ADSORPTION REMOVAL OF TH (IV) FROM AQUEOUS SOLUTIONS USING INVERSE SPINEL NICKEL FERRITE NANOCOMPOSITE BASED ON GRAPHENE OXIDE (GONF)

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Abstract- In the present study, synthesized GO based nickel ferrite (GONF) by chemical precipitation and was well characterized with suitable spectroscopy techniques in order to use for adsorption removal of Th(IV) from aqueous solutions. The synthesized GONF was well characterized using X-ray diffraction (XRD), Fourier transform-infrared resonance (FT–IR), and X-ray photoelectron (XPS) spectroscopes. The morphology, the surface area and pore volume of GONF was evaluated by scanning electron microscopy (SEM) and BET analysis, respectively. Batch adsorption of Th(IV) was successfully done by the prepared GONF and the kinetics studies revealed the sorption of Th(IV) onto GONF was well described by pseudo-second-order equation. The sorption equilibrium data of Th(IV) was well tune to the Langmuir isotherm model than the Freundlich and Temkin's isotherm models. Hence, the sorption of Th(IV) onto GONF occurred through monolayer chemisorptions on homogeneous surface of GONF. The maximum adsorption capacities (Q_{max}) of the GONF for Th(VI) is 88.49 mg/g. Thermodynamic studies reveal that the sorption was increased as increase temperature from 298 to 328 K, indicates the chemisorptions. The overall obtained results demonstrated that the GONF as an effective sorbent for Th(IV) removal from aqueous acidic solutions.

Keywords- Graphene oxide based nickel ferrite, Nanocomposite materials, Adsorption, Th(IV) removal

I. INTRODUCTION

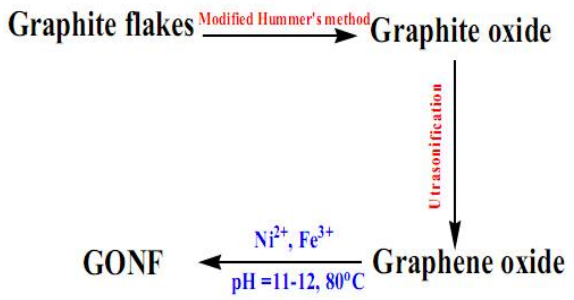
Thorium is one of the radioactive actinide occurs in the environment as tetravalent form. It is used as a fuel in the nuclear reactors for the production of non-fossil energy. The release of thorium contamination into the environment reaches the top of the food chain and be ingested by humans, causing several health problems like kidney or liver damage and even death [1]. Due to increasing demand of thorium as a nuclear fuel for production of non-fossil energy and complexity of nuclear waste management, there is great need to develop advanced analytical technique for recovery of thorium from contaminated wastewaters in order to prevention of its environmental impact and demand.

Carbon materials are very often used for as excellent adsorbents [2-5]. In recent years, adsorption techniques based on carbon or graphene materials has been used for the removal of uranium from aqueous environment [6-8]. Graphene has been chosen for the removal of radioactive elements because of it possesses a large surface area, open porous structure, flexibility, high electrical and thermal conductivity with great radiation resistivity than the organic exchange resins, and high chemical stability than the regular inorganic sorbents in the strong acidic nuclear wastes [7]. However, the recovery of loaded graphene or graphen oxide has been challenged. GO is a good candidate for constructing graphene-based composite materials with metal oxides [9]. Moreover, graphene based nanocomposites has become a hot topic of research due to their enhanced functionalities that cannot be achieved by either component alone, and therefore holds a great promise for a wide variety of applications in catalysis, surface enhanced Raman scattering, biomedical fields, drug delivery and removal of contaminants from wastewater [10-12]. In the present study, synthesized GO based nickel ferrite (GONF) by chemical precipitation and was well characterized with suitable spectroscopy techniques in order to use for adsorption removal of Th(IV) from aqueous solutions.

II. METHODS AND MATERIALS

Preparation of porous GONF

As shown in the Scheme 1, prepared GONF from GO and nickel ferrite by thermal co-precipitation method. The GO was prepared from Graphite flakes oxidation using Hummer's method and subsequently utrasonication. The prepared GO was used for the preparation of GONF.



Scheme 1. Schematic representation for the preparation GONF.

