJ mol}^{-1}$ , but in chemisorption is between 80 and 400  $\text{KJ mol}^{-1}$  [28]. The negative value of  $\Delta H$  (CoF:  $\Delta H = -1.24$ ; CuF:  $\Delta H = -3.49$ ) reveals the adsorption is exothermic and physical in nature. Furthermore, the positive value of  $\Delta S$  reveals the increased randomness at solid-solution interface during the fixation of the active sites of the metal ferricyanide.

## APPLICATIONS

Dyeing effluent has a serious environmental impact causing damage to aquatic biota or humans by mutagenic and carcinogenic effects. So the present work is more useful for removal of Dye Alizarin red-S from solution by using Synthetic metal ferricyanides as adsorbents.

## CONCLUSIONS

An effective adsorbent, metal ferricyanide (CoF and CuF) synthesized in the form of fine particles and successfully applied for the removal of ARS 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 4 h and maximum removal of ARS for CoF and CuF at a pH of 4.15

and it decreased before and after this pH, depends upon the surface charges corresponds to  $pH_{zpc}$ . The Langmuir and Freundlich adsorption isotherm model were used for the mathematical description of the adsorption data but the correlation coefficient values showed that the adsorption data better fitted the Langmuir model. Maximum adsorption capacity of CoF and CuF were 6.41 and 50.51  $mg\ g^{-1}$ , respectively for the adsorption of ARS. Thermodynamic parameters indicated that the adsorption was exothermic in nature. The study also proved that the increased randomness at the solid/solution interface.

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