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Ligand exchange used as double-edged sword for the removal of ammonia and dyes from wastewater

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Abstract
Cationic ligand exchange is one of the most predominant mechanisms for the removal of ammonia from wastewater through complex formation. The complexation technique occurs between the metal ions loaded on the surface of Amberlite IR-120 (R-H) and ammonia which is present in medium. Cu(II)-loaded Amberlite IR-120 (R-Cu$^{2+}$) was prepared and described using FT-IR, TGA, XRD, SEM, EDX techniques. The prepared R-Cu$^{2+}$ was applied for elimination of ammonia from aqueous solution. Different cations such as Co$^{2+}$, Ni$^{2+}$ were loaded onto Amberlite IR-120 to study the impact of counter cation on the removal efficiency of ammonia. The ammonia removal percentage followed the order; R-Cu$^{2+}$ > R-Ni$^{2+}$ > R-Co$^{2+}$. The removal of ammonia using R-Cu$^{2+}$ obeyed Freundlich isotherm model. Thermodynamic parameters characteristics of the adsorption of ammonia onto R-Cu$^{2+}$ were determined. The time-adsorption data were followed the pseudo-second-order and intraparticle diffusion models. Moreover, the resulting product (R-Cu(II)-amine composite) from the adsorption process exhibited high catalytic activity and could be applicable as low cost catalyst for enhancement the elimination of dyes from wastewater.

Keywords: Ammonia, Amberlite IR-120, Complexation, R-Cu(II)-amine composite, Dyes, Removal

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1. Introduction

Water is the most indispensable thing for the life on the earth. water contamination is one of the most serious issues facing humans and living organisms over the worldwide due to agricultural activities, industrialization and rapid-growing global population (Elkady, Salama et al. 2020). Ammonia nitrogen (NH$_3$-N) plays an essential role in marine life, it represents a nutrient for plant growth. However, it is the primary pollutant in wastewater, it results from municipal sewage, industrial wastewater and agricultural sources or from the decomposition of organic nitrogen compounds which discharged into water streams (Zhu, Chen et al. 2019). Fertilizers industry, manufacturing of many industrial products such as fibers, explosives, plastics, rubber, pulp, paper, chemicals and pharmaceuticals are considered the major source of ammonia contaminated water (Karri, Sahu et al. 2018).

Large amount of contaminated water that contains high concentrations of NH$_3$-N leak into the surrounding water resources. As a result, serious environmental problems were caused such as the eutrophication of surface water due to algae growth that leads to reduce of dissolved oxygen in water, and toxicity to fish and aquatic life (Adam, Othman et al. 2019, Zhu, Chen et al. 2019).

According to the World Health Organization (WHO) and the U.S. environmental protection agency (EPA), the level of NH$_3$-N in surface water more than 10 mg N L$^{-1}$ is more dangerous to human health and other aquatic organisms’ life (Liu, Chen et al. 2018). However, the maximum concentration of NH$_3$-N in drinking water and in natural water should be 1.5 mg N L$^{-1}$ and 0.2 mg L$^{-1}$, respectively.

Nowadays, with increasing toxic effect of NH$_3$-N on human health and aquatic organisms, the removal of NH$_3$-N from wastewater is the main task. NH$_3$-N They include chemical precipitation (Han, Butterly et al. 2021), photocatalytic oxidation (Yu, Yu et al. 2021), air stripping, break-point chlorination (Zhang, Yin et al. 2022), biological method such as nitrification and denitrification (Adam, Othman et al. 2019), membrane filtration (Rohani, Yusoff et al. 2021), reverse osmosis (Gui, Mai et al. 2020), adsorption (Vocciante, De Folly D'Auris et al. 2018), ion exchange and others (Qin, Zhu et al. 2020). Specifically, ion exchange and adsorption technique are regarded a better choice for treatment NH$_3$-N contaminated wastewater. This is due to high removal efficiency, ease of application and operation. Moreover, the adsorbents should be effectively low cost, environmentally friendly, practicable alternative properties and

Large number of adsorbents applied for removal of NH$_3$-N from wastewater, among of these adsorbents various type of zeolites (Peng, Chai et al. 2017), clays, bentonite (Cheng, Zhu et al. 2019), fly ash (Tang, Xu et al. 2020), activated carbon (Ghany, Ahmed et al. 2017) and synthetic organic resin (Han, Butterly et al. 2021). However, these conventional adsorbents have low adsorption capacity and required secondary physical and chemical treatments that increase the adsorption operation costs (Chen, Zhou et al. 2017). The existence of other competing ions such as (Na$^+$, K$^+$, Ca$^{2+}$) reduce the selectivity of imitative ion exchange resins, the maximum adsorption capacity ($q_{\text{max}}$) of zeolite for removal of NH$_4^+$ is 1.54 mol kg$^{-1}$, while in the presence of Na$^+$ removal efficiency decreased from 90% to 36% (Jiang, Minami et al. 2018).

Ligand exchange technology was suggested to enhance the removal efficiency of NH$_3$-N by ion exchange resins (Chen, Zhou et al. 2017). Cation exchange resin was loaded with metal ion, which formed complex with the polluted substance. The term "ligand exchange" was suggested by Helfferich in 1962, who studied the selectivity of the ion exchanger toward ammonium ion (Chen, Zhou et al. 2017).

