Adsorption of uranium from aqueous solution as well as seawater conditions by nitrogen-enriched nanoporous polytriazine

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HIGHLIGHTS

- NENP-1 as an adsorbent efficiently capture uranium from aqueous and simulated seawater.
- Remarkable adsorption capacity of 489 mg g\textsuperscript{-1} at 25 °C and at a pH of 7 was estimated.
- The adsorption of uranium by NENP-1 leads to achieve the WHO and USEPA targets.
- The adsorption behavior was fitted using linear and nonlinear regression analysis model.
- Retention of adsorption efficiency of 93\% after five consecutive adsorption cycles.

ABSTRACT

Efficient removal of uranium from both aqueous and simulated seawater conditions using a nitrogen enriched nanoporous polytriazine (NENP-1), is reported. A maximum adsorption capacity of 489 mg g\textsuperscript{-1} with 97.8\% adsorption efficiency was estimated at 25 °C and pH of 7, when 10 mg of NENP-1 was introduced to 10 mL of 500 mg L\textsuperscript{-1} aqueous uranium solution. Both linear and non-linear regression analyses have been performed. The adsorption follows a pseudo second order kinetics and fitted well with the Langmuir adsorption isotherm model. The negative values of \(\Delta S (-52.08 \text{J mol}^{-1} \text{K}^{-1})\), \(\Delta H (-24.37 \text{kJ mol}^{-1})\) and \(\Delta G\) indicate that the uranium adsorption is a spontaneous exothermic process with a reduced entropy. Retention of 93\% activity even after five consecutive cycles, achieving (0.012 mg L\textsuperscript{-1}) the permissible limits of the WHO (0.015 mg L\textsuperscript{-1}) and USEPA (0.03 mg L\textsuperscript{-1}) and adsorption of uranium (50 mg g\textsuperscript{-1}) from simulated seawater have made this a potential adsorbent for industrial applications.

A R T I C L E  I N F O

Keywords:
Uranium removal
WHO and USEPA permissible limits
Microwave-assisted synthesis
Nitrogen enriched nanoporous polytriazine (NENP)
Simulated seawater

1. Introduction

The high demand of energy after the industrialization has led to the excessive use of fossil fuels resulted in an extraordinary global warming scenario \cite{1-3}. To sustain the growth, renewable and nuclear energies are the sources of energy for electricity generation leaving less carbon footprints \cite{4}. It was suggested by Intergovernmental Panel on Climate Change (IPCC) that the share of renewable energy and nuclear power...
for electricity generation needs to increase from approximately 30 to 80% by 2050. [5]. Nuclear energy has much higher energy density compared to all other energy options. The renewable sources like wind, solar, and hydroelectric power are inconsistent and could not perform in adverse environmental conditions such as during dry, overcast (or overnight), and drought-riddled times. [6]. Moreover, large magnitude of required battery storage capabilities is a bottleneck. Similarly, the major limitations of nuclear energy include the availability of nuclear fuel, effluent management and uncertainty of the nuclear safety. [7]. At present, around 31 countries having a total of 388 reactors with a combined installed capacity of 333 GW are operating. [8]. These produce enormous amount of nuclear waste rich in uranium, which is a hazard to the environment and humans owing to its radioactive and chemical toxicity. [9–11]. Thus, efficient removal of uranium from these nuclear waste as well as other water bodies could make the uranium based nuclear energy economically and environmentally sustainable. [12,13].

World Health Organization (WHO) and United States Environmental Protection Agency (USEPA) have defined the maximum permissible level of uranium in drinking water to be 0.015 and 0.030 mg L$^{-1}$, respectively. [14,15]. This, in turn has forced the scientific community to develop suitable technology for removing uranium from the effluents prior to disposal. [16–20]. Moreover, recovery of uranium from the effluent would help in the sustainable development of nuclear energy. Among various methods, the noteworthy processes include precipitation [21], solvent extraction [22], membrane processes [23], ion-exchange [24], chelation [25], and adsorption by high surface area nanoporous materials. [21,26].

