Analytical Instrumentation Techniques of FT-IR, XRD, SEM, and EDX for Adsorption Methods of Ni\textsuperscript{2+} Ions onto Low Cost Adsorbent

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http://dx.doi.org/10.13005/ojc/370608

(Received: November 22, 2021; Accepted: December 23, 2021)

ABSTRACT

In present investigate the possible removal of Ni\textsuperscript{2+} ions from aqueous solution by using low-cost *Hygrophila auriculata* activated nano carbon (HA-ANC) as an adsorbent. The activated nano carbon had been prepared from *Hygrophila auriculata* stem waste as well; the raw material was carbonized with con. H\textsubscript{2}SO\textsubscript{4} and activated by thermal action. Batch experiments were performed in order to calculate the percentage removal of Ni\textsuperscript{2+} ions for 90.737\% at 60\(^\circ\)C. The properties of treated carbon and untreated carbon are compared using instrumental techniques such as FT-IR, XRD, SEM and EDX, which confirms Ni\textsuperscript{2+} ions adsorption onto HA-ANC. FT-IR showed that the surface of HA-ANC had more oxygen containing functional groups which enhanced the adsorption of Ni\textsuperscript{2+}. XRD showed the nature of adsorbent, SEM images implies morphological deviance of before and after adsorption of Ni\textsuperscript{2+} onto HA-ANC and EDX showed that the C content of HA-ANC were higher than that of Ni\textsuperscript{2+}/HA-ANC.

Keywords: Adsorption, *Hygrophila auriculata* activated nano carbon (HA-ANC), Batch method, Ni\textsuperscript{2+} ions, FT-IR, XRD, SEM, EDX.

INTRODUCTION

Pollution of heavy metals has attracted global attention due to their toxicity, hard decay and accumulation in organisms. Heavy metals accumulate in the tissues of various living organisms and as a result attach to the food chain, affecting humans, posing a health risk\textsuperscript{1-3}. Therefore, the treatment of wastewater polluted by heavy metals is an important environmental concern. Ion exchange, solvent extraction, chemical precipitation, ultra-filtration, reverse osmosis, electro dialysis and adsorption are the traditional methods for removing heavy metal ions from polluted water\textsuperscript{4-6}. However, absorption is considered to be one of the most popular methods for removing heavy metals from wastewater due to its low cost, in effect, biodegradability, ease of design and high removal efficiency. There are many absorbent materials available, but activated carbon is used to remove heavy metals by the adsorption method because activated carbon has a numerous pores and a large surface area\textsuperscript{7,8}. 
The literary study shows that no work has been done on *Hygrophila auriculata* activated nano carbon (HA-ANC) as an adsorbent, as well as low cost and high abundance. Therefore this study focused on the removal of Ni$^{2+}$ ions from the aqueous solution using the HA-ANC by batch adsorption method.

**MATERIALS AND METHODS**

**Chemicals**

Analytical reagent grade chemicals were used. Stock Ni$^{2+}$ ion solution (1000ppm) was prepared by dissolving required amount of NiSO$_4$.6H$_2$O in 1000 mL of double distilled water. Working standards were prepared by diluting the stock solution of Ni$^{2+}$ ions using double distilled water. The ionic solutions of 0.1M HCl and 0.1MNaOH were made for to alter the solution pH.

**Procedure for adsorbent preparation and activation**

The *Hygrophila auriculata* stem waste was obtained from the agricultural sites near at Poompuhar, Mayiladuthurai district, Tamilnadu, India. The stem was cut into small pieces, dried in the absence of sunlight and treated with concentrated H$_2$SO$_4$ in W/V ratio. The carbonized material washed away by double distilled water until it becomes neutral one and dried further inside the hot air oven at 110$^\circ$C for 24 hours. The carbon was activated by using muffle furnace at 1000$^\circ$C for 6 h and the activated carbon (HA-ANC) was powdered well and stored in desiccators in order to perform the experiment.

**Batch adsorption method**

The batch experiments for Ni$^{2+}$ ions removal was determined under various initial pH like 3, 4, 5, 6, 7, 8 and 9 besides temperature ranges from 30 to 60$^\circ$C at an initial Ni$^{2+}$ ion solution concentration was varied from 10 to 50ppm with different adsorbent doses and different time intervals such as 15, 30, 45, and 60 minutes. The effect of initial Ni$^{2+}$ ions concentrations was investigated by using 25 mg biomass, initial pH 6 and volume of Ni$^{2+}$ ion solution 50 mL are constant but varied initial Ni$^{2+}$ concentrations at room temperature (30$^\circ$C). The Ni$^{2+}$ ion solution samples were collected after 60 min of shaking then centrifuged at 120rpm, the filtrate was analyzed. The unadsorbed Ni$^{2+}$ ions were measured by using UV-Visible spectrophotometer. The removal percentage and amount of Ni$^{2+}$ ions adsorption were calculated using equation 1 and equation 2 correspondingly.