The removal of NH$_3$-N from wastewater by ligand exchange reactions can be represented as the following (Chen, Zhou et al. 2017):

$$R_2[\text{Cu(H}_2\text{O)}_4]^{2+} + 4\text{NH}_3(\text{aq}) \rightleftharpoons R_2[\text{Cu(NH}_3)_4]^{2+} + 4\text{H}_2\text{O}$$

(1)

Where R denotes the cation exchange resin such as Amberlite IR-120.

Several transition metals such as Cu$^{2+}$, Ni$^{2+}$, Co$^{2+}$ and Zn$^{2+}$ were loaded onto cation exchange resin served as a ligand exchanger (Chen, Zhou et al. 2017, Chen, Chen et al. 2019). There is an electrostatic interaction between active group of ion exchange resin and metal ions. A complex between the metal ion and NH$_3$-N was formed and NH$_3$-N replaced the aqua molecule in the solvation shell of metal (Clark and Tarpeh 2020).

There are several studies showed that NH$_3$-N removal from wastewater using titanate by cation exchange process (Zhang, Wang et al. 2021). Chen Yan et al used Zn(II)-supported on poly ligand exchange resin for the removal of NH$_3$-N from wastewater (Chen, Chen et al. 2019). It was also removed by high silica zeolite granules regenerated with ozone (Doekhi-Bennani, Leilabady et al. 2021) and manganese oxides (MnOs) (Zhang, Wang et al. 2020). Moreover, Iron oxide nanoparticles dispersed on zeolite by
green synthesis was utilized for the removal of NH$_3$-N from aqueous solution (Xu, Li et al. 2020).

Strongly cation exchange resins such as Amberlite IR-120 (R-H) used as adsorbent for removal of NH$_3$-N from wastewater. R-H is sulfonated polystyrene cross-linked with divinylbenzene (Alguacil 2019). It is characteristics by gel form of active site strongly cationic sulfonated group, which plays an essential role in the separation of charged species from aqueous solution. It has thermal stability about 120 °C, high surface area, non-toxic, its total exchange capacity 2 meq/mL, particle size 0.6-0.8 mm (16-45 mesh), and moisture content 45–50 % (Meshram, Sahu et al. 2012, Alguacil 2019).

So, in this work, the removal of NH$_3$-N from wastewater by ligand exchange technique was studied. R-H was loaded with Cu(II) ions, (R-Cu$^{2+}$), and used for the removal of NH$_3$-N from wastewater via the complexation. Afterward, the loaded R-H with copper ammonia complex was applied as a catalyst for the oxidative decolorization of some organic polluted dyes. Therefore, ligand exchange resin has a dual role for consecutive removal of NH$_3$-N and dyes from wastewater.

2. Experimental
2.1. Materials

Strongly acidic exchange resin, Amberlite IR-120 (R-H) was purchased from Fluka chemie AG, CH-9470 Buchs which was packed in Switzerland. Thymol (5-Methyl-2-isopropylphenol) and sodium nitroprusside dihydrate (pentacyano nitrosyl ferrate II) were purchased from LANXESS AG 50569 cologne (Germany) and used without further purification. Ammonium hydroxide (36 %), sodium hypochlorite (4-5%), acetic acid (99%) were obtained from ADWIC (Egypt). Phosphoric acid (99%) and hydrochloric acid (30%) were purchased from SDFCL (India). Sodium hydroxide, sodium carbonate, sodium hydrogen carbonate, boric acid, cobalt (II) chloride, nickel (II) chloride and copper sulphate were obtained from Sigma-Aldrich. Hydrogen peroxide (50%, as an oxidant) was obtained from Merck (Germany), and potassium permanganate was used to determine its initial concentration (Leonard 1990). Aniline blue (AB), methyl green (MG) and Methyl violet 2B (MV 2B) were purchased from Sigma-Aldrich.

2.2. Instrumental Measurements

The UV/Vis measurements were carried out on a high-performance double beam SPECORD 210 PLUS spectrophotometer with an electronic temperature controller
(Analytic jena, Germany). AD1030 pH-temperature bench meter was used to adjust pH
(Adwa, Hungary). Water shaker thermostat (Julabo D-7633 Seelbach, Germany) was
used to shake the mixtures during the adsorption process. The concentration of metals
was determined by inductively coupled plasma emission spectroscopy (ICP-
OES) Optima 7000 DV with double monochromator and a simultaneous CCD array
detector (Perkin Elmer, USA). The thermogravimetric analysis (TGA) was recorded on
Shimadzu TG-50 thermal analyzer (Japan) from 30 °C up to 800 °C with scanning rate
of 10 °C min⁻¹ under N₂. FT-IR analysis was performed using JASCO FT-IR-4100
(Japan) within the wavenumber range of 4000-400 cm⁻¹. To confirm the structure of the
adsorbent, powder X-ray diffraction (XRD) with GNR, APD 2000 PRO diffractometer
(Italy) was used. X-ray radiation with Cu-Kα (λ = 1.5405 Å) and operated at 40 kV and
30 mA was directed to the samples. The diffraction patterns were measured within the
scanning range of (4–50°)2θ with a step size 0.03°. Scanning electron microscope
(SEM) measurements were performed with (QUANTA FEG250 microscope). The
energy dispersive X-ray spectroscopy (EDX) analysis was investigated using IT100LA
operating at an accelerating voltage of 20.00 keV attached to an SEM device.