Among various explored methods, solar light induced degradation and adsorption are considered as widely used technologies for wastewater treatment in industries because of various advantages such as low cost, high efficiency, low energy consumption and simple operation. [27–30]. Recently, adsorbents such as metal oxides [31], activated carbon [32], barium titanate [33], activated carbon-silica aerogel composite materials [34], gallo-cyanine grafted hydro-gel [35], ion-imprinted polymers [36], polyphenolic compounds [37], mesoporous silica [38], porous organic polymers (POPs) [26], metal organic frameworks (MOFs) [39], zeolites [40], and graphene oxide [19], have been employed. Moreover, functionalization of the adsorbents also improves the performance. For example, mesoporous silica functionalized with phosphonic [41,42], amidoxime [38], and alkylphosphine oxide [43], groups have shown improved uranium adsorption. Similarly, a wide variety of functionalities have been introduced into the graphene oxides to enhance the adsorption efficiency. [44,45]. In some of the recent reports, MOFs [46], chitosan [47], zeolites [48], and POPs [26], functionalized with amine and amidoxime groups have been explored. From all these literatures, a common phenomenon was observed that the increase in the electron density on the surface of the adsorbents have improved the adsorption capacity. However, a common practice followed in most of the reported research is the functionalization of the pristine materials by post-synthesis methods. Although, the post-synthesis functionalization is advantageous for incorporation of functional group distribution in the adsorbents, pore blockage and use of expensive precursors for the post-synthesis functionalization. In this article, a nitrogen enriched nanoporous polytriazine (NENP-1) framework is reported that shows efficient capture of uranium in both low and high concentration in aqueous solution as well as from simulated seawater conditions. Moreover, the material has shown to adsorb uranium to an extent that satisfy the permissible limits of both the WHO and USEPA.

2. Experimental section

2.1. Synthesis of nitrogen enriched nanoporous polytriazine (NENP-1)

The synthesis of NENP-1 was carried out following our recent reports using precursors melamine and cyanuric chloride [59–61]. Typically, 1 mmol each of melamine and cyanuric chloride dissolved in 20 mL of DMSO reacted to form NENP-1 in a microwave reactor at 140 °C for 30 min with microwave power of 400 W. The obtained white powder was filtrated and washed with water and THF and dried at 100 °C.

2.2. Characterization

FTIR (Perkin Elmer Spectrum Two spectrophotometer) and XPS (PHI 5000 Versa Probe III) were used for the structural characterization of the NENP-1. The C/H/N/S elemental analysis was carried out using Thermo Flash 2000. The FE-SEM images and EDAX were recorded in TESCAN MIRA3. The N$_2$ sorption experiment was performed using Autosorb-iQ2 (Quantachrome Instruments, USA) at 77 K and pore size distribution (PSD) was determined by DFT method. The uranium content was estimated using inductively coupled plasma optical emission spectroscopy (ICP-OES; Teledyne Leeman Labs, Prodigy SPEC).

2.3. Uranium adsorption in aqueous solution

Uranium sorption experiments were carried out using a stock solution [2.11 g of UO$_2$(NO$_3$)$_2$·6H$_2$O in 1 L of DI water]. In the adsorption studies, 10 mg of NENP-1 was introduced into 10 mL of uranium solution of desired concentration. The adsorption experiments at pH of 3, 4, 5, 6, 7 and 8 were investigated by adjusting the pH using 0.1 M HNO$_3$ and 0.1 M NaOH. The adsorption isotherms and adsorption capacities were investigated at various uranium concentrations from 5 to 1000 mg L$^{-1}$. The adsorption kinetics was investigated at contact times.
of 5, 30, 60 and 120 min and the thermodynamics was studied at 278, 298, 308, 328 and 348 K.

The equilibrium adsorption capacity and adsorption efficiency were estimated using Eqs. (1) & (2) respectively [50];

\[
q = \frac{(C_0 - C_e)V}{W}
\]

\[
\%E = \frac{(C_0 - C_e)}{C_0} \times 100
\]  

(1)

(2)

where, \(q\) is the adsorption capacity (mg g\(^{-1}\)), \(C_0\) and \(C_e\) are the initial and equilibrium concentrations of adsorbate (mg L\(^{-1}\)), \(V\) is the volume of test solution (L), \(W\) is the weight of adsorbent (g) and \(E\) is the adsorption efficiency (%).

