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DESIGN OF A NICKEL BASED MIXED-LIGAND COORDINATION COMPOUND FOR REMOVAL OF CONGO RED DYE FROM WATER

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ABSTRACT

Adsorptive uptake of congo red (CR) dye from water by a Ni(II) coordination compound containing carboxylate and N-donor ligands, formulated as [Ni(TDPH)(BPY)] **1**, is herein reported (4,4-bipyridine= BPY; 3,3-thiodipropionate= TDPH). Characterization of the compound was done by Scanning Electron microscopy (SEM), Thermogravimetric analysis (TGA), Infrared spectroscopy (FTIR), and X-ray diffraction (XRD) analysis. Experimental data were subjected to isotherm and kinetics studies, an R^2 value of 0.9953 was obtained for the Langmuir isotherm while the pseudo-second-order model was observed to be best fit for the experimental data with a correlation coefficient value of 0.9918.

Keywords: Coordination compound; Carboxylate; N-donor; Characterization; Langmuir isotherm; Pseudo-second-order model

INTRODUCTION

Coordination chemistry generally concerns itself with interaction of metal cations and ligands. Synthesis of coordination compounds generally involve conventional and non-conventional methods with the advent of new synthetic method recently [1, 2]. One-pot synthesis approach is mostly common in conventional methods which involve reacting both the metal ions and ligand(s) in one vessel by directly mixing solutions of the ligand(s) and metal salts. Conventional hydrothermal or solvothermal approach of heating organic and inorganic reacting precursors suitably dissolved in solvents using closed vessels subjected to autogenous conditions has been widely reported for conventional methods. This has generated coordination polymers having interesting properties such as porosity [3-7]. Experimental conditions of temperature, pressure and reaction time is usually keenly monitored in this approach for the formation of the desired framework structures [5]. Mechanochemistry majorly finds application in the non-conventional methods of synthesis. It mainly involves grinding or milling the mixture of solid reactants (metal salt and ligand). it is also a powerful approach for a rapid and clean environmentally friendly synthesis of coordination compounds and polymers [8]. This method generally avoids bulk

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solvent and limits solution-based occurrences like solvent complexation. Furthermore, molecular self-assembly could be achieved by liquid-assisted grinding approach. Mechanochemical reactions can be achieved easily at ambient temperature free of solvents with the advantage of avoiding organic solvents that can pollute the environment [9-11]. Quantitative yields can also be achieved over a short reaction with possibility of achieving interesting properties such as porosity and high surface area in the synthesized coordination compound/polymer. Coordination compounds have been reported to find applications in numerous processes such as catalysis, environmental remediation, among others [12-16].

To the best of our knowledge, there is no reported information on the synthesis of a Ni(II) coordination compound containing a combination of 4,4-bipyridine and 3,3-thiodipropionate ligands for their use in the uptake of Congo red dye from water.

MATERIALS AND METHOD

Reagents of aanalytical grade were uutilized for this research as received from Sigma Aldrich Co., Germany. CR dye in deionised water solution was employed. SHIMADZU UV-1650 UV-Vis spectrophotometer was used for UV-Visible spec. analysis. FTIR spectroscopy was done on a Nicolet IR Spectrophotometer. PXRD analysis was done using a Rigaku diffractometer. SEM analysis was carried out on a JEOL Scanning Electron Microscope. BET analysis was carried out on a JW-DA:75025 BET Instrument. Thermogravimetric analysis (TGA) was done using a TGA V6.7 Build thermogravimetric analyser.

Synthesis of the [Ni(TDPH)(BPY)] 1

The [Ni(TDPH)(BPY)] compound was synthesized by a refluxing technique [10]. The TDPH, BPY and Ni(II) salt (1 mmol each) were dissolved in ethanol, dimethyformamide (DMF) and methanol respectively, mixed together in a round-bottom flask and refluxed for 2 h at 120 °C. Precipitates formed (light green) were filtered after cooling to room temperature. The residue obtained was washed with a mixture of methanol, ethanol and DMF, dried and stored for analysis.