2.3. Preparation of metal ions supported on ligand exchange resin (R-M²⁺)
An appropriate amount of R-H was washed repeatedly with distilled water to remove
any fine particles and non-adhesive impurities, then filtrated and air-dried before used.
It was regenerated with (0.1 M HCl) to increase the capacity of the exchanger and then
was washed with distilled water to remove excess of Cl⁻ ions which was detected by
AgNO₃ test and dried at room temperature for overnight (Salem 2001).
25 g of R-H was dispersed and saturated with 500 ml of CuSO₄ solution (0.5 M). This
mixture was magnetically stirred for 24 h to achieve the equilibrium state and the resin
was converted to Cu²⁺-form. Afterwards, it was filtered and washed thoroughly with
distilled water until the filtrated solution became colorless. The R-Cu²⁺ product was
dried in an oven at 50 °C for 12 h. The loaded amount of Cu (II) ions onto the resin was
determined by measuring the concentration of copper ions before and after loading
process using ICP spectroscopy (Chen, Chen et al. 2019). R-Ni³⁺ and R-Co²⁺ were
similarly prepared using the same circumstances procedure for R-Cu²⁺.

2.4. Batch equilibrium measurements
To investigate the adsorption capacity of cationic ligand exchange resin (R-M²⁺) for the
removal of NH₃-N from aqueous solution. A fixed amount of R-M²⁺ (0.1 g) was added
into a series of Erlenmeyer conical-flasks (100 mL) with stoppers that contain a certain
volume of distilled water (19 mL). A definite volume (1 mL) of ammonia solution (3395 mg/L) was taken by micropipette then added to each flask and all of these flasks were immediately shaken at 130 rpm in shaker water thermostat at controlled temperature 30 ± 0.2 °C for given period. The adsorption capacities of (R-M²⁺) at different time intervals was defined by determining the concentration of NH₃-N that is free in the solution. The concentration of NH₃-N was determined using indothymol blue method by UV/Vis spectrometer (SPECORD 200 PLUS) (Zamora-Garcia, Correa-Tome et al. 2021).

The removal efficiency percentage, R(%) and the adsorption capacity at time t, qₜ (mg/g) of NH₃-N solution onto R-M²⁺ at different time were estimated using Equs. 2 and 3.

\[ R(\%) = \frac{C_o - C_t}{C_o} \times 100 \]  \hspace{1cm} (2)

\[ q_t = \frac{(C_o - C_t) \times V}{m} \]  \hspace{1cm} (3)

Where \( C_o \) represents the initial concentration of NH₃-N (mg/L), \( C_t \) represents the non-adsorbed concentration of NH₃-N, V is the volume of solution (L), and m (g) is the mass of adsorbent.

For R-Cu²⁺ as an adsorbent, the influence of temperature on NH₃-N uptake was performed at 20, 30 and 40 °C ± 0.2 °C, respectively using fixed initial NH₃-N concentration and amount of R-Cu²⁺ (0.1 g). Universal buffers of pH range from 2 to 12 were utilized to know the impact of pH in the removal efficiency of NH₃-N.

2.5. Catalytic oxidation of dyes

The recovery and reusability of R/Cu(II)-amine composite after washing with distilled water several times and drying in oven at 50 °C for 12 h were studied. It was used for catalytic decolorization of different types of dyes by the oxidation process. The stock solutions (1 x 10⁻³ mol L⁻¹) of AB, (5 x 10⁻⁴ mol L⁻¹) of MG, and (2.4 x 10⁻³ mol L⁻¹) of MV2B dyes were prepared. The optimum reaction mixture was set up in a 100 mL Erlenmeyer flask, which containing known concentration of mixture of the dye and appropriate concentration of H₂O₂ solution. The flasks were put in a water shaker thermostat at 30 °C ± 1 °C and agitated at 120 rpm for a given period. A specific amount of R-Cu (II) amine composite (0.05 g) was added, and the change of the absorbance of each dye solution was determined with time.

The decolorization efficiency was determined using Equ. 4.
Removal efficiency (%) = \frac{A_o - A_t}{A_o} \times 100 \quad (4)

Where, \( A_o \) is the initial absorbance of dye (at time 0) and \( A_t \) is the absorbance at time \( t \) (min).

3. Results and discussion

3.1. Loading of metal ions on R-H

R-H was loaded with different amounts of copper (II), nickel (II) and Co (II) as measured by ICP spectroscopy. It was found that 1g of R-H has been loaded with 245.6 mg L\(^{-1}\), 52.8 mg L\(^{-1}\), and 10 mg L\(^{-1}\) of copper (II), nickel (II) and Co (II), respectively. This can be attributed to the selectivity of the sulfonate (-SO\(_3\)H) functional group of R-H towards loaded metal ions. It was written that this selectivity increases with increasing the atomic size of metal ions (Chandrasekara and Pashley 2015). The ionic radius of three metals decreases according to the order Cu(II) > Ni(II) > Co(II). As a result, the highest loaded amount on R-H was found for Cu(II).