Batch sorption experiments

The stock solution (1000 mg/L) of metal ion, Th(IV), was prepared from thorium ICP standard (ICP-61N-1). Typical batch sorption experiment were carried out with 50 mL of 8 mg/L aqueous solution of Th(IV) initial concentration at pH 4.0 in a falcon tube at room temperature. To this added each 0. 3 g/L of GONF. Then, mixture was shaken for pre-determined equilibrium time intervals (120 min), and the adsorbent was separated using external magnetic field, then the samples were filtered out through a 0.45 µm membrane syringe filter for measuring the metal ion concentration using Optima 2100 DV inductive coupled plasma-optical emission spectroscopy (ICP–OES) (Perkin-Elmer, USA). The amount of Th(IV) adsorbed onto GONF was calculated from the mass balance between the initial (C_o) and equilibrium (C_e) concentrations (mg/L) of metal ions. The metal uptake capacity (q_e, mg/g) of nanocomposite materials was calculated by the following equation:

$$q_e = \frac{(C_o - C_e)V}{m} \quad (1)$$

where V is the volume of Th(IV) solution and m (g) is the weight of GONF. All pH measurement was carried out by 340i pH meter (WTW, Germany). The sorption experiment was also performed at different pH values by adjusting pH with 0.1 moles/L HCl and NaOH solutions. Desorption studies were conducted using pH 1.0 aqueous HNO_3 acid solution. All the investigations were carried out in triplicate to avoid discrepancies in experimental results and the values reported are mean ± standard deviation (SD). Origin 8.0© was used to fit the kinetics and equilibrium models using linear regression analysis. Metal solution controls were also utilized to maintain quality control.

III. RESULTS AND DISCUSSIONS

The X-ray diffraction results (XRD) (Fig.1) observed that the strong peaks at $2\theta = 8.9^o$ confirmed the presence of GO at the GONF [13]. The peaks at $2\theta = 26.6$, 35.65 and 44.5^o values indicated the presence of inverse spinel nickel ferrite in the GONF [14]. The size GONF was also clearly observed from the X-ray diffraction studies and i.e. 41.0 nm. It was calculated from well-known Scherer formula: $D = 0.94\lambda / \beta \cos\theta$, where D is the crystallite size (nm), β is the full width of the diffraction line at half of the maximum intensity measured in radians, λ is the X-ray wavelength of Cu Kα = 0.154 nm, and θ is the Bragg angle. Finally the XRD results were confirmed that the formation of GO-based cubic inverse spinel nickel ferrite nano composite, GONF.

Further FT-IR results (Fig.2) suggest that the presence of epoxy and carbonyl functional groups along with carboxylic groups which confirming the formation of GO. FT-IR spectrum of GONF indicates that the wavelengths of such functional groups present in GO were shifted to lower wavelengths regions upon magnetization of GO. It is a common phenomenon for the formation of new product from bare compound by reduction

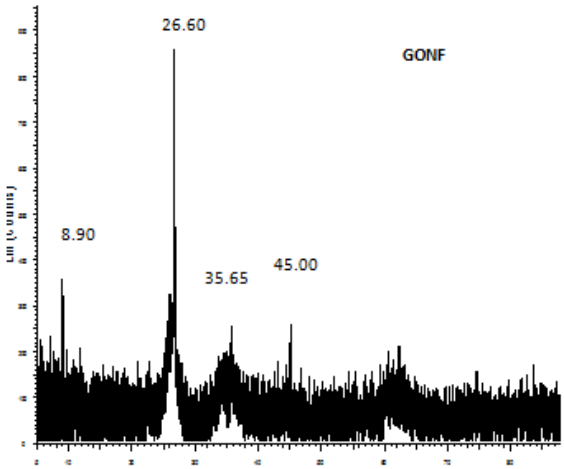


Fig.1. X-ray diffraction studies of prepared GO and GONF nanocomposite.

