Adsorption removal of U(VI) from aqueous solutions using reduced graphene oxide based inverse spinel nickel ferrite nanocomposite as sorbent

(Remval of U(VI) by reduced graphene
oxide based inverse spinel nickel ferrite)

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Abstract— **The synthesized rGONF was 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. rGONF was successfully used for the removal of U(VI) by batch adsorption techniques. Batch kinetics studies revealed the sorption of U(VI) onto rGONF was well described by pseudo-second-order equation. The sorption equilibrium data of U(VI) was well tune to the Langmuir isotherm model than the Freundlich and Temkin's isotherm models. Hence, the sorption of U(VI) onto rGONF occurred through monolayer chemisorptions on homogeneous surface of rGONF. The maximum adsorption capacities (Q_{max}) of the rGONF for U(VI) is 200 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 rGONF as an effective sorbent for U(VI) removal from aqueous acidic solutions.**

Keywords— *reduced graphene oxide based nickel ferrite, U(VI) removal, adsorption.*

I.   Introduction

Uranium is one of the toxic and radioactive element occurs in the environment as hexavalent form. Uranium is used as a fuel in the nuclear reactors for the production of non-fossil energy. In 2008, the global uranium production for power generation was recorded as 40,000 tons, supplying approximately 15% of the world's electrical energy [1]. The release of uranium 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 [2]. Moreover, the recommended standard for [238]U in a drinking water is 20 mg/L [3].

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Due to increasing demand of uranium 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 uranium from contaminated wastewaters in order to prevention of its environmental impact and demand.

Among the purification techniques, the adsorption is considered as a simple and economical technique, when used low-cost adsorbents [4-5]. Carbon materials are very often used for as excellent adsorbents [6-8]. In recent years, adsorption techniques based on carbon or graphene materials has been used for the removal of uranium from aqueous environment [9-11]. Graphene has been chosen for the removal of uranium 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 [10]. However, the recovery of loaded graphene or graphen oxide has been changed. GO is a good candidate for constructing graphene-based composite materials with metal oxides [12]. 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 [13-15]. In the present study, synthesized GO based reduced nickel ferrite (rGONF) by chemical precipitation and was well characterized with suitable spectroscopy techniques in order to use for adsorption removal of U(VI) from aqueous solutions. Developed adsorption mechanism of U(VI) onto GONF and rGONF by means of surface characteristics studies.

II.   Materials and methods

A. *Preparation of rGONF*

For the preparation of rGONF, hydrazine hydrate (10 mL) was slowly added to the solution containing 0.5 g GO, 2:1 molar ratio of Fe^{3+}: Ni^2 (2.5g of $Fe(NO_3)_3 \cdot 9H_2O$ and

0.875g of Ni(NO$_3$)$_3$·9H$_2$O) at pH ≥12 at nitrogen atmosphere for the reduction of GO. Then, the solution temperature rose to 80°C with constant stirring, resulting in a black precipitation in the solution. After rapid stirring for 5 h, the solution was cooled down to room temperature. The resulted black precipitate was thoroughly washed with double distilled de-ionized water/ethanol and collected by magnetic separation, dried at 60°C under vacuum for 12 h.

B. *Adsorption removal of U(VI)*

U(VI) adsorption experiments were performed in a 50 mL of polyethylene falcon tube containing 0.2 g/L of rGONF and 50 mL of uranium standard solutions those pH were adjusted to 4.0. The Falcon tubes were shaken using a rotator shaker at room temperature for pre-determined equilibrium time (180 min) to get complete equilibration. The adsorbents were separated by using 0.45 μm membrane syringe filter and the concentration of U(VI) in the filtrate solution was determined using ICP–OES. The amount of adsorbed U(VI) was estimated from the difference of the U(VI) concentration in the aqueous phase before and after the adsorption studies.

III. Results and discussion

A. *Spectral Characterization of rGONF*

The X-ray diffraction results (XRD) (Fig.1) observed that the crystalline property of GO decreased as meso-pours carbonaceous material increased .in the modified rGONF. The strong peak at 2θ = 11.3^o confirmed the formation GO and was shifted to lower range (2θ = 8.9 and 5.6^o) at the rGONF [16]. The peaks at 2θ: 26.35, 35.60 and 43.20^o values indicated the presence of spinel nickel ferrite in the rGONF [17]. The size of rGONF was also clearly observed from the X-ray diffraction studies of rGONF, i.e. 32.12 nm (rGONF). 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 spinel nickel ferrite nano composites, GONF and rGONF.

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

Further FT-IR results (Fig.2) suggest the presence of epoxy and carbonyl functional groups along with carboxylic groups which confirming the formation of GO. FT-IR spectrum of rGONF indicates that the wavelengths of such functional groups present in GO were shifted to lower wavelengths regions upon magnetization of GO or the reduction of GONF. It is a common phenomenon for the formation of new product from bare compound by reduction magnetization. The shifting of absorption peaks is associated with the formation of GONF and rGONF from the GO. The sharp peaks at 550 – 500 cm^{-1} indicates the tetrahedral and octahedral Fe–O or Ni–O bonds.