3.2. Characterization

3.2.1. FT-IR

The FTIR spectra of R-H, R-Cu\(^{2+}\) and R-Cu\(^{2+}\) after adsorption of NH\(_3\)-N (R/Cu(II)-amine composite) are shown in Fig. 1(a). For parent R-H, there is a stretching vibration of O–H groups which originated from H\(_2\)O molecule due to moisture are shown around 3434 cm\(^{-1}\). The peaks at 2920 cm\(^{-1}\) are corresponded to the symmetric and asymmetric C–H stretching vibration of C–H and –CH\(_2\) groups, the peaks observed at 2370 cm\(^{-1}\) is due to O–H stretching mode that is originated from the polymer (Singare, Lokhande et al. 2011). The band at 1637 cm\(^{-1}\) indicates C=C stretching vibration of aromatic rings, stretching vibration of O–S–O group of sulfonic acid was recorded at 1388 cm\(^{-1}\) and the peaks observed at 1170 cm\(^{-1}\) and 999 cm\(^{-1}\) are represented to symmetric stretching of –SO\(_3\) group (Prekob, Hajdu et al. 2019). The band at 835 cm\(^{-1}\) represented bending C–H out-of-plane deformation of the aromatic ring and at 679 cm\(^{-1}\) attributed to –SO\(_3\)H groups (Ghosh, Dhole et al. 2015). The stretching –OH peak at 3434 cm\(^{-1}\) was shifted to 3460 cm\(^{-1}\) and 3468 cm\(^{-1}\) according to (R-Cu\(^{2+}\)) and R/Cu(II)-amine composite, respectively. The intensity of C=C was strengthened in case of (R-Cu\(^{2+}\)) and (R/Cu(II)-amine composite). The change in the intensity of peaks at 1172 cm\(^{-1}\), 1036 cm\(^{-1}\) and 833 cm\(^{-1}\) due to the complex formation between Cu (II) ion and –SO\(_3\)H groups (Jha, Van Nguyen et al. 2009). After the complexation of ammonia with Cu\(^{2+}\), the peak of SO\(_2\) group further shifted from 1388 cm\(^{-1}\) to 1401 cm\(^{-1}\) and a new band appeared at 517 cm\(^{-1}\).
due to the stretching vibration of N–Cu which confirm the complex formation between Cu (II) ion and ammonia in solution (Chen, Chen et al. 2019).

3.2.2. XRD analysis

Figure 1(b) presents that the X-ray diffractogram of R-H which has a narrow diffuse peak in the spectrum, indicating that it is amorphous in nature (Yousef and Malika 2020). In case of R-Cu\(^{2+}\), the main peak of Amberlite IR-120 (\(2\theta = 18.6^\circ\)) was shifted to lower value (\(2\theta = 15.6^\circ\)) due to the loading of Cu\(^{2+}\) on the surface of Amberlite IR-120 (Manivannan, Starvin et al. 2010). A new peak was appeared at (\(2\theta = 23.3^\circ\)) due to the complexation between Cu\(^{2+}\) and ammonia in solution with keeping the amorphous nature of R-H.

3.2.3. TGA

Thermal stability of R/Cu(II)-amine composite was investigated via TGA technique as displayed in Fig. 1(c). The thermogram of R/Cu(II)-amine composite demonstrated that the total loss of weight of about 93.08 % in three separate steps. The first step showed about 19.42 % loss of weight at the temperature range of 28-100 °C. This is attributed to the evaporation of adsorbed water molecules from the surface. The second step represents the complete decomposition of amino ligand in the complex of Cu (II)–amine with a weight loss of 9.677 % in the range of 100–295 °C (Jeslin Kanaga Inba, Anmaraj et al. 2013). The last weight loss step was noted above 295 °C with 63.96 % degradation. This corresponds to the degradation of organic polymer of R-H leaving thermally stable metal oxide as a residue (Singare, Lokhande et al. 2011).

3.2.4. SEM

The surface morphology of R-H, R-Cu\(^{2+}\), and R/Cu(II)-amine complex was investigated by SEM, Fig. 2(a, b, c). The surface of pure R-H is a plane spherical structure. But in the case of R-Cu\(^{2+}\), it was observed that some grains have generated on its surface which indicates the impregnation of R-H with Cu\(^{2+}\) (Singare, Lokhande et al. 2011). Also, the grain species turned to be a coarse coating at the surface of R/Cu(II)-amine composite which indicated the complex formation between ammonia and the Cu\(^{2+}\) ions at the surface of R-Cu\(^{2+}\).

3.2.5. EDX

The adsorption of ammonium ions on the surface of R-Cu\(^{2+}\) was confirmed by EDX measurement. Figure 2(d) presents the EDX spectra of R/Cu(II)-amine composite. EDX
composition analysis for R/Cu(II)-amine complex indicate the presence of C, N, O, S, and Cu elements, Table (1).