2.4. Linear and nonlinear methods for equilibrium isotherm analysis and kinetic study

Linear regression method is one of the most common methods to determine the best-fitted adsorption isotherms and kinetic models. However, the transformation of nonlinear equations to linear forms provides erroneous result and hence, misrepresent the fit. On the other hand, the nonlinear method is rigorous, comparatively more complex, and requires an error analysis to evaluate the fit of an equation to the given experimental data. In the present study, both linear and nonlinear regression methods were used. Two isotherms (Langmuir and Freundlich) and two kinetic models (pseudo first order and pseudo second order) have been used. For nonlinear regression method, MATLAB® was employed for optimization of the parameters. Three error analysis methods were used in this optimization procedure as well as for comparison with linear method on the basis of goodness-of-fit [Eqs. (3)–(5)]: coefficient of determination (R\(^2\)), residual root mean square error (RMSE) and chi-square (\(\chi^2\)).

\[
R^2 = 1 - \frac{\sum (q_{-exp} - q_{-pred})^2}{\sum (q_{-exp} - \bar{q}_{-exp})^2}
\]

\[
RMSE = \sqrt{\frac{1}{n-2} \sum_{i=1}^{n} (q_{exp} - q_{pred})^2}
\]

\[
\chi^2 = \sum \frac{(q_{exp} - q_{pred})^2}{q_{exp}}
\]

(3)

(4)

(5)

where, \(q_{exp}\) is the adsorption capacity obtained from experiment, \(q_{pred}\) is the adsorption capacity predicted from the isotherms or kinetic models, \(\bar{q}_{exp}\) is the average of \(q_{exp}\) and \(n\) is the number of experimental observations. Higher R\(^2\) and smaller values of standard errors (RMSE and \(\chi^2\)) signify the better fitting of the data.

2.5. Uranium desorption

To evaluate the reusability of the adsorbent, the adsorption and desorption experiments were performed for five consecutive cycles. In a typical experiment 50 mg of NENP-1 was introduced to 50 mL of stock solution (\(C_0 = 500\) mg L\(^{-1}\)) and stirred for 60 min at 25 °C, followed by centrifugation. The regeneration of the adsorbent was performed by washing with 0.1 M HCl solution, three times and finally dried at 80 °C for 12 h.

2.6. Uranium adsorption from simulated seawater condition

The performance of NENP-1 for the uranium adsorption in seawater condition was evaluated following the previous report [38]. Simulated seawater was prepared by dissolving 0.017 g of UO\(_2\)(NO\(_3\))\(_2\)-6H\(_2\)O, 25.6 g of NaCl and 0.193 g of NaHCO\(_3\) in 1 L of DI water. To 200 mL of the simulated seawater, 50 mg of NENP-1 was added and the resulting suspension was stirred for 24 h. To calculate the uranium content, the supernatant was subjected to ICP-OES investigation.

3. Results and discussion

3.1. Structural and textural characterisation of NENP-1

The successful condensation of NENP-1 (Fig. S1) was investigated by FTIR [59–61]. The elemental composition of NENP-1 investigated using C/H/N/S analyzer indicates the composition of 37.9, 50.5 and 2.4 wt% of C, N and H, respectively, which matched with the theoretical values of 35.8, 62 and 1.49 wt% with some deviation as expected considering the nature of the specimen [59–61]. Further, the chemical environment of the elements present in the specimen was studied using XPS (Fig. 1a) and high resolution XPS spectra [59,61]. For example, the high-resolution C 1s spectrum (Fig. 1b) shows the peaks at 284.7, 286.4 and 288.1 eV assigned to sp\(^3\)-C, sp\(^2\)-C of the triazine ring and oxidized carbon or graphitic impurity arises from the carbon tape used for XPS, respectively [59,61–68]. Similarly, the peaks at 398.3 and 399.6 eV in the N 1s XPS spectrum (Fig. 1c) are due to pyridine (N6) and pyrrolic (N5) nitrogen, respectively [59,61–68].