The BET surface area of GO increases from 2.59 to 167.26 m^2/g as particle size decreases from 1000 nm to 34.46 nm from the conversion of GO to rGONF. It may be due to the formation of end product, rGONF by the intercalation of cubic spinel NiFe$_2$O$_4$ with GO. The reduction or modifications of GO with 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 and rGONF indicates the nano-crystalline meso-porous composite particles. The magnetic hysteresis curves (*M–H*) of nano magnetic spinel rGONF composite were recorded at 300 *K* indicated that the paramagnetic property of rGONF was confirmed from magnetic susceptibility (χ) determined from the slope of *M–H* curve. Magnetic susceptibility (χ) is +1.45 × 10^{-4} emu/cm^3·Oe.

B. *Adsorption removal of U(VI) using rGONF*

In order check the adsorption removal capacity of rGONF for the removal of U(VI), studied the adsorption characteristics. The effect of contact time for adsorption of U(VI) onto rGONF was investigated to evaluate the equilibrium point. Fig. 2 showed the adsorption of U(VI) at different time intervals with an initial U(VI) concentration 4.0 and 7.0 mg/L at pH 4.0 and 298 K. From the results, it can be clearly observed that the U(VI) adsorption was very fast during the first 45 min, and then slowly increased and reached an equilibrium at 180 min. The initial very fast adsorption of U(VI) can be explained by that rGONF have more freely available reactive sites with high surface area and relatively large pore sizes.
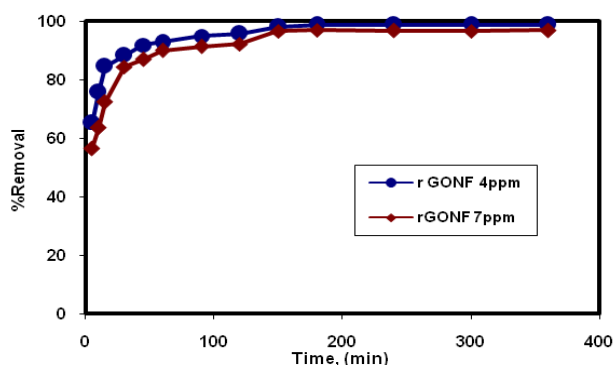

GO

rGONF

8.90   35.65
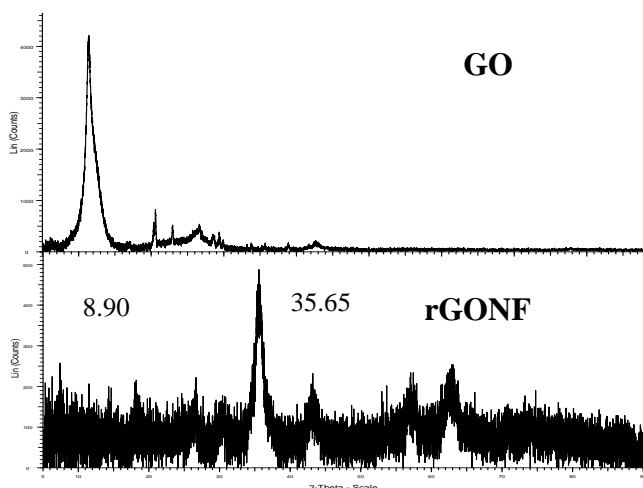
Fig.2. Contact time affect on the adsorption of U(VI) onto rGONF

Table 1. Isotherm parameters of U(VI) adsorption onto rGONF at pH 4.0 and room temperature (n=3, mean±SD).

Langmuir			Freundlich		
$q_{max, mgg}{}^{-1}$	$K_{L,}$ Lmg^{-1}	R^2	$KF,$ $mgg^{-1}(Lmg^{-1})^{1/n}$	n	R^2
200.00	1.78	0.995	141.65	1.43	0.977

The kinetics of U(VI) adsorption was evaluated by applying the pseudo-first order and pseudo-second-order kinetic models in order to understand the adsorption behavior of the prepared nanocomposites, GONF and rGONF. The resultant regression coefficient (R^2) and U(VI) uptake capacity (q_e) (from calculated and theoritical) (Fig, Table) values indicated that the pseudo-second-order kinetic was well fitted to the kinetic data for the adsorption of U(VI) onto rGONF. The kinetic results concluded that the adsorption kinetics of U(VI) onto rGONF was rate limiting diffusion kinetics. The Langmuir and Freundlich isotherm models were applied to the adsorption data and the results shown in the Tabe 1. The resultant correlation coefficients (R^2) value and SD values found that the U(VI) adsorption on rGONF, was well tune with Langmuir isotherm model than the other two isotherm models. The maximum adsorption capacities (q_{max}) of the rGONF, for U(VI) at 298K is 20 mg/g. The results indicate that the rGONF has higher adsorption capacity than the bare GO (60.0 mg/g).

IV. Conclusions

The prepared rGONF nanocomposites were confirmed by means of instrumental techniques, XRD, FT-IR, and BET results. The size of rGONF is 34.46 nm confirmed by BET X-rd results. The sorption kinetics was rate-limiting kinetics. The sorption of rGONF is 200 mg/g and was more than the bare GO(60.0 mg/g).

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