3.3. Kinetics of NH$_3$-N removal by metal ions supported on ligand exchange resin (R-M$^{n+}$)

A comparison study between the removal efficiency of NH$_4^+$ using R-Cu$^{2+}$, R-Ni$^{2+}$, and R-Co$^{2+}$, at the same initial concentration of NH$_4^+$ was carried out. It was found that the uptake amount of NH$_4^+$ by R-Cu$^{2+}$ ($q_e = 200$ mg/g) more than that by R-Ni$^{2+}$ ($q_e = 158.55$ mg/g) and by R-Co$^{2+}$ ($q_e = 143.18$ mg/g), as shown in Fig. 3(b). The highest removal efficiency in the case of R-Cu$^{2+}$ can be attributed to the highest loaded concentration of Cu$^{2+}$ ion on the surface of R-H than Ni$^2$ and Co$^{2+}$ (Demirbas, Pehlivan et al. 2005). So, R-Cu$^{2+}$ was established as the best adsorbent which can be applied for the removal of NH$_3$-N from wastewater. So, detailed experiments concentrated on the removal efficiency of NH$_4^+$ using R-Cu$^{2+}$ were achieved under different conditions. The adsorbed amount of NH$_4^+$ onto R-Cu$^{2+}$ changing within time. It was increased sharply in the first 20 min and attained the equilibrium state within 50 min, Fig. 3(a). The initial rapid adsorption of NH$_3$-N onto R-Cu$^2$ can be assigned to large number of the exchangeable active sites which increase the complexation’s rate between loaded Cu$^{2+}$ ions and NH$_3$-N in solution. After that, the adsorption process became slower and slower till reached the equilibrium due to no vacant Cu$^{2+}$ ions on the surface. The maximum adsorption capacities ($q_{max}$) of NH$_4^+$ on various other adsorbents reported in the literature are shown in Table (2). R-Cu$^{2+}$ has the highest the adsorption capacity of NH$_4^+$, reflecting that R-Cu$^{2+}$ is a good candidate for the removal of NH$_4^+$ from aqueous solution.

Three kinetic models namely, pseudo-first-order, pseudo-second-order and intraparticle diffusion models (Eqs. 5, 6 and 7, respectively) are applied to find out the relation between NH$_3$-N concentration and adsorption rate and fitting the experimental data of adsorption (Cheng, Zhu et al. 2019).

\[
\ln(q_e - q_t) = lnq_e - k_1 t
\]

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}
\]

\[
q_t = k_p t^{1/2} + C
\]

Where, $q_e$ and $q_t$ (mg/g) are the adsorbed amount of NH$_3$-N at equilibrium and at contact time t, respectively. $k_1$ (min$^{-1}$), $k_2$ (g/mg min) and $k_p$ (mg.g$^{-1}$.min$^{1/2}$) are the rate constant of pseudo-first-order, pseudo-second-order and the intra-particle diffusion,
respectively. C (mg.g\(^{-1}\)) is a constant term that represents the thickness of the boundary layer.

The values of kinetic parameters, the correlation coefficient, R\(^2\), and the calculated adsorption capacity (q\(_{e,cal}\)) were presented in Table (3). According to this Table, the adsorption of NH\(_3\)-N onto R-Cu\(^{2+}\) does not fit the pseudo-first-order model due to the low value of the correlation coefficient (R\(^2\) ≈ 0.81). In addition, the values of (q\(_{e,cal}\)) and the experimental one (q\(_{e,exp}\)) were not compatible. However, the calculate (q\(_{e,cal}\)) from the pseudo-second-order equation was matched with the experimental one (q\(_{e,exp}\)). Additionally, the value of (R\(^2\)) was close to unity, indicating that pseudo-second-order model is the best one to describe the adsorption of NH\(_3\)-N from an aqueous solution onto the surface of R-Cu\(^{2+}\). Moreover, the adsorption mechanism was carried out by the chemical adsorption process (Zhang, Wang et al. 2020). The fitting data of the intraparticle diffusion model involved two steps as presented in Fig. 4, indicating that the adsorption mechanism was involve two steps. The first step was mainly due to the film diffusion and the fitting lines away from origin implying that the adsorption of NH\(_3\)-N occurring over the external surface. Therefore, the intraparticle diffusion was not the rate-controlling step. The second step was assigned to the intraparticle diffusion (Elsherbiny, Gemeay et al. 2020). The values of k\(_{p1}\) and k\(_{p2}\) are listed in Table (3), where the value of k\(_{p1}\) is greater than that of k\(_{p2}\).

### 3.4. Impact of pH

pH of the medium is one of the most critical factors for the removal of NH\(_3\)-N by R-Cu\(^{2+}\). Since it possesses a significant role of the ratio of two forms of ammonia and the adsorbent surface. The impact of pH in the removal of NH\(_3\)-N was examined in the pH range from 2 to 12 using universal buffer, while the initial concentration of NH\(_3\)-N, amount of R-Cu\(^{2+}\) and temperature were kept constant. Fig. 5. NH\(_3\)-N in an aqueous solution is available in two forms, ammonium ion (NH\(_4^+\)) and unionized ammonia (NH\(_3\)) and the proportion of both forms depends on pH and temperature. At the pH lower than 4, the amount of NH\(_3\)-N uptake is slightly increased, this is due to the predominant form of ammonia in this range is NH\(_4^+\). On the other hand, when the pH increases from 4 to 8, the removal efficiency increased significantly from 10.6 % to 65.2 %. This increasing is attributed to ammonium ion is gradually converted to NH\(_3\) which react with Cu\(^{2+}\) to form Cu (II)-amine complex as shown in eq (1). However, above pH 8, the NH\(_3\)-N removal efficiency decreased, because of the considerably increasing in the concentration of hydroxide ion developed in alkaline medium. This
increasing can be form a precipitate of copper (II) hydroxide Cu(OH)$_2$, which leads to
decrease the amount of copper loaded on the resin (Chen, Chen et al. 2019).