The N\(_2\) sorption isotherm of NENP-1 (Fig. S2a) is a type-I isotherm indicating the microporous nature. A narrow hysteresis in the high pressure region further indicates the presence of mesopores forming a hierarchical pore structure. This was confirmed by the observation of a narrow PSD centred at 1.3 nm along with mesopores centred at 4.4 and 7.1 nm (Fig. S2b). The specific surface area estimated using the BET
comes almost zero at a dominating species in the aqueous solution and its concentration be-

the neutral species UO$_2$(OH)$_2$, and anion species [(UO$_2$)$_3$(OH)$_7$] and [(UO$_2$)$_3$(OH)$_5$]$^+$. Moreover, there may be slight deviation in the concentration of these species at different pH values. Among the various models used to study the adsorption isotherms, the Langmuir and Freundlich models were more acceptable and have been extensively used in the literatures [50,73–75]. The linear and nonlinear forms of Langmuir and Freundlich models can be presented as [76–78];

\[
\text{Langmuir (Linear) } C_e = \frac{C_e^{max}}{q_{eq}} + \frac{1}{q_{max}b}
\]

\[
\text{Langmuir (Nonlinear) } q_e = \frac{q_{max}bC_e}{1 + bC_e}
\]

\[
\text{Freundlich (Linear) } \log q_e = \frac{\log C_e}{n} + \log k_f
\]

was performed at different pH values. Moreover, both lower and higher uranium concentrations of 5 and 500 mg L$^{-1}$ were employed to check the validity. As shown in Fig. 2b, in both the lower and higher uranium concentrations, as expected the maximum adsorption capacity was achieved at pH of 7 when 10 mg of the adsorbent was introduced to 10 mL of the adsorbate solution. Either increasing or decreasing the pH has adversely affected the adsorption capacity. A maximum adsorption capacity of 489 mg g$^{-1}$ was achieved when the initial concentration of the solution was 500 mg L$^{-1}$ with an adsorption efficiency of 97.8%. Similarly, at the lower concentration of 5 mg L$^{-1}$, an adsorption capacity of 4.7 mg g$^{-1}$ was recorded with the efficiency of 84%. These results indicate the effectiveness of the adsorbent for uranium removal in both lower and higher uranium concentrations.

Further, the adsorption experiments were carried out by varying the adsorbent dosage of 5, 10, 20, 30, 40 and 50 mg with an initial absorbate concentration of 500 mg L$^{-1}$. As shown in Fig. 3a, although, there was a marginal decrease in the adsorption capacity from 570 to 489 mg g$^{-1}$ on increasing the adsorbent dose from 5 to 10 mg, but the substantial increase in the adsorption efficiency from 57 to 97.8% has indicated that 10 mg of adsorbent is ideal for the adsorption experiments. Moreover, on further increasing the adsorbent dose to 50 mg, no further increase in the adsorption efficiency was observed and rather a substantial decrease in the adsorption capacity could be seen. Thus, an adsorbent amount of 10 mg was chosen as the optimum dose for subsequent experiments. The observed adsorption capacity of 489 mg g$^{-1}$ is better than some of the reported porous adsorbents such as, mCMC-g-PANI [71], amidoxime-functionalized PAF-1 [26], (COF-TpDb-AO) [9], nitro and amino-functionalized MOFs [39], Sx-LDH [13], and comparable to the amino functionalized SBA-15 [16], manganese oxide nanoparticles [31], and PA/PANI/FeOOH [72] (Table S1).

The initial adsorbate concentration is another important parameter that determines the effectiveness of an adsorbent. In the present research, concentration of uranium was systematically varied from 5 to 1000 mg L$^{-1}$ keeping the adsorbent amount fixed at 10 mg. As shown in Fig. 3b, there was a continuous increase in the adsorption capacity on increasing the molar concentration of uranium up to 500 mg L$^{-1}$, however, there was no appreciable change above this concentration. This indicates that the uranium concentration of 500 mg L$^{-1}$ is the equilibrium concentration and this concentration was chosen to investigate the physical parameters. The effect of contact time on the adsorption capacity provides useful information on the adsorption kinetics. On varying the contact time from 5 to 120 min, a maxima of adsorption capacity was achieved at the contact time of 60 min and on further increasing the contact time didn’t improve the adsorption capacity (Fig. 3c). Therefore, 60 min was considered to be the optimum contact time for the efficient adsorption. The effect of temperature on the adsorption capacity was further studied to estimate the thermodynamic parameters (Fig. 3d). As expected, the adsorption capacity decreases on increasing the temperature which confirms the exothermic nature of the adsorption process.

