Sequestration of p-nitrophenol from liquid phase by poly(acrylonitrile-co-acrylic acid) containing thioamide group

J. W. Soo, L. C. Abdullah, S. N. A. M. Jamil, and A. A. Adeyi

ABSTRACT

In this paper, the adsorptive performance of synthesized thiourea (TU) modified poly(acrylonitrile-co-acrylic acid) (TU-P(AN-co-AA)) polymeric adsorbent for capturing p-nitrophenol (PNP) from aqueous solution was investigated. TU-P(AN-co-AA) was synthesized via the redox polymerization method with acrylonitrile (AN) and acrylic acid (AA) as the monomers, then modified chemically with thiourea (TU). Characterization analysis with Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), elemental microanalysis for CHNS, zeta potential measurement, Brunauer–Emmett–Teller (BET) surface analysis and thermal analyses were carried out to determine the morphology and physico-chemical properties of the synthesized polymer. The characterization results indicated successful surface modification of polymer with TU. The performance of TU-P(AN-co-AA) for the removal of PNP was investigated under various experimental parameters (adsorbent dosage, initial adsorbate concentration, contact time and temperature). The results demonstrated that the Freundlich isotherm model and pseudo-second-order kinetic model best described the equilibrium and kinetic data, respectively. Thermodynamic studies showed that the uptake of PNP by TU-P(AN-co-AA) was spontaneous and exothermic in nature. The results of the regeneration studies suggested that the TU-P(AN-co-AA) polymer is a reusable adsorbent with great potential for removing PNP from wastewater.

Key words: p-nitrophenol, poly(acrylonitrile-co-acrylic acid), polymeric adsorbent, regeneration, thioamide groups

HIGHLIGHTS

- Poly(AN-co-AA) was synthesized using free radical polymerization and modified with thiourea.
- The polymeric adsorbent possessed multi-functional groups with negative surface charge.
- PNP sequestration onto TU-P(AN-co-AA) adsorbents was high.
- Equilibrium and kinetic models were employed for the experimental data analyses.
- The regeneration study indicated the stability and reusability of the thioamide-modified polymer.

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INTRODUCTION

Water scarcity is one of the main global challenges that, to be solved, requires urgent attention. At the same time, the rate of water pollution increases daily, due to the rising water demand for rapid industrialization and steady population growth (Muthamilselvi et al. 2016). The uses of p-nitrophenol (PNP) in recent times by numerous industries for producing various products including pesticides, fungicides and engineering polymers to cope with the increasing demands from consumers and disposal of industrial wastewater has added PNP to the environment (Ofomaja & Unuabonah 2013; Muersha & Pozan Soylu 2018). PNP is known to be highly toxic, highly bio-accumulative in food chains and carcinogenic to living things; it is capable of causing adverse impacts to biological systems and serious damage to internal organs (Govindhan et al. 2015; Aamir et al. 2019; He et al. 2019; Karami & Zeynizadeh 2019). Hence, it is important to treat water sources polluted with PNP for the safety of the environment and public health.

Wastewater treatment methods developed for PNP removal include adsorption, electrochemical oxidation, biological treatment and photocatalysis (Villegas et al. 2016; Ramírez et al. 2017). Adsorption stands out amongst the available treatment methods due to its cost efficiency, simplicity and high pollutant removal efficiency (Karami & Zeynizadeh 2019). However, the performance of adsorbents depend on the affinity of the adsorbate and the adsorbent. Various adsorbent materials have been investigated for their potential for pollutant removal from wastewater, including natural clay, silica gel and activated carbon (Khireddine et al. 2018; Tien 2019). However, some of the adsorbents have major drawbacks, including high regeneration cost, low adsorption capacity and generation of unwanted products.