### 3.5. Effect of R-Cu$^{2+}$ dose

The effect of the amount of R-Cu$^{2+}$ on the removal efficiency of NH$_3$-N was carried out
using the variable amounts of R-Cu$^{2+}$ and the other factors were kept constant. As the
amount of R-Cu$^{2+}$ increased, the amount of NH$_3$-N uptake increased significantly as
shown in Fig. 6. It was noticed that the removal efficiency increased from 32.7 to 90.8
% as the amount of R-Cu$^{2+}$ increased from 0.02 g to 0.2 g, respectively. This increment
is due to the large surface area of the adsorbent and increasing the adsorbent dose which
in turn leads to increase the number of exchangeable active site. Moreover, the loading
copper concentration increased so that the rate of complexation between metal and
NH$_3$-N increased (Clark and Tarpeh 2020).

### 3.6. Impact of initial NH$_3$-N concentration.

The impact of the initial NH$_3$-N concentration [NH$_4^+$]$_o$ was studied by changing its
concentration between 398.6 to 1686.18 mg. L$^{-1}$, Fig. 7. The removal efficiency of
NH$_3$-N using R-Cu$^{2+}$ at given time increases from 89.22 to 93.98 % as the initial
concentration of NH$_3$-N increases from 398.6 to 1686.18 mg. L$^{-1}$. This is due to an
enhancement of the concentration gradient of NH$_3$-N in solution that leads to a large
mass transfer driving force (Wang, Xu et al. 2020). Also, the available adsorption active
site of adsorbent (R-Cu$^{2+}$), becomes fewer due to continuous blocking of this site with
NH$_3$-N to form (R/Cu(II)-amine composite). on the other hand, some of ammonia
molecules don't get absorbed and remain free in the solution (Ding and Sartaj 2016).

### 3.7. Adsorption isotherms models

To obtain information about the distribution of adsorbate molecules between the liquid
phase and solid phase at the equilibrium state, adsorption isotherm was studied. NH$_3$-
N adsorption isotherm has been investigated at several initial concentrations and three
different temperatures. The adsorption isotherm was evaluated using four models,
Freundlich, Langmuir, Temkin and Dubinin-Radushkevich (D-R) isotherms (Eqs. 8, 9,
10, and 11, respectively).

\[
\frac{C_e}{q_e} = \frac{C_e}{q_{\text{max}}} + \frac{1}{q_{\text{max}} K_L} \tag{8}
\]

\[
\ln q_e = \frac{1}{n} \ln C_e + \ln K_F \tag{9}
\]

\[
q_e = B_1 \ln K_T + B_1 \ln C_e \tag{10}
\]
\[ \ln q_e = \ln q_m - Be^2 \]  \hspace{1cm} (11)

Where, \( C_e (\text{mg L}^{-1}) \) is the concentration of NH\(_3\)-N at equilibrium, \( q_{\text{max}} (\text{mg/g}) \) is the maximum adsorption capacity of NH\(_3\)-N and \( K_L (\text{L/mg}) \) is Langmuir adsorption constant that is related to the adsorption energy (Doekhi-Bennani, Leilabady et al. 2021). \( K_F (\text{mg/g}) \) and \( 1/n \) are Freundlich constants related to the adsorption capacity and adsorption intensity, respectively. \( K_T (\text{L/mg}) \) is the Temkin equilibrium constant that is connected to the maximum binding energy, and \( B_1 (\text{J/mol}) \) is a constant representing the heat of adsorption which is calculated from the following expression:

\[ B = RT/b; \ R \text{ is the gas constant, } T \text{ is the absolute temperature (K), and } b \text{ is the adsorption potential (Chen, Zhou et al. 2017). } q_m \text{ is the monolayer capacity (mg g}^{-1}\text{), and } \varepsilon \text{ is the Polanyi’s potential. The value of } \varepsilon \text{ can be written as: } \varepsilon = RT \ln[1 + 1/C_e]. \]

The value of \( B \) gained from the slope of D-R’s plot is utilized to calculate the mean adsorption energy (\( E, \text{kJ/mol} \)) which was obtained from the following equation:

\[ E = 1/(-2B)^{0.5} \]  \hspace{1cm} (12)

All parameters obtained from the isotherm models along with their correlation coefficient (\( R^2 \)) were listed in Table (4). By comparing the values of (\( R^2 \)) it was found that the adsorption NH\(_3\)-N on R-Cu\(^{2+}\) not obeyed Langmuir model. Whereas, it can be described by Freundlich, Temkin and D-R models. The highest value of (\( R^2 \)) was found that of the Freundlich model, revealing that the Freundlich model is the best one for representing the adsorption process with a formation of the monolayer coverage.

According to the data in Table (4), the values of \( 1/n \) were larger than unity and decreased with increasing the temperature, indicating the adsorption process becomes less unfavorable at higher temperatures. However, the \( K_F \) values increase with increasing temperature. This suggesting that the adsorption process is of an endothermic nature and favorable at higher temperatures (Fu, Zhao et al. 2021).