Adsorption studies

Prior to the uptake of CR dye, **1** was activated in an oven at a 160 ºC for 24 h, cooled and stored. Calibration curve for CR dye uptake experiment was obtained by dissolving 0.25 g of the CR dye in 250 ml of deionized water to obtain 1000 mg/L dye solution. A value of 500 nm was obtained as the λ_{max}. Concentrations of 5 – 30 mg/L were further prepared from the stock solution and their absorbance taken at the λ_{max}. A calibration curve (Fig, 2.1) was thereafter plotted from the absorbance values.

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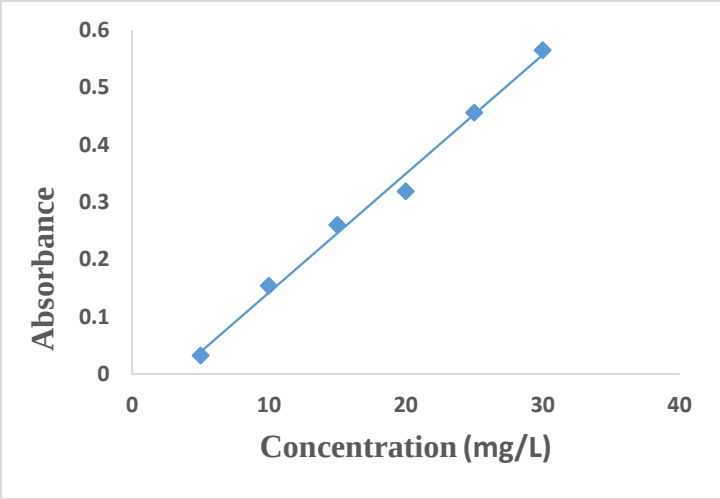

Fig. 1: Calibration curve for CR uptake study

Adsorption experiment was conducted by studying the effect of change in CR dye concentration (5-30 mg/L) using 7 ml of each concentrations with 0.01 g of **1**, effect of contact time using 7 ml CR solution of 25 mg/L in the time range of 1 – 5 h. The pH range of 3 – 13 (adjusted using 0.1 M HCl or 0.1 M NaOH) was utilized to study the effect of change in pH on CR adsorption. Effect of temperature was investigated within the temperature range of 30 - 70 °C. The supernatant of each solutions were obtained after isolating **1** from the CR solutions after each experiments and analysed using a UV-Vis spectrophotometer at a λ_{max} value of 500 nm [11, 16-17]. The amount of CR removed per gram of **1** was obtained using equation 1 while the % removal was calculated using equation 2 [5, 10]:

$$q_e = \frac{(C_o - C_e)V}{W} \quad [1]$$

$$\%\, removal = \frac{(C_o - C_e)}{C_o} X100 \quad [2]$$

Where Co is initial concentration (mg/L) of CR, Ce= equilibrium concentration (mg/L) of CR, V= dye volume (L), W= mass of **1** used (g).

Data obtained were further analysed using isotherm and kinetic models.

RESULTS AND DISCUSSION

Characterization of the Adsorbent

Tests for solubility were carried out on the prepared adsorbent **1** and compared with its starting materials. It was observed that **1** was insoluble in solvents used while the precursors were soluble in solvents tested. In addition, melting point test gave a melting point >400 for the adsorbent.

Spectroscopic analysis of **1**

FTIR spectra **1** taken before and after adsorption showed that there was no change in the spectra of the material after the adsorption experiments (Fig. 2). However, a shift in wavenumber values were mainly observed after adsorption.

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Powder X-ray diffraction analysis

The XRPD patterns of **1** before and after adsorption were compared. The patterns showed similarity in 2Θ values, however a shift to lower 2Θ values were observed for the pattern after adsorption obtained after adsorption of CR dye.

Thermogravimetric analysis

TGA analysis of the adsorbent **1** gave a two stage decomposition pattern at 190 °C with a percentage weight loss of 11.5 % and also at 370 °C with a percentage weight loss of 68.5 % (Fig. 3).