Therefore, polymeric adsorbents have been selected due to their ease of preparation, efficiency, low cost and feasible regeneration. Many studies involving investigation of the surface modification or functionalization of polymeric adsorbents for adsorptive performance enhancement and pollutant selectivity have been published recently. For instance, Shao & Huang (2017) prepared N-vinylimidazole-modified hyper-cross-linked resins as the adsorbent for the removal of PNP from aqueous solution. Similarly, Wang et al. (2017) reported the effect of different aminiating agents in the preparation of amino-modified hyper-cross-linked resins on the sorption performance of p-chlorophenol (PCP). In addition, Ali & Saeed (2016) investigated the effect of chemical modification on banana peel as an adsorbent for the removal of phenol from aqueous medium. Istratie et al. (2017) synthesized styrene-divinylbenzene copolymer functionalized by carboxylic acid groups to investigate its performance for the removal of PNP.

In this study, thiourea-modified poly(acrylonitrile-co-acrylic acid), denoted as TU-P(AN-co-AA), was synthesized through the redox polymerization process and further modified chemically with thiourea (TU) to introduce thioamide functional groups to the polymer chain. The selection of TU as a modification agent was for the incorporation of thioamide functional groups that could act as proton donors, with the nitro functional group of PNP being proton acceptors. This allowed the formation of hydrogen bonds between the two functional groups, thereby enhancing PNP removal from aqueous solution (Liu et al. 2014). The characterization, adsorption isotherms, adsorption kinetics and thermodynamics of the synthesized adsorbent were investigated.

MATERIALS AND METHODS

Materials and chemicals

Acrylonitrile (AN), acrylic acid (AA) were purchased from Acros Organics, New Jersey, USA. Sodium bisulphate (SBS), potassium persulfate (KPS), methanol, ethanol and thiourea (TU) were purchased from R&M Chemicals, Essex, UK. All chemical reagents were analytical grade and no further purification were carried out prior to use. The p-nitrophenol (PNP) (C₆H₅NO₃; molecular weight: 139.11 g/mol; maximum wavelength: 401 nm) used as the adsorbate was procured from Acros Organics, New Jersey, USA.

Preparation of thiourea-modified poly(acrylonitrile-co-acrylic acid)

Redox polymerization, with AN and AA at a feed ratio of 97:3, was conducted at 60 °C under nitrogen gas (N₂) in a three-necked round-bottom flask, which was fitted with a water condenser. The 200 mL deionized water that acted as the reaction medium was purged with N₂ gas for 0.5 hour prior to the addition of monomers and initiators. 2.16 g of KPS and 2.09 g of SBS were added to the reaction medium as the reaction initiator, together with a 275 mmol of AN and 29 mmol of AA as monomers. The mixture was stirred with a magnetic stirrer for 2 hours at 200 rpm. The resulting P(AN-co-AA) polymer was precipitated in methanol for 1 hour and washed successively with a mixture of methanol and deionized water. The
polymer was then dried until it reached a constant weight in an oven at 40 °C. This polymer synthesis method is based on Adeyi et al. (2019).

The synthesized P(AN-co-AA) polymer was then modified with TU: 6 g of TU and 100 mL of ethanol/deionized water (1:2 by volume) were stirred and mixed at 70 °C at 200 rpm agitation speed for 0.5 hour. Next, 5 g of the prepared P(AN-co-AA) polymer was added to the mixture and the modification reaction was left for 5 hours at 100 °C. The resulting TU-P(AN-co-AA) polymer solids were rinsed with an ethanol/deionized water mixture, filtered and dried overnight in an oven at 50 °C. The drying process continued until a constant weight was reached. The overall synthesis and modification process for TU-P(AN-co-AA) are shown in Figure 1.

Instrumentation
The morphologies of synthesized polymers were analyzed using a scanning electron microscope (SEM; Hitachi model S-3400N SEM by Hitachi High-Technologies Corporation, Japan). Fourier transform infrared spectroscopy (FTIR) analysis was conducted using a Perkin Elmer 1750X FTIR spectrometer and elemental microanalysis for CHNS was executed with a LECO CHNS-932 spectrometer together with a C-31 Microbalance for combustion and weighing of the sample. In addition, a 3Flex Surface Characterization Analyzer (Micromeritics Instrument Corporation) was used to analyze the Brunauer–Emmett–Teller (BET) specific surface area of both P(AN-co-AA) and TU-P(AN-co-AA) polymers with N2 gas as the adsorbing gas. The surface charge of synthesized polymers was measured using a Zeta-sizer Nano Series (Malvern Panalytical Limited, United Kingdom). The thermal stability analysis of both polymers was conducted using a simultaneous thermal analyzer (STA) 6,000 instrument (Perkin Elmer Corporation).