From Temkin model, it was found that, the value of \( B_1 \) decreased with increasing the temperature (Elsherbiny, Gemeay et al. 2020). In addition, the better fitting results of Temkin model indicated that the adsorption of NH\(_3\)-N is dominated by chemisorption, which is in agreement with the results of pseudo-second-order model. The value of \( E \), which was calculated form D-R model gives information about the mechanism of adsorption. Its value was higher than 20 kJ/mol, indicating the adsorption of NH\(_3\)-N onto R-Cu\(^{2+}\) is governed by chemical adsorption (Elsherbiny, Gemeay et al. 2020) coinciding with Temkin model. This value confirms that the removal of ammonia from
aqueous solution using R-Cu\textsuperscript{2+} was through complexation and R/Cu(II)-amine composite was formed. Additionally, this value was increased with increasing the temperature.

3.8. Thermodynamic parameters

Deep insight on the changes in the energetic parameters related to the adsorption process was provided from thermodynamic studies. The parameters of adsorption thermodynamics can be calculated by introducing the experimental data at three different temperatures into the following Equations (Elsherbiny 2013).

\[
\ln K_d = -\frac{\Delta H_{ads}}{RT} + \frac{\Delta S_{ads}}{R} \tag{13}
\]

\[
\Delta G_{ads} = -RT \ln K_d \tag{14}
\]

\[
\Delta G_{ads} = \Delta H_{ads} - T\Delta S_{ads} \tag{15}
\]

Where; \(K_d\) is the distribution coefficient (\(K_d = q_e/C_e\)), \(\Delta G_{ads}\) is the change in Gibbs-free energy of adsorption process, \(\Delta H_{ads}\) (kJ.mol\textsuperscript{-1}) is the enthalpy change, and \(\Delta S_{ads}\) (J.mol\textsuperscript{-1}.K\textsuperscript{-1}) is the entropy change. The distribution coefficient (\(K_d\)) and the thermodynamic parameters were presented in Table 5. As shown in Table 5, the value of \(K_d\) enhanced as temperature increased from 293 to 313 K. The values of \(\Delta S_{ads}\) and \(\Delta H_{ads}\) were determined by plotting Van't Hoff ’s equation (Eq. 13). The positive value of \(\Delta H_{ads}\) indicates endothermic nature of the adsorption process. While, the positive value of \(\Delta S_{ads}\) revealed that the degree of disorder increased at solid-liquid interface during the adsorption of NH\textsubscript{3}-N onto R-Cu\textsuperscript{2+} (Pan, Zhang et al. 2019). The negative values of \(\Delta G_{ads}\) demonstrated that the adsorption of NH\textsubscript{3}-N is a feasible and spontaneous process. Furthermore, the value of \(\Delta G_{ads}\) becomes more negative with increasing the temperature, suggests the adsorption of NH\textsubscript{3}-N onto R-Cu\textsuperscript{2+} was more favorable and spontaneous at higher temperatures.

3.9. Catalytic activity application of R/Cu(II)-amine composite for the oxidative degradation of dyes

Wastewater discharge during dyes manufacturing and textile dyeing cause serious problems for both the environment and human life. This type of pollutant is produced by manufacturing poisonous and potential carcinogenic materials, that contain highly colored organic compounds that have a low degradation ability (Salem, El-Ghamry et al. 2014). The valorization of the resulting product R/Cu(II)-amine composite was carried out. This product was applied to remove three different organic dyes namely, aniline blue
(AB), methyl green (MG), and methyl violet (MV 2B) from aqueous solution. The removal of these dyes was done in the presence of H$_2$O$_2$ as an eco-friendly oxidant. Fig. 8, presents the time decay of the absorbance of the three dyes. A glance to Fig. 8, the color of MG dye was completely disappeared in about 40 min. However, about 92.64 % and 90.26 % of AB and MV dyes were removed after 80 min. These results confirmed the ability of R/Cu(II)-amine composite as an efficient catalyst for removal of both anionic and cationic dyes from wastewater.

4. Conclusion

In conclusion, Amberlite IR-120 (R-H) was successfully loaded with Cu$^{2+}$, Ni$^{2+}$ and Co$^{2+}$ through cation exchange mechanism to form R-M$^{n+}$. The highest loaded amount was found in case of Cu$^{2+}$ with value of 245.6 mg L$^{-1}$ for 1g of R-H. The loaded resin R-M$^{n+}$ was applied to get rid of ammonia from aqueous solution and the highest removal efficiency was found in the case of R-Cu$^{2+}$. The adsorption of NH$_3$-N from an aqueous solution onto the surface of R-Cu$^{2+}$ obeyed pseudo-second-order model and Freundlich isotherm. The removal mechanism was governed by chemical adsorption and formation of R/Cu(II)-amine composite. The formed R/Cu(II)-amine composite was used as an efficient catalyst for removal of aniline blue, methyl green, and methyl violet dyes from aqueous solution in presence of H$_2$O$_2$.