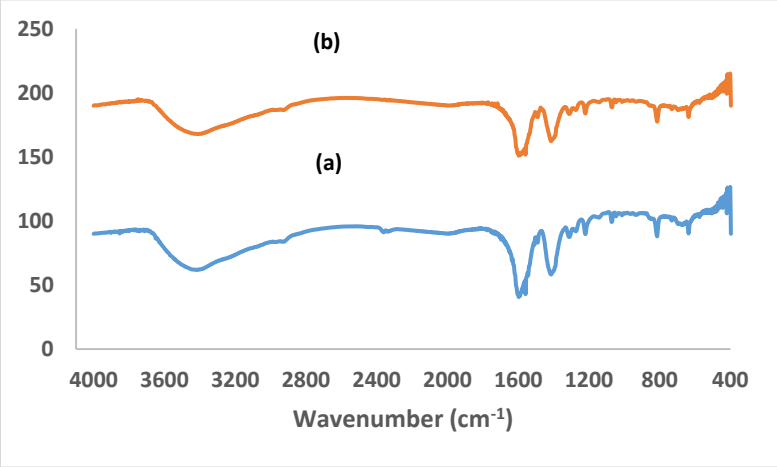

Fig. 2: FTIR Spectra of **1** (a) before adsorption; (b) after adsorption

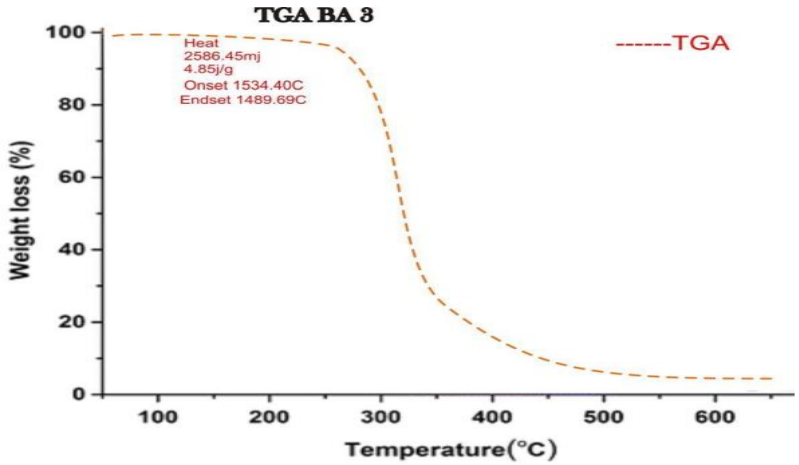

Fig. 3: TGA analysis results

SEM analysis results

SEM images of **1** showed the surface morphology having stick like particles with presence of void between the particles before adsorption of CR dye. However, after the adsorption experiments, SEM images showed the disappearance of these void presumably filled up by the dye molecules (Fig. 4).

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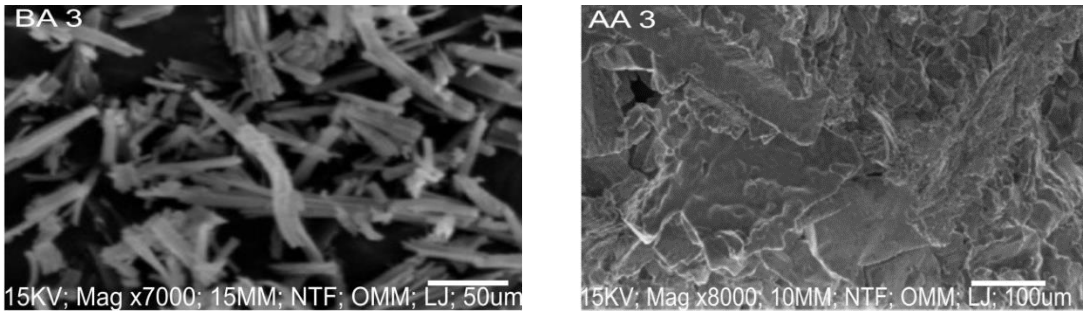
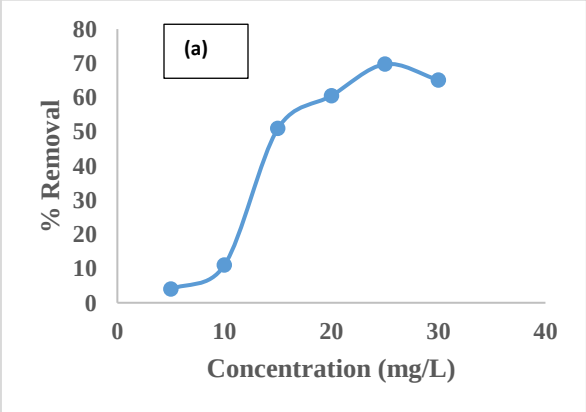
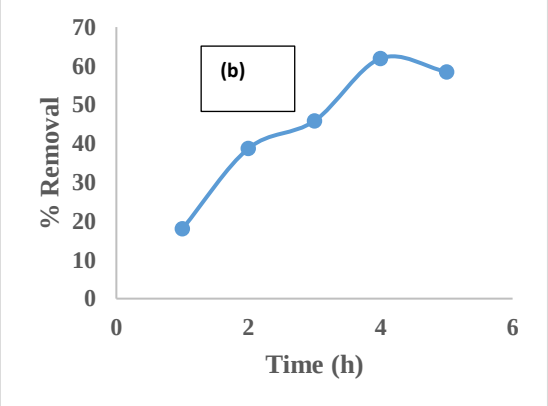