Batch adsorption experiments
The adsorption performance of TU-P(AN-co-AA) polymer in the removal of PNP was evaluated via batch adsorption experiments. 50 mL of PNP solutions with desired concentrations (5–500 mg/L) were prepared and a measured mass of adsorbent was added into the solution. The solution was shaken continuously at 100 rpm at a desired temperature using a water bath shaker (Model-903, Tech-Lab Mfg Sdn, Malaysia). At set experiment time intervals, the sample was extracted, filtered and the concentration of PNP remaining in the sample was determined using a Lambda 35 UV-vis spectrophotometer (Perkin Elmer Life and Analytical Science Incorporated, Singapore) at the maximum wavelength of 401 nm. The percentage of PNP removal (% Re) and equilibrium adsorption capacity ($q_e$) was determined by using Equations (1) and (2), respectively.

$$\% \text{Re} = \frac{C_o - C_e}{C_o} \times 100$$  \hspace{1cm} (1)

$$q_e = \frac{C_o - C_e}{m} \times V$$  \hspace{1cm} (2)

Figure 1 | The redox polymerization of P(AN-co-AA) (a), and chemical modification of P(AN-co-AA) with TU.
where \( C_0 \) and \( C_e \) represent the initial and equilibrium concentrations of PNP in solution (mg/L); \( V \) represents the volume of the solution (L); and \( m \) represents the mass of adsorbent (g).

The desorption studies for the regenerability of saturated adsorbent were conducted by agitating 0.1 g of TU-P(AN-co-AA) with 150 mL of 500 mg/L PNP solution for 24 hours in order to prepare saturated adsorbent samples. These were rinsed with distilled water, dried and mixed with 100 mL of solution mixture consisting of ethanol/deionized water in the ratio of 4:1. The samples were shaken for 3 hours. The regenerated samples were then extracted, rinsed with distilled water and dried overnight in an oven at temperature of 50 °C. The regenerated samples were used for the subsequent adsorption studies and the regeneration efficiency (\( RE \)) was calculated with Equation (3).

\[
RE = \frac{q_{e,n}}{q_{e,0}} \times 100\% \tag{3}
\]

where \( n \) is the number of times the adsorbent was regenerated, \( q_{e,n} \) is the adsorption capacity of regenerated adsorbent for \( n \) time (mg/g) and \( q_{e,0} \) is the adsorption capacity of fresh adsorbent.

RESULTS AND DISCUSSION

Characterization of synthesized polymers

Figure 2 shows the FTIR spectra of the synthesized P(AN-co-AA) and TU-P(AN-co-AA) polymer in the range of 4,000 cm\(^{-1}\) to 400 cm\(^{-1}\). The adsorption peaks at 3,516 cm\(^{-1}\) could be attributed to the O-H groups, while the characteristic peak at 2,932 cm\(^{-1}\) were assigned to the stretching modes of C-H bonds (Buapeth et al. 2019). The adsorption peaks at 2,244 cm\(^{-1}\) and 1,725 cm\(^{-1}\) represented the nitrile group (C≡N) and carbonyl group (C=O), respectively (Yang et al. 2017; Ren et al. 2018). After chemical modification with TU, the FTIR spectra of polymer had showed significant changes, where the adsorption peak at 2,244 cm\(^{-1}\) had disappeared and new adsorption peaks at 1,614 cm\(^{-1}\) and 729 cm\(^{-1}\) had appeared. These could be attributed to the C≡N group and stretching vibration of C=S bonds, respectively (Karthik et al. 2017; Ren et al. 2018). This indicated that the chemical modification with TU was successful and thioamide groups were incorporated to the surface of polymer.