3.2. Uranium batch adsorption studies

Before starting the investigation on the uranium adsorption by the NENP-1, a thorough literature studies on the speciation of uranium ion as a function of pH in the aqueous solution was carried out. It was well documented by several reports that at lower pH of < 4, UO$_2^{2+}$ is the dominating species in the aqueous solution and its concentration becomes almost zero at a pH greater than 6 [16,44–47]. At pH ~ 7, the dominating species is cationic [(UO$_2$)$_3$(OH)$_3$]$^+$ both at lower and higher uranium concentration. However, at a higher pH of 8 and above, the neutral species UO$_2$(OH)$_2$, and anion species [UO$_2$(OH)$_3$]$^-$ and [(UO$_2$)$_3$(OH)$_7$]$^-$ are the dominating species [16,39,44–47,69,70]. Moreover, there may be slight deviation in the concentration of these species at different uranium concentration as reported by Huynh et al. [16]. In order to understand the feasibility of the adsorbent for the uranium adsorption in aqueous solution, the surface charge of NENP-1 was investigated by zeta potential (ζ). As can be seen in Fig. 2a, ζ value varies from positive to negative on increasing the pH with the isoelectric point reached at the pH of 6.4. Thus, on comparing the speciation of uranium and the ζ-values, it can be expected that a lower pH may not be suitable for the adsorption of uranium by NENP-1 due to the positive charges both at the surface of the adsorbent as well as the dominating species UO$_2^{2+}$. However, at pH of 6 or 7 we can expect a better adsorption capacity due to the attractive interaction between the negatively charged adsorbent surface and the dominating ion [(UO$_2$)$_3$(OH)$_3$]$^+$. In order to support the assumptions, the adsorption of uranium ion equation (SA$_{BET}$) of the specimen was found to be 840 m$^2$ g$^{-1}$ with a total pore volume of 0.71 cm$^3$ g$^{-1}$ at P/P$_0$ of 0.95.
Freundlich (Nonlinear) \[ q_e = k_f q_e^{1/n} \] (9)

where, \( q_{\text{max}} (\text{mg g}^{-1}) \) is the maximum monolayer adsorption capacity, \( b \) is a Langmuir equilibrium constant \((\text{L mg}^{-1})\) which is related to the energy of adsorption, \( K_f \) is a Freundlich constant \([\text{mg g}^{-1} (\text{L mg}^{-1})^{1/n}]\), and \( n \) is the Freundlich exponent (dimensionless) indicating the extent of adsorption and degree of nonlinearity between solution concentration and adsorption.

Linear [Eqs. (6) and (8)] and nonlinear [Eqs. (7) and (9)] regression methods were employed to the experimental data and the parameters were calculated (Table 1). Fig. 4 illustrates the fitting of different forms of above mentioned isotherms. Among these isotherms, higher \( R^2 \) and lower RMSE and \( \chi^2 \) were observed for Langmuir model in comparison to Freundlich model. When linear and nonlinear methods were compared for Langmuir model, the parameters obtained were slightly different. However, the error functions indicate that better fitting obtained by non-linear regression method. On the other hand, the parameters generated by linear and nonlinear methods were different for Freundlich isotherm. This could be attributed to difference in efficiency of both methods as well as limitations of linear regression method. The higher value of \( R^2 \) and lower values of RMSE and \( \chi^2 \) obtained for nonlinear method indicates that nonlinear method provides better fitting and therefore better estimation of parameters [78].

3.4. Kinetics study

To predict rate of adsorption, kinetic parameters have been calculated by plotting the linear and nonlinear form of pseudo first order and pseudo second order kinetic models as given in following equations [76–78];

Pseudo first order (linear) \[ \ln(q_{\text{max}} - q_t) = \ln q_{\text{max}} - k_{\text{ad}} t \] (10)

Pseudo first order (nonlinear) \[ q_t = q_{\text{max}} (1 - e^{-k_{\text{ad}} t}) \] (11)

Pseudo second order (linear) \[ \frac{t}{q_t} = \frac{1}{k_{\text{ad}} q_{\text{max}}} + \frac{1}{q_{\text{max}}} t \] (12)

Pseudo second order (nonlinear) \[ q_t = \frac{k_{\text{ad}} q_{\text{max}}^2 t}{1 + k_{\text{ad}} q_{\text{max}}^2 t} \] (13)

where, \( q_{\text{max}}, q_t, \) and \( k_{\text{ad}} \) are maximum adsorption capacity, adsorption capacity at time \( t \) and adsorption rate constant, respectively.

