Adsorption of Copper Ion using Acrylic Acid-g-Polyaniline in Aqueous Solution

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Abstract A conductive polymer, polyaniline (PANI) has unique electrical behaviour, stable in the environment, easy synthesis and have wide application in various fields. Modification of PANI in order to improve its adsorption capacity has been done. In this study, the polyaniline-grafted acrylic acid has been prepared and followed by adsorption of copper ion in aqueous solution. Acrylic acid, PANI and acrylic acid-g-polyaniline (Aag-PANI) were characterized by FTIR and SEM to determine its characteristic. The adsorption capacity was investigated to study the removal capacity of Cu ion from aqueous solution. Two parameters were selected which are pH (2, 4 and 6) and initial metal ion concentration (50 mg/L, 100 mg/L and 200 mg/L). The maximum adsorption capacity for PANI and Aag-PANI are 1.7 mg/g and 64.6 mg/g, respectively, at an initial concentration of 100 mg/L. The Langmuir adsorption isotherm model and Freundlich adsorption isotherm model have been used and showed that it is heterolayer adsorption by follows the Freundlich isotherm model.

1. Introduction
Water pollution by heavy metals is a major environmental problem due to the high toxicity of these elements to human being and ecosystem. Most of the heavy metals are coming from industrial wastewater such as cadmium (Cd), zinc (Zn), nickel (Ni) and copper (Cu). They affect all living organism by accumulation through a food change and enter in an ecological system [1, 2, 3]. For instance, an excessive intake of Cu (II) can lead to gastrointestinal problems, kidney and liver damage, headaches and nausea [4]. Lack of wastewater management from industries such as electroplating, cadmium-nickel batteries, galvanizing, phosphate fertilizers, etc. generate a massive amount of wastewater that contains heavy metal that pollutes the water resources. This waste actually is a valuable material that can be reused in electronic device manufacturing such as in solar cell component, batteries and others electrical component [5].

There are various treatment processes for the removal of metal ions from wastewater such as chemical stabilization [6], chemical precipitation [7], chemical oxidation [8], chemical coagulation [9], ion exchange [10] and adsorption [11, 12]. However, adsorption process seems to be the better choice due to the accessibility of the materials, cheaper and effective.
In recent years, use of conducting polymer materials as adsorbent has gained a substantial attention due to their outstanding adsorption performance, low cost, wide availability and the presence of various functional groups. Polymeric polyaniline (PANI) is widely used as metal ion adsorbent [12, 13, 14, 15, 16, 17]. PANI has great properties as an adsorbent with high adsorption capacity and selectivity towards heavy metal ions because of its accessible for active sites, large surface area and short diffusion length [18]. Acrylic acid has amazing properties containing a hydrophilic group which usually use to increase the water solubility property of many polymers [19, 20]. Grafting using high-energy radiation offers several advantages over conventional redox grafting method. Grafting via ionization radiation by gamma and electron beam irradiation through the formation of radicals is an environmental friendly than the chemical process. It has been extensively used for grafting of various monomers on a different type of polymers. This simple, clean and cheap grafting procedure could enhance the adsorbent properties for PANI. The objective of this study is to investigate the possibility of copper ions removal from aqueous solution by acrylic acid-g-PANI (Aag-PANI) by isotherm study. The modification of PANI by adding acrylic group via grafting irradiation will increase the ability and efficiency of adsorption of copper ion onto PANI. The Aag-PANI was characterized by FT-IR and SEM (EDX). The experimental data were fitted to Langmuir and Freundlich isotherm models.

2 Material and methodology

2.1 Material
Copper Nitrate (R&M), Acrylic Acid (R&M), Aniline (R&M), Sodium Hydroxide pellet R&M), Chloroform (R&M), nitric acid 70% (QREC), Ammonium persulfate (R&M) and Acetone (QREC). All chemicals are in analytical grade.

2.2 Preparation of acrylic acid-g-polyaniline
PANI was prepared by polymerization of aniline by ammonium persulfate as an oxidizing agent in acidic condition. The obtained PANI which is in the form of emeraldine salt was later converted into its base form by stirred for 5 hours in 0.5M sodium hydroxide. This emeraldine base (EB) PANI was then filtered and washed several times with excess water and followed by acetone. The obtained dark blue powders were dried under vacuum for spectroscopic characterization and grafting irradiation.

Aag-PANI was prepared by radiation of PANI using electron beam irradiation. 10 g of EB PANI were soaked in 50% of 80ml acrylic acid for 2 hours and immediately sent for irradiation. The irradiation was carried out by using Nisshin High Voltage (Japan) in 2.5 MeV beam current, 10 mA at 10 kGy. The grafted PANI was then soaked in distilled water at 90°C and repeatedly wash until the pH 7 is obtained. This process was to remove the homopolymer. Finally, it was then filtered and dried in a vacuum oven until constant weighed. The Aag-PANI was characterized by Fourier transform infrared (FTIR) Spectroscopy, (Thermo Scientific Nicolet 6700, USA) to analyze the organic functional groups present in the adsorbent and using field emission Scanning Electron Microscope, CARL ZEISS EVO MA10, UK to examine its surface morphologies.