Fig. 4: SEM image of the synthesized compound

Results of Adsorption Studies

The CR dye adsorption experiment using the synthesized adsorbent **1** was investigated under conditions of varying pH, dye concentration, temperature, contact time, and mass of adsorbent [17]. The effect of changing concentration on CR adsorption was investigated using 10 ml each of of 5, 10, 15, 20, 25 and 30 mg/L of dye in the presence of 0.01 g of adsorbent for 2 h. Maximum % removal was observed to be 69.72 % with the 25 mg/L dye concentration (Fig. 5a). This may be attributed to the saturation of the active sites of **1** at a concentration of 25 mg/L leading to reduced adsorption at higher concentrations [16]. By varying the time between 1 – 5 h, it was observed that % removal increased with time up to 4 h before equilibrium was obtained with a removal efficiency of 63.61 % (Fig. 5b). A study of the pH effect on adsorption between within the pH range of 1 – 13 showed a maximum adsorption at pH of 7 with removal efficiency of 90.57 % (Fig. 5c). Increasing temperature was observed to lead to increased adsorption of CR dye (Fig. 5d). This may be attributed to increased kinetic energy attained by the dye molecules leading to increased collision between the molecules of CR and **1** [16, 17].





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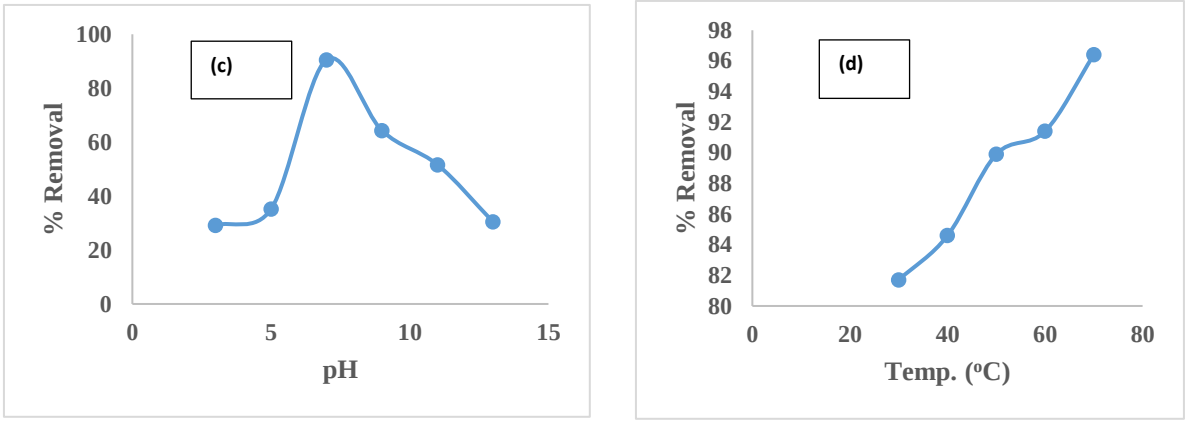
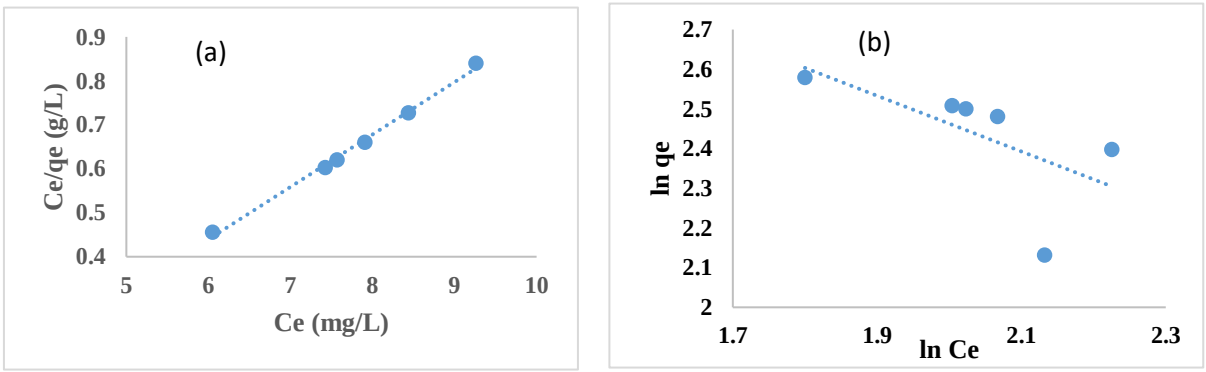