Pseudo first order kinetics assumes that the rate of adsorption depends upon diffusion step, however, for pseudo second order kinetics it

Table 1

<table>
<thead>
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<th>Models</th>
<th>Langmuir</th>
<th>Freundlich</th>
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<tbody>
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<td>Linear method</td>
<td>Nonlinear method</td>
</tr>
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<td>758.316</td>
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<td>Parameters ( b (\text{L mg}^{-1}) )</td>
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<td>RMSE</td>
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<tr>
<td></td>
<td>( \chi^2 )</td>
<td>20.382</td>
</tr>
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</table>
depends upon the number of vacancies on adsorbent and mainly con-
trolled by chemical adsorption mechanism [79,80]. Fig. 5 depicts the
fitting of linear and nonlinear forms of kinetic models, and Table 2
summarizes the values of kinetic parameters and error function corre-
sponding to these fittings. The pseudo second order kinetic model ex-
hibits higher $R^2$ and lower RMSE and $\chi^2$ values as compared to the
pseudo first order model. Therefore, the adsorption of uranium follows
pseudo second order adsorption process. As observed during isotherms
study, the higher value of $R^2$ and lower values of RMSE and $\chi^2$ were
obtained for nonlinear method in both types of kinetic models. There-
fore, it can be concluded that nonlinear method provides better fit-
ting and therefore better estimation of parameters. These observations
support our assumption that the adsorption is mainly due to exchange
of electrons between adsorbent and adsorbate. Therefore, the adsorp-
tion of uranium on the surface of NENP-1 could be due to chemisorp-
tion.

3.5. Thermodynamic study

To get the better understanding of thermodynamics of the adsorp-
tion process, the thermodynamic parameters like $\Delta H$ and $\Delta S$ were cal-
culated using the following equations:

$$k_d = \frac{q_d}{C_e}$$  \hspace{1cm} (14)

$$\ln(k_d) = \frac{\Delta S}{R} - \frac{\Delta H}{RT}$$  \hspace{1cm} (15)

$$\Delta G = -RT \ln(k_d)$$  \hspace{1cm} (16)

where, $R$, $T$ and $k_d$ are universal gas constant, temperature (K) and
distribution coefficient, respectively (Fig. 6).

The values for $\Delta S$ and $\Delta H$ were estimated to be $-52.08 \text{ J mol}^{-1} \text{ K}^{-1}$
and $-24.37 \text{ kJ mol}^{-1}$, respectively. Negative $\Delta H$ value confirms the
exothermic nature of adsorption process. Moreover, it is well known
that for pure physical adsorption, the value of $\Delta H$ lies below
$-20 \text{ kJ mol}^{-1}$ [75]. As the estimated $\Delta H$ value is marginally higher
than the pure physisorption, the conclusion derived from the kinetic
study was again supported by the thermodynamic investigation.
Moreover, negative $\Delta S$ value specifies that randomness decreased at the
adsorbent and adsorbate interface during the adsorption process. The
$\Delta G$ values calculated by using Eq. (16), were found to be $-9.40$,
$-9.40$, $-8.13$, $-7.05$ and $-6.35 \text{ kJ mol}^{-1}$ at 278, 298, 308, 328 and
348 K, respectively. The negative values indicate that the adsorption
process is spontaneous in nature.

3.6. Possible mechanism

In order to understand the interaction that leads to a higher ur-
nium adsorption, XPS analysis of the specimen after uranium ad-
sorption (NENP-1U) was carried out and compared with the pristine
sample (Fig. 1). It can be seen from Fig. 1c that the N 1s of triazine ring
has shifted from 398.3 to 398.6 eV and N 1s of the NH group has shifted
from 399.6 to 400.1 eV. This indicates that the electron density of the
electron rich NENP-1 has interacted with the positively charged ur-
nium ion. This was further con

formed from the C 1s spectra, where a
shift in the binding energy of the carbon in the triazine ring from 286.4
to 286.5 eV was recorded while leaving C 1s peaks from other carbons
unchanged (Fig. 1b). Such shifts in the binding energy of different
elements in the XPS spectra were also earlier reported by several re-
search groups [13,31,69,81]. A schematic representation showing the
possible interactions of the uranium ion with the pore surface is shown
in Scheme 1. The quantitative EDAX analysis confirms the presence of
uranium (Tables S2 & S3). Further, the EDAX mapping indicates a
uniform distribution of the uranium throughout the specimen as shown
in Fig. S3.
3.7 Reusability studies

For practical application, it is very much important to investigate the adsorption recyclability as it is significant for an effective and economical adsorption process. Herein, reusability of the adsorbent was investigated by performing five consecutive adsorption-desorption cycles (Fig. 7). It is important to note that even after five consecutive cycles, the remarkable adsorption efficiency of 93% was retained, which further signifies its applicability as a superior adsorbent for uranium removal from industrial effluent.