Ethical Approval

Not applicable

Consent to Participate

All the authors are agreed to participate in this work

Consent to Publish

All the authors are agreed to publish this work in *Environmental Science and Pollution Research*

Authors Contributions

Marwa A. El-Ghobashy, Mohamed M. Khamis, Abeer S. Elsherbiny, Ibrahim A. Salem: validation; Marwa A. El-Ghobashy, Mohamed M. Khamis, Abeer S. Elsherbiny: formal analysis; Mohamed M. Khamis: investigation and data curation; Abeer S. Elsherbiny, Marwa A. El-Ghobashy, Mohamed M. Khamis: writing-original draft preparation; Marwa A. El-Ghobashy, Abeer S. Elsherbiny: review and editing; Ibrahim A. Salem; Put the idea of the work and final revision.

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Competing Interests

There are no conflicts to declare
Availability of data and materials

All the data and materials are available in the manuscript

References


**Legends of Figures**

**Fig. 1.** (a) FT-IR spectra of R-H, R-Cu$^{2+}$, and R/Cu(II)-amine composite; (b) XRD patterns of R-H, R-Cu$^{2+}$, and R/Cu(II)-amine composite; (c) TGA curve of R/Cu(II)-amine composite.

**Fig. 2.** (a) SEM images of R-H; (b) SEM images of R-Cu$^{2+}$; (c) SEM images of R/Cu(II)-amine composite; (d) EDX image of R/Cu(II)-amine composite.

**Fig. 3.** (a) Effect of contact time on the adsorption capacities of NH$_4^+$; (b) The removal efficiency of NH$_4^+$ onto R-Cu$^{2+}$, R-Ni$^{2+}$ and R-Co$^{2+}$ (0.1 g) using [NH$_4^+$]$_0$ =1060 mg. L$^{-1}$, 130 rpm and 30 °C.

**Fig. 4.** Intra-particle diffusion plot of the adsorption of NH$_4^+$ onto (0.1 g) of R-Cu$^{+2}$ at 30 °C.

**Fig. 5.** The effect of initial pH on the removal efficiency of NH$_3$-N, [NH$_4^+$]$_0$ = 1032.9 mg. L$^{-1}$ using R-Cu$^{2+}$ (0.1 g) at 30 °C.

**Fig. 6.** The effect of dose (R-Cu$^{2+}$) on the removal efficiency of NH$_3$-N, [NH$_4^+$]$_0$ = 1032.9 mg. L$^{-1}$, pH = 8.6 and temperature 30 °C.

**Fig. 7.** Influence of initial concentration of NH$_3$-N solution on the removal efficiency at different time using R-Cu$^{2+}$= 0.1 g, pH= 8.6 at 30 °C.

**Fig. 8.** Absorbance-time plots for the catalytic degradation of different types of organic dyes using 0.05 g of R/Cu(II)-amine composite as a catalyst in the presence of [H$_2$O$_2$] = 0.01 mol L$^{-1}$ at 30 °C: (A) [MV] = 1.86 x 10$^{-4}$ mol L$^{-1}$, (B) [AB]= 7.5 x 10$^{-5}$ mol L$^{-1}$, and (C) [MG]= 2.5 x 10$^{-5}$ mol L$^{-1}$.
Graphical Abstract
Figure 1

(a) FT-IR spectra of R-H, R-Cu$^{2+}$, and R/Cu(II)-amine composite; (b) XRD patterns of R-H, R-Cu$^{2+}$, and R/Cu(II)-amine composite; (c) TGA curve of R/Cu(II)-amine composite.

Figure 2
(a) SEM images of R-H; (b) SEM images of R-Cu$^{2+}$; (c) SEM images of R/Cu(II)-amine composite; (d) EDX image of R/Cu(II)-amine composite.

Figure 3

(a) Effect of contact time on the adsorption capacities of NH$_4^+$; (b) The removal efficiency of NH$_4^+$ onto R-Cu$^{2+}$, R-Ni$^{2+}$ and R-Co$^{2+}$ (0.1 g) using [NH$_4^+$]$_0$ = 1060 mg L$^{-1}$, 130 rpm and 30 °C.
Figure 4

Intra-particle diffusion plot of the adsorption of NH$_4^+$ onto (0.1 g) of R-Cu$^{+2}$ at 30 °C.
The effect of initial pH on the removal efficiency of NH$_3$-N, [NH$_4^+$]$_o$ = 1032.9 mg. L$^{-1}$ using R-Cu$^{2+}$ (0.1 g) at 30 °C.
Figure 6

The effect of dose (R-Cu$^{2+}$) on the removal efficiency of NH$_3$-N, [NH$_4^+$]$_0$ = 1032.9 mg L$^{-1}$, pH = 8.6 and temperature 30 °C.
Figure 7

Influence of initial concentration of NH$_3$-N solution on the removal efficiency at different time using R-Cu$^{2+}$ = 0.1 g, pH = 8.6 at 30 °C.
Figure 8

Absorbance-time plots for the catalytic degradation of different types of organic dyes using 0.05 g of R/Cu(II)-amine composite as a catalyst in the presence of $[\text{H}_2\text{O}_2] = 0.01 \text{ mol L}^{-1}$ at 30 °C:

- (A) $[\text{MV}] = 1.86 \times 10^{-4} \text{ mol L}^{-1}$,
- (B) $[\text{AB}] = 7.5 \times 10^{-5} \text{ mol L}^{-1}$, and
- (C) $[\text{MG}] = 2.5 \times 10^{-5} \text{ mol L}^{-1}$. 