2.3 Adsorption by batch kinetic
Adsorption isotherm and kinetic experiment were performed by shaking 0.1 g of the acrylic-g-polyaniline with 100 mL of the Cu ion solution. For equilibrium isotherm studies, Cu metal ion solutions of different initial concentrations (50, 100, 200 mg/L) was taken in batches of 100mL and agitated using laboratory shaker at 160rpm at 25 ±2°C for 1 hours at pH 6 in a series of 250mL Erlenmeyer flask. For kinetic studies, the samples were collected at different time intervals (2, 5, 10, 20, 40, 60 min) and filtered each time through a 0.45µm Whatman filter membrane with a syringe. The experiments were carried out by varying the initial metal ions concentrations, pH and temperature. The left out concentrations in the filtrate solution after the adsorption process and the initial solution before the adsorption process will be analysed using flame atomic absorption spectrophotometer with an air-acetylene flame. Cu hollow cathode lamp will be used. The quantity of adsorbed metal ions on adsorbent
will be calculated as the difference between initial concentration and concentration at any time, t. Each experiment was duplicated at least under identical conditions.

2.4 Mathematical Model
The percentage removal can be calculated following the equation

$$\% R = \frac{C_i - C_t}{C_i} \times 100$$  \hspace{1cm} (1)

Where, $C_i$(mg/L) and $C_t$ are the concentration in the solution at time $t=0$ and at time $t$. The amount of metal adsorbed $q_t$(mg g$^{-1}$) was determined by using the following mass balance relationship:

$$q_t = \frac{(C_0 - C_t)V}{m}$$  \hspace{1cm} (2)

where, $q_t$ is the amount of metal adsorbed per gram of Aag-PANI, $C_0$ and $C_t$ are the initial and final copper concentration in the solution for time $t$ (mg L$^{-1}$).

The Langmuir isotherm theory pictures a saturated monolayer of solute molecules on the adsorbent surface with no migration of adsorbates molecules and a constant energy of adsorption. The non-linear equation of Langmuir isotherm model is expressed as:

$$q_e = \frac{q_{max}K_LC_e}{1+K_LC_e}$$  \hspace{1cm} (3)

where $q_e$ is the equilibrium adsorption capacity of ions on the adsorbent (mg/g); $q_m$, the maximum capacity of the adsorbent (mg/g); $K_L$, the Langmuir adsorption constant (L/mg); and $C_e$, the equilibrium concentration of ions in solution. The isotherm constants were calculated from the linear plot between $1/q_e$ and $1/C_e$.

The Freundlich model describes the adsorption of a reversible heterogeneous surface and is not restricted to a monolayer adsorption capacity. The equation is described as:

$$q_e = K_FC_e^{1/n}$$  \hspace{1cm} (4)

where, $q_e$ is the amount of Cu adsorbed per gram of Aag-PANI at equilibrium (mg g$^{-1}$), $C_e$ is the Cu concentration in the solution at equilibrium (mg L$^{-1}$), $K_L$ is Langmuir constant that corresponds to adsorption energy (L mg$^{-1}$), $q_{max}$ is maximum adsorption capacity (mg g$^{-1}$), $K_F$ is Freundlich constant that indicates the relative adsorption capacity (mg$^{1/(1/n)}$ L$^{1/n}$ g$^{-1}$), and $n$ is related to the intensity of adsorption.

3 Result and discussion
3.1 Characteristic of Aag-PANI
FT-IR spectroscopy was used to confirm the changes in functional groups of grafted PANI. Figure 1 represented the FTIR spectra of PANI and grafted PANI exhibits that grafting reaction occurs between acrylic acid and PANI. The addition of new peak at 1700 cm$^{-1}$ in spectra of grafted PANI can be attributed to -CO- of -COOH- group belonging to poly (acrylic acid). This peak is not found on PANI curve verified that monomer acrylic acid grafted successfully on the PANI molecule [21, 22, 23, 24]. The accompanying key characteristic bands were observed: 3315 cm$^{-1}$ (overlapping of O-H stretching), 2966 cm$^{-1}$ (aliphatic C-H stretching), 1596 and 1477 cm$^{-1}$ (non-symmetric vibration mode of C=C in benzenoid and quinoid ring system); 1212 cm$^{-1}$ (C-N stretching vibration mode in benzenoid ring system) and 1315 cm$^{-1}$(C-N stretching vibration of secondary aromatic amine).
Figure 1. FT-IR spectra of Aag-PANI

FESEM image of acrylic acid-g-polyaniline has been taken before and after copper ion adsorption are shown in figure 2 (a) and (b), respectively. The same nanofiber structure with short length size of fibre before and after adsorption process reveals the stability of acrylic acid-g-PANI along adsorption process. However, figure 2b shows that the nanofiber is encrusted, assumed that the Cu metal ions were adsorbed on its surface and causes it looks more compact and stick to each other compared to the previous one.