3.8 Achieving the WHO and USEPA permissible limits

The high adsorption capacity and efficiency, along with the recyclability of the adsorbent is very important for practical applications. These have been achieved using the NENP-1 as adsorbent. However, another important parameter that can be the bottleneck in using the adsorbent for practical applications is the effectiveness of the adsorbent for removing the uranium from the industrial effluent to an extent that satisfy the permissible limits of two of the major organizations, WHO and USEPA.

As the uranium concentration in most of the effluents lies below 5 mg L\(^{-1}\), a thorough investigation has been carried out at a lower uranium concentration of 5 mg L\(^{-1}\). As expected, the isotherms (Fig. S4) and kinetics (Fig. S5 and Table S4) of the adsorption followed the same trend also at a lower concentration of 5 mg L\(^{-1}\). However, there was a substantial difference in the adsorption efficiency. Unlike for 500 mg L\(^{-1}\) solution where the maximum adsorption efficiency was achieved when 10 mg of the adsorbent was introduced, at a lower concentration of 5 mg L\(^{-1}\) as shown in Fig. 8, there was a continuous increase in the adsorption efficiency recorded up to 99.8% for the 50 mg of the adsorbent. This leads to almost complete adsorption of the uranium leaving only 0.012 mg L\(^{-1}\) in the solution, which is below the WHO limit of 0.015 mg L\(^{-1}\) and USEPA limit of 0.03 mg L\(^{-1}\).

3.9 Adsorption in simulated seawater condition

Uranium enrichment from seawater using suitable adsorbent is of
great significance for resource sustainability and environmental safety concerns. It has been observed that uranium adsorption capacity of 50 mg g\(^{-1}\) could be achieved using NENP-1 as an adsorbent under seawater conditions, when 50 mg of NENP-1 is introduced into 200 mL of simulated seawater with contact time of 24 h. Herein, high adsorption capacity and high affinity of NENP-1 towards uranium species makes the material an attractive adsorbent for uranium recovery in seawater conditions.

4. Conclusions

The NENP-1, a nitrogen enriched (N of \(~50\) wt\%) nanoporous polytriazine with specific surface area of 840 m\(^2\) g\(^{-1}\) and hierarchical pore structure, has been used as an adsorbent for the removal of uranium from aqueous solution and simulated seawater. Remarkable adsorption capacity of 489 mg g\(^{-1}\) and adsorption efficiency of 97.8\% were recorded at 25 °C and at a pH of 7 in aqueous medium.
In this direction, the adsorbent NENP-1 has been recognized as a good candidate for practical applications. In their experimental outcome and thorough literature investigation, they concluded that the NENP-1 could be used as a superior adsorbent for the removal of uranium from industrial effluents leading to address the environmental concerns of the nuclear power plant effluents with reusability of the collected uranium as well as uranium enrichment from seawater.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/jcej.2019.122236.

References


Fig. 8. Effect on adsorption capacity of NENP-1 as a function of adsorbent amount at lower uranium concentration of 5 mg L−1.

Thermodynamic calculations revealed a spontaneous exothermic adsorption process with negative ΔG and ΔH values. The recyclability up to five continuous cycles has shown a remarkable retention of adsorption efficiency of 93%. The efficiency of the adsorbent both at higher and lower uranium concentration of 500 and 5 mg L−1, respectively, have made this adsorbent a good candidate for practical applications. In this direction, the efficient adsorption of uranium at a lower initial concentration of 5 mg L−1 by the adsorbent NENP-1 leaving behind a concentration that is better than the permissible limits of the WHO and USEPA have made it stand out among its peers. Thus, based on the experimental outcome and thorough literature investigation, it can be concluded that the NENP-1 could be used as a superior adsorbent for removal of uranium from industrial effluents leading to address the environmental concerns of the nuclear power plant effluents with reusability of the collected uranium as well as uranium enrichment from seawater.