Figure 3 shows the morphologies of synthesized unmodified and modified P(AN-co-AA) polymer. The morphologies of both polymers were similar and showed agglomerations of rough surfaced spherical morphology that provide appropriate binding sites for adsorption. The occurrence of this phenomenon could be due to the attractive interaction between monomers and the complex nature of the polymerization reactions (Yu et al. 2016; Adeyi et al. 2019). The mean particle size of P(AN-co-AA) and TU-P(AN-co-AA) polymer were found to be 300 nm and 308 nm, respectively. The slight increase in particle size of TU-P(AN-co-AA) could be attributed to the successful introduction of thioamide functional groups to the P(AN-co-AA) polymer and further confirmed the successful modification with TU. A similar finding was also reported by Do et al. (2017).

The elemental microanalyses (CHNS) of P(AN-co-AA) and TU-P(AN-co-AA) synthesized polymer are shown in Table 1. The observable percentage increase in weight of sulphur, carbon and nitrogen in the modified polymer indicated successful chemical modification of P(AN-co-AA) polymer with TU and incorporation of the thioamide functional group into the
polymer. This statement could be supported by the FTIR spectra of TU-P(AN-co-AA) as shown in Figure 2, where the adsorption peak C≡N groups disappeared and adsorption peaks that indicated the presence of C=S and C=N bonds appeared. The increase in carbon, nitrogen and sulphur content could be due to the successful conversion of nitrile groups in P(AN-co-AA) and modification with thioamide groups.

The zeta potentials or surface charge of both TU-P(AN-co-AA) and P(AN-co-AA) polymers were measured and are shown in Figure S1 (see Supplementary Information). It was found that both polymers possess negative surface charges when exposed to different pH environments, including acidic, alkaline and neutral pH environments. Stronger negative surface charge was observed in TU-P(AN-co-AA) at every pH compared to the unmodified polymer. This can be ascribed to the successful modification of the polymer with TU that introduced the thioamide groups to the synthesized P(AN-co-AA) polymer. Similar observations in zeta potential variation after modification have been reported in other studies (Kim et al. 2016; Maleki et al. 2017; Majedi et al. 2018).

The textural properties and N₂ gas adsorption/desorption isotherms for both TU-P(AN-co-AA) and P(AN-co-AA) polymers are shown in Table 2 and Figure S2 (Supplementary Information), respectively. According to the International Union of Pure and Applied Chemistry (IUPAC), both isotherms are similar to the type-IV isotherm, where significant hysteresis loops at P/P₀ = 0.6–0.95 were observed, which could be due to the occurrence of capillary condensation in mesopores through an increase in relative pressures (Yurdakal et al. 2019). The mesoporous characteristics were further confirmed, with the measured pore sizes shown in Table 2. The pore sizes range from 2 nm to 50 nm. The BET surface area determined for P(AN-co-AA) and TU-P(AN-co-AA) were 22.99 m²/g and 26.31 m²/g, respectively. The pore size determined for both unmodified and modified polymers were 41.60 nm and 47.93 nm, respectively. This suggested that

| Table 1 | Elemental composition of P(AN-co-AA) and TU-P(AN-co-AA) |
|---|---|---|
| Element in weight percentage (wt%) | P(AN-co-AA) | TU-P(AN-co-AA) |
| Carbon | 54.19 | 61.94 |
| Hydrogen | 5.274 | 5.618 |
| Nitrogen | 20.83 | 25.06 |
| Sulphur | 2.510 | 3.187 |

| Table 2 | Textural properties of TU-P(AN-co-AA) and P(AN-co-AA) |
|---|---|---|
| Polymer | Surface area (m²/g) | Average pore volume (cm³/g) | Average pore size (nm) |
| TU-P(AN-co-AA) | 26.31 | 0.1576 | 47.93 |
| P(AN-co-AA) | 22.99 | 0.2492 | 41.60 |
TU-P(AN-co-AA), with a higher BET surface area, possessed more binding sites for capturing PNP as compared to the unmodified polymer, and the increased pore size could potentially lead to a higher mass transport rate that could enhance the adsorption capacity.