**Analytical tools for HA-ANC and Ni$^{2+}$/HA-ANC**

The determination of surface area, volume and diameter of pores for HA-ANC, BET-BJH methods were used. The FT-IR spectrum is an important tool to study the changes in frequency due to the interaction between adsorbent and adsorbate. The XRD pattern confirms the nature of the adsorbent as well as adsorption of Ni$^{2+}$ ions onto HA-ANC in order to changes of 2θ values. SEM is a substantial tool to evaluate the morphological features and surface characteristics of the fresh adsorbent and treated adsorbent materials and also EDX study gives details about the element compositions.

**RESULTS AND DISCUSSIONS**

The equilibrium data was calculated with the help of batch methodology it’s incorporated some of the effective parameters such as contact time, solution pH, adsorbent dose, temperature. The data was given in Table 1, the result says that the nature of effectiveness of *Hygrophila auriculata* activated nano carbon (HA-ANC), which indicates the amount of adsorbed Ni$^{2+}$ ions onto HA-ANC increased with increasing temperature. The removal was high (90.737%) at 60$^\circ$C it’s also declared the removal of Ni$^{2+}$ ions onto adsorbent favored in elevation of temperature as well as low concentration of Ni$^{2+}$ ion solution by 25 mg of adsorbent.
Table 1: Equilibrium Data for the Adsorption of Ni²⁺ ions onto HA-ANC

| C₀ (Mg / L) | 30°C | 40°C | 50°C | 60°C | qₑ (Mg / L) | 30°C | 40°C | 50°C | 60°C | Removal% |
|-------------|------|------|------|------|-------------|------|------|------|------|----------|
| 10          | 1.804| 1.463| 0.976| 0.926| 16.393      | 18.048| 18.147| 81.963| 85.375| 90.238   |
| 20          | 5.363| 4.877| 4.408| 3.414| 29.275      | 30.246| 31.184| 73.188| 75.614| 77.960   |
| 30          | 11.149| 10.630| 9.263| 8.582| 37.702      | 38.741| 41.475| 42.836| 64.568| 69.125   |
| 40          | 17.103| 15.641| 14.837| 13.917| 45.793      | 48.718| 50.327| 52.139| 62.908| 65.208   |
| 50          | 25.350| 24.471| 23.931| 22.510| 49.300      | 51.059| 52.139| 54.581| 62.908| 54.981   |

According to the BET-BJH method, the surface area, volume and diameter of pores was obtained as 90.067 m²/g, 0.115 cc/g and 3.520 nm, respectively.

Fourier transform infrared was used to determine the changes of vibration frequency in the functional groups of the adsorbent due to Ni²⁺ ions adsorption. The FT-IR spectrum within 500-4000 cm⁻¹ for the HA-ANC before and after the adsorption of Ni²⁺ is shown in order to Fig. 1 and Fig. 2. The peak point of frequency; 2500 to 4000 cm⁻¹ indicates the single bonds (C-H, O-H, N-H), 2000 to 2500 cm⁻¹ indicates the triple bonds (C≡C, C≡N), 1500 to 2000 cm⁻¹ indicates the double bonds (C=C, C=N, C=O) and 500 to 1500 cm⁻¹ indicates fingerprint region. The FT-IR spectrum of HA-ANC indicates that there is remarkable change in the peaks at 2997.49 cm⁻¹, 2888.47 cm⁻¹, 1860.25 cm⁻¹, 1560.72 cm⁻¹, 1184.19 cm⁻¹, 1123.42 cm⁻¹, 1035.85 cm⁻¹, 795.09 cm⁻¹, and 525.96 cm⁻¹ respectively which it can be due to Ni²⁺ binding with functional groups adsorbent. The formation of new peaks, demolition of old peaks and higher to lower as well as lower to higher shifting of peaks were reason for that HA-ANC adsorbed with Ni²⁺ ions.

The result of XRD diffractogram for HA-ANC (Fig. 3) revealed that the Hygrophila auriculata activated nano carbon is crystalline in nature and resembles the graphite structure. After adsorption of Ni²⁺ ions (Fig. 4) the surface of adsorbent was disturbed this one leads to new theta values, HA-ANC given in Table 2 and Ni²⁺/HA-ANC given in Table 3 respectively.