Fig. 5: Effect of (a) initial concentration; (b) time; (c) pH; and (d) temperature on adsorption of CR dye by **1**

The experimental data were subjected to the Langmuir and Freundlich adsorption isotherm models (equations 3 and 4) to understand the mechanism of dye adsorption on **1** [16-18]. The plot of Ce/qe vs Ce (Fig. 6a) for Langmuir isotherm model gave an R^2 value of 0.9953 while a plot of ln qe vs ln Ce (Fig. 6b) for the Freundlich isotherm model gave an R^2 value of 0.4012. Correlation coefficient values obtained indicated the suitability of the Langmuir isotherm model to best explain the adsorption experiment and suggesting monolayer adsorption of CR dye molecules on to **1** [17].



Fig, 6: (a) Langmuir and (b) Freundlich isotherm plots

$$\frac{C_e}{q_e} = \frac{1}{K_L Q_m} + \frac{C_e}{Q_m} \quad [3]$$

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad [4]$$

The rate and mechanism of CR dye uptake by **1** was studied using the pseudo first-order and pseudo second-order kinetic models (equations 5 & 6). The results indicated the experimental data is best explained by pseudo second order model with $R^2 = 0.9918$ suggesting chemical interaction between the adsorbate and the adsorbent [17].

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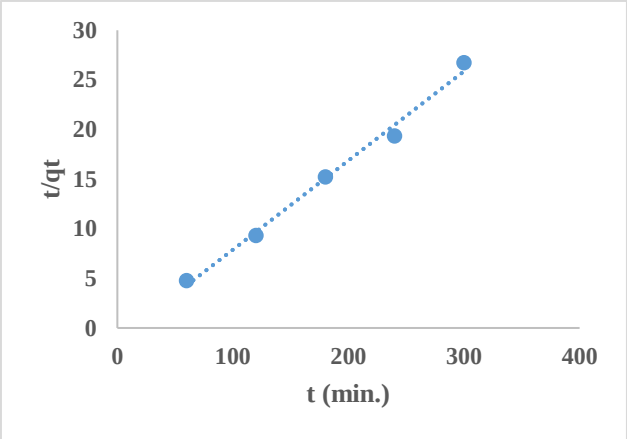

Fig. 7: Pseudo-second-order plot of CR dye uptake by **1**

$$\ln(q_e - q_t) = \ln(q_e) - K_1 t \quad (5)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (6)$$

CONCLUSION

A nickel-based coordination compound formulated as [Ni(TDPH)(BPY)] **1** was synthesized and applied as adsorbent for CR dye removal from water. The process gave an optimum CR dye removal condition of 25 mg/L concentration for 4 h, at a pH of 7. Removal efficiency was observed to increase with increase in temperature and adsorbent dosage. The sorption experimental data was better-fitted to the Langmuir adsorption isotherm model while the pseudo-second order model better explained the kinetics of the experiment. Results obtained from the uptake of CR dye by the synthesized compound **1** showed that it can be a good adsorbent for processes involving removal of water contaminants and waste water treatment.

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