Figures S3 and S4 (Supplementary Information) show the thermal stability analysis of the synthesized P(AN-co-AA) and TU-P(AN-co-AA) polymers. The TU-P(AN-co-AA) polymer had degraded earlier than the unmodified P(AN-co-AA) polymer as temperature increased. The TU-P(AN-co-AA) decomposed at about 200 °C, while P(AN-co-AA) only started significant degradation at around 290 °C. This could be due to the weakening or disruption of the dipolar interactions of the nitrile groups in P(AN-co-AA) with the incorporation of thioamide functional groups into the polymer chain through chemical modification with TU (Zahri et al. 2015). The difference in degradation point of P(AN-co-AA) and TU-P(AN-co-AA) further confirmed the successful polymer modification with TU and the result also indicated that both of the polymer samples were stable for water treatment processes.

Preliminary evaluation on PNP adsorption performance by synthesized polymer samples

The effect of chemical modification with TU on the performance of synthesized polymer for the removal of PNP from aqueous solution is shown in Figure S5 (Supplementary Information). The removal efficiency of unmodified P(AN-co-AA) was significantly lower when compared to the modified one, as depicted in Figure S5. This could be due to the limited functional groups, such as carboxyl and hydroxyl groups, which are available for bonding with PNP molecules in the aqueous solution (Zheng et al. 2017). The incorporation of thioamide functional groups to the polymer surface through chemical modification with TU offered higher affinity and availability of abundant active binding sites for PNP adsorption via hydrogen bonding (Zhou et al. 2017). Other than that, the modification of P(AN-co-AA) polymer had also improved the textural properties of the polymer as adsorbent, by increasing the BET surface area and the pore size, as shown in Table 2. This could further enhance the adsorption capacity and performance. Therefore, TU-P(AN-co-AA) was selected for successive PNP sequestration experimental studies.

Effect of adsorbent dosage

In order to determine the optimal dosage of adsorbent, the adsorbent dosage was varied from 1 to 5 g/L; the effect of adsorbent dosage is shown in Figure 4. It can be seen that with the increase in adsorbent dosage from 1 to 2 g/L, the removal efficiency showed a slight increase in terms of PNP removal from aqueous solution. The increase in removal efficiency with increasing adsorbent dosage is due to the increased availability of active binding sites for adsorption as a surface area is available (Shakoor & Nasar 2016). Further increases in adsorbent dosage led to insignificant increases in PNP removal. Hence, the adsorbent dosage of 2 g/L was selected as the optimum adsorbent dosage for the subsequent experiments.

Effect of initial adsorbate concentration

The effect of the initial concentration of adsorbate on the uptake of PNP by the synthesized TU-P(AN-co-AA) polymer was examined by varying it from 5 to 500 mg/L. The experimental results shown in Figure 5 show that the amount of adsorbate

![Figure 4](http://iwaponline.com/wst/article-pdf/84/1/242/913200/wst084010237.pdf)
that can be adsorbed onto the TU-P(AN-co-AA) per mass unit ($q_e$) increases as the initial concentration of adsorbate (PNP) increases. This could ascribed to the high driving force that overcome the obstacles for the mass transfer of PNP between the solid and aqueous phases at high initial adsorbate concentration (Ali et al. 2016). This means that more PNP molecules will interact with the active sites of the adsorbent when the concentration of the PNP solution is high, resulting in increased $q_e$ values. The reduction in PNP removal percentage at higher initial concentrations of PNP solution was due to the lower ratio of active binding sites to PNP molecules available in the solution, where most of the active binding sites were occupied so more adsorbates remained in the aqueous phase (Etim et al. 2016). A similar result trend were also reported by Ooi et al. (2017).