Figure 2. Micrograph of Aag-PANI a) Before adsorption b) After adsorption

3.2 Percentage removal of Cu using Aag-PANI

Percentage removal of Cu ion onto AAg-PANI was investigated at the initial concentration of 50, 100 and 200 mg/L as shown in figure 3. Adsorption of Cu ion onto AAg-PANI and PANI for each initial concentration reach the equilibrium at 5 and 10 minutes, respectively. However, the highest percentage of Cu removal of 92.8% was at the initial concentration of 50 mg/L. Increasing of the initial concentration up to 200 mg/L decrease the percentage removal of 80%. This is due to the sufficient site for Cu metal ions to adsorb onto the surface of Aag-PANI [27]. Increasing the concentration of Cu ions in the system, significantly increase the number of Cu ion adsorb on the available site of the surface of the adsorbent, however, it also depends on the available site for the adsorption process take place. Therefore, the removal percentage decreases by increasing the initial concentration up to 200 mg/L. PANI took a longer time to reach equilibrium with a low percentage of adsorption due to the non-
availability of an active site of the functional group for the Cu metal ions adsorption compared with AAg-PANI.

Figure 3. Effect of initial concentration on the removal percentage of Cu metal ions using AAg-PANI and PANI at 27°C and pH 6. (Conc.: 50, 100 and 200 ppm)

Figure 4. Effect of pH on the removal percentage of Cu metal ions using AAg-PANI at 27°C and initial concentration of 100 mg/L.

The initial pH of the metal ion solution is the main factor as it affects the kinetic reaction of proton ions in aqueous solution and the availability of hydroxyl sites on the surface of AAg-PANI. In figure 4, AAg-PANI showed a decrease in the copper ion percentage of removal at pH below 6. It shows, in a high acidic condition which is pH 2 and 4, hydrogen ion dominate most on the adsorption site of the surface of AAg-PANI compare with copper ion itself. This trigger the electrostatic repulsion in the system [16]. Increasing the pH up to pH 6 give more adsorption site for Cu ions by decreasing the competition with hydrogen ions. The optimum pH for adsorption of copper ion is pH6 with a maximum percentage removal up to 83%. Increasing the pH to above the pH 6 will cause the precipitation of copper hydroxide in the solution [28].

3.3 Adsorption isotherm of Cu using AAg-PANI
Langmuir and Freundlich model were analyzed to understand the adsorption mechanism of Cu metal ions onto AAg-PANI. The R2 value of Freundlich isotherm model is closer to 1 compared to Langmuir, therefore, AAg-PANI follows the Freundlich isotherm model as shown in table 1. The 1/n values for this experimental data indicate that the type of this isotherm is favourable. While the n value is greater than 1 indicates that the adsorption expected to happen by the force within the surface [15, 25]. The
Freundlich model assumed that the adsorption of Cu metal ions onto the surface of AAg-PANI are heterogeneous adsorption [26, 13].

### Table 1. Values of Langmuir and Freundlich constants for adsorption of Cu with AAg-PANI

| Adsorbate   | Langmuir constants | Freundlich constants |
|-------------|--------------------|----------------------|
|             | $q_{\text{max}}$ (mg/g) | $K_L$ (L/mg) | $R^2$ | $1/n$  | $n$ | $K_F$ (L/mg) | $R^2$ |
| AAg-PANI    | 64.6               | 0.1817             | 0.9448 | 0.3826 | 2.6137 | 13.6263 | 0.9937 |

### 4. Conclusion

In this research, the AAg-PANI was prepared as an adsorbent for the adsorption of Cu metal ions in aqueous solution. The kinetic and isotherm study has been done to measure its adsorption capacity for metal ions removal, especially in wastewater. The simple characterization analysis has been done and showed that its content functional group that support the adsorption of metal ions on its surface as well as SEM images that shows the compact sample after the adsorption process compares to the before adsorption. The initial concentration and pH played a major role in the copper ion adsorption capacity onto acrylic acid-g-PANI. The removal percentage of copper increased with the increasing of initial concentration, however, stop when there was no more vacant area on its surface. The optimum pH for the removal of copper was found to be pH 6. Freundlich isotherm model was fit the best for the adsorption of Cu metal ions on AAg-PANI. The maximum adsorption capacity of AAg-PANI was measured to be 64.6 mg/g at the concentration of 100 mg/L and the temperature of 27°C. This study proved that AAg-PANI is potential adsorbent for removal of metal ions from polluted wastewater or industrial effluents.

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