Table 2: XRD measurements of HA-ANC

| Pos.[°2θ] | Height[cts] | FWHM | Left[°2θ] | d-spacing[Å] | Rel.Int.[%] |
|-----------|-------------|------|-----------|--------------|------------|
| 25.2589   | 1233.20     | 8.7438| 3.52305   | 100.00      |
| 43.5468   | 384.92      | 4.5991| 4.35492   | 2.98        |
| 23.8854   | 1206.41     | 5.9034| 3.72244   | 5.07        |
| 26.5138   | 209.24      | 9.0362| 3.35909   | 0.88        |
| 42.5192   | 718.56      | 0.9656| 2.12441   | 3.02        |

Table 3: XRD measurements of Ni²⁺/HA-ANC

| Pos.[°2θ] | Height[cts] | FWHM | Left[°2θ] | d-spacing[Å] | Rel.Int.[%] |
|-----------|-------------|------|-----------|--------------|------------|
| 5.0131    | 23772.90    | 0.0520| 17.61333  | 100.00      |
| 20.3762   | 708.42      | 3.3002| 4.35492   | 2.98        |
| 23.8854   | 1206.41     | 5.9034| 3.72244   | 5.07        |
| 26.5138   | 209.24      | 9.0362| 3.35909   | 0.88        |
| 42.5192   | 718.56      | 0.9656| 2.12441   | 3.02        |

SEM images have been used for morphological study of HA-ANC. The SEM...
micrographs of HA-ANC before and after adsorption of Ni²⁺ ions are shown in Fig. 5 and Fig. 6 respectively. In the SEM image of HA-ANC, the porous structure is obvious, but in the case of the used particles, the pores have been covered by the Ni²⁺ ions²⁰,²¹.

Fig. 5. SEM image for HA-ANC in different magnifications 10 µm, 1 µm and 300 nm

The EDX spectrum²²,²³ of HA-ANC before and after adsorption of Ni²⁺ ions were evaluated shown in Fig. 7 and Fig. 8 respectively. The spectrum clearly indicates the peak of element C, there was significant reduction in the intensity of peak of C in the after adsorption of Ni²⁺ ions comparing with the before adsorption. And also the peak of Ni²⁺ ions was notable on the after adsorption of Ni²⁺ ions onto HA-ANC in addition the elemental compositions statistics were given in Table 4 and Table 5 respectively for before and after adsorption Ni²⁺ ions onto HA-ANC. In addition the atomic percentage of carbon reduced form 99.7% to 88.8% based on Table 4 and Table 5, it can be usable as remarkable reduction.

Fig. 6. SEM image for Ni²⁺ / HA-ANC in different magnifications 10 µm, 1 µm and 300 nm

Fig. 7. EDX for HA-ANC

Fig. 8. EDX for Ni²⁺ /HA-ANC

Table 4: EDX of Smart Quant Results for HA-ANC

| Element | Weight% | Atomic% | Error% | Kratio |
|---------|---------|---------|--------|-------|
| CK      | 85.6    | 89.7    | 4.4    | 0.5959 |
| OK      | 11.7    | 9.2     | 13.9   | 0.0133 |
| MgK     | 0.5     | 0.2     | 13.2   | 0.0029 |
| AlK     | 0.4     | 0.2     | 13.2   | 0.0026 |
| SiK     | 0.7     | 0.3     | 7.2    | 0.0056 |
| SK      | 0.3     | 0.1     | 18.3   | 0.0028 |
| CIK     | 0.4     | 0.1     | 19.9   | 0.0035 |
| CaK     | 0.4     | 0.1     | 27.7   | 0.0034 |

Table 5: EDX of Smart Quant Results for Ni²⁺ /HA-ANC

| Element | Weight% | Atomic% | Error% | Kratio |
|---------|---------|---------|--------|-------|
| CK      | 84.8    | 88.8    | 4.0    | 0.6254 |
| OK      | 13.5    | 10.6    | 13.6   | 0.0158 |
| AlK     | 0.4     | 0.2     | 9.9    | 0.0031 |
| SK      | 0.4     | 0.2     | 15.4   | 0.0038 |
| CIK     | 0.2     | 0.1     | 30.2   | 0.0020 |
| NiK     | 0.6     | 0.1     | 20.0   | 0.0062 |

CONCLUSION

The Hygrophila auriculata activated nano carbon (HA-ANC) has been used successfully with an initial concentration of 10ppm at pH 6 in 60 minutes. The appearance, disappearance and shifting of peaks in the FT-IR spectrum confirmed the adsorption of Ni²⁺ ions onto HA-ANC as well as XRD analysis also provided reasonable evidence for adsorption to the adsorbent. In addition to supporting, the SEM study gives difference in the
surface morphology of the adsorbent before and after the adsorption of Ni²⁺ ions as well as EDX also given elemental composition evident of removal of Ni²⁺ ions onto HA-ANC. Finally, it was concluded that the present adsorbent HA-ANC could be a good alternative adsorbent for the removal of heavy metals from aqueous solutions in a very efficient and economical manner.

ACKNOWLEDGEMENT

The authors sincerely thank the Government of Tamil Nadu Adi Dravidar and Tribal Welfare Department for providing the fund from Full Time Ph. D Scholars incentive Scheme.

Conflict of interest

The author declare that we have no conflict of interest.

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