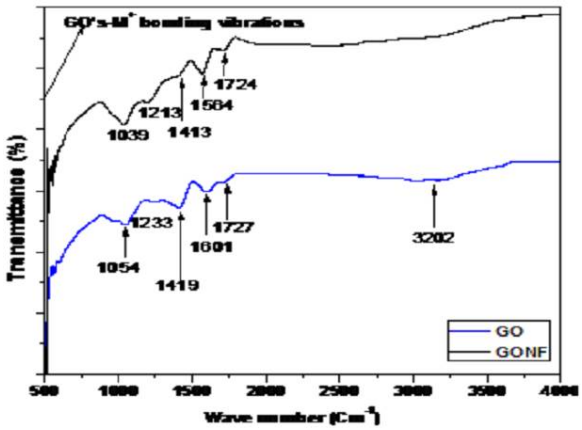


Fig.2. FT-IR spectrum of prepared GO, GONF nanocomposite.

or magnetization. The shifting of absorption peaks is associated with the formation of GONF from the GO. The sharp peaks at 550 – 500 cm^{-1} indicates the tetrahedral and octahedral Fe–O or Ni–O bonds.

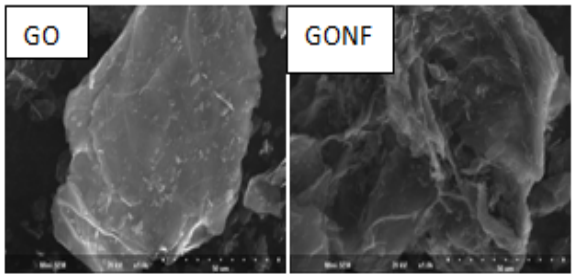


Fig.3. Scanning Electron Microscopy (SEM) images of bare GO, GONF, nanocomposite.

The BET surface area of GO increases from 2.59 to 135.99 m^2/g as particle size decreases from 1000 nm to 44.12 nm from the conversion of GO to GONF. It may be due to the formation of end product, GONF by the intercalation of cubic inverse spinel $NiFe_2O_4$ with GO. The modifications of GO with inverse spinel nickel ferrite increases its surface area in a

large size and is favorable for enhances its adsorption capacity. The significant changes in surface texture of GO upon intercalation of nickel ferrite lead to increases porosity with increasing surface area of GONF and rGONF. The resultant average pore volume and pore diameter of GONF indicates the nano-crystalline meso-porous composite. The BET size of GONF was closely agreement with XRD particles size (41.0 nm). The magnetic hysteresis curves (M–H) of nano magnetic inverse spinel GONF composite was recorded at 300 K indicated that the paramagnetic property of GONF was confirmed from magnetic susceptibility (χ) determined is $+1.8 \times 10^{-3}$ emu/cm^3·Oe. The SEM images of GO, GONF were shown in Fig. 3. The obtained surface images clearly indicate increase of porosity as decreasing particle size along with significant difference in surface morphology due to the formation of GONF from GO. The obtained porous surface morphology is favorable for surface interface studies such as adsorption. Hence, the prepared GONF can be used as adsorbents. In order to check the water treatment performance, Th(IV) batch adsorption studies were performed using the prepared GONF at pH 4.0. The effect of contact time for adsorption of Th(IV) onto GONF was investigated at fixed 0.3 g/L adsorbent dosage, pH 4.0, 8 mg/L initial metal ion concentration and 298 K to evaluate the equilibrium point and the results found that 120 min contact time is required for maximum adsorption of Th(IV). In order to check sorption mechasim of Th(IV) on to GONF pseduo-first and second-order kinetics models applied to the kinetic data of Th(IV) and the results confirmed that the sorption of Th(IV) was rate-limiting pseudo-second-kinetics. The Langmuir, Freundlich and Temkin's isotherm models were applied to the adsorption data and the obtained results observed that the sorption data was well tune with Langmuir isotherm. Hence, the sorption of Th(IV) onto GONF occurred through monolayer chemisorptions on homogeneous surface of GONF. The maximum adsorption capacities (Q_{max}) of the GONF for Th(VI) is 88.49 mg/g. Thermodynamic studies reveal that the sorption was increased as increase temperature from 298 to 328 K, indicates the chemisorptions. The overall obtained results demonstrated that the GONF as an effective sorbent for Th(IV) removal from aqueous acidic solutions.

CONCLUSIONS

The prepared GONF nanocomposite was confirmed by means of instrumental techniques, XRD, FT-IR, SEM and BET results. The average size of GONF is around 42 nm. The sorption kinetics was rate-limiting pseudo-second- order kinetics. The sorption of GONF is 88.49 mg/g. Thermodynamic studies reveal that the sorption was increased as increase temperature from 298 to 328 K, indicates the chemisorptions.

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