Effect of temperature
The effect of temperature on the sorption of PNP from aqueous solution was studied from 298 to 328 K while maintaining other experimental parameters constant. From the results depicted in Figure S6 (Supplementary Information), it was found that the adsorption capacity of the TU-P(AN-co-AA) adsorbent decreased as the temperature increased. This indicated that the sorption process that took place between the TU-P(AN-co-AA) polymer and the PNP molecules was exothermic in nature, where higher temperatures are not favourable for adsorption (Mishra et al. 2019). Exothermic adsorption processes may suffer from lower adsorption capacity due to lower interactive forces between active sites of adsorbent and adsorbate as the temperature increases (Akhtar et al. 2016). Hence, solution temperature was kept constant at 298 K (25 °C) for the subsequent adsorption experiments.

Effect of contact time
The effect of contact time on the adsorption of PNP onto the synthesized TU-P(AN-co-AA) was investigated and the experimental results are shown in Figure 6. It can be seen that the uptake efficiency of PNP by the TU-P(AN-co-AA) polymer increased sharply from the start of the experiment up to 20 min, and equilibrium was established within 1 hour. The high adsorption rates at the beginning of the experiment were due to the availability of abundant active adsorption sites and the high concentration gradient (Dehghani et al. 2016). The adsorption rate reduced gradually as contact time increased due to the occupation of the active adsorption sites by the adsorbate. The insignificant changes in amount of PNP uptake by the adsorbent observed with further increases in contact time signified that all the active sites had been fully occupied/exhausted and an equilibrium state had been achieved. Similar trends were also observed in studies done by other researchers (Ali et al. 2015; Awual et al. 2016).

Adsorption isotherm study
The investigation of the equilibrium relationship established between the concentration of the adsorbate and the quantity of adsorbate was carried out with adsorption isotherm models in order to further understand the mechanism of the adsorption
The Langmuir and Freundlich adsorption isotherm models were selected to simulate the PNP adsorption onto TU-P(AN-co-AA). The linear forms of both isotherm models and the Langmuir separation factor or equilibrium parameter ($R_L$) equation are shown in Equations (4)–(6), respectively (Freundlich 1907; Langmuir 1918; Fierro et al. 2008).

\[
\frac{C_e}{q_e} = \frac{1}{QK_L} + \frac{C_e}{Q}
\]  
\[
\ln q_e = \ln K_F + \frac{1}{n} \ln C_e
\]  
\[
R_L = \frac{1}{K_L C_o}
\]

where $Q$ (mg/g) and $K_L$ (L/mg) represents the Langmuir adsorbent monolayer adsorption capacity and Langmuir constant related to adsorption energy, respectively. $K_F$ (mg/g) is the Freundlich constant related to adsorbent adsorption capacity and $1/n$ is the Freundlich constant related to intensity of adsorption. The value of $R_L$ indicates the favourability of Langmuir adsorption, where the adsorption is unfavourable when $R_L > 1$, linear when $R_L = 1$, favourable when $0 < R_L < 1$ and irreversible when $R_L = 0$.

The adsorption isotherm model parameters and the correlation factor ($R^2$) from the Langmuir and Freundlich adsorption isotherm models are presented in Table 3. The table shows that the equilibrium data could be fitted into the Langmuir adsorption isotherm models with $R^2$ value of 0.7428, which is an acceptable fit for monolayer adsorption (Farouq & Yousef 2015). The values of $R_L$ calculated ranged from 0.0055 to 0.3561, which are both between 0 and 1. This indicated that the adsorption of PNP onto the TU-P(AN-co-AA) was favourable. However, the Freundlich isotherm model was found to fit the equilibrium data better with an $R^2$ value of 0.9853, which is higher and closer to unity, indicating that the Freundlich adsorption isotherm is more suitable to describe the adsorption behaviour of PNP.

Table 3 | Isotherm parameters and correlation factor of PNP adsorption onto TU-P(AN-co-AA)

<table>
<thead>
<tr>
<th>Adsorption isotherm models</th>
<th>Langmuir model</th>
<th>Freundlich model</th>
</tr>
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<tbody>
<tr>
<td>$Q$ (mg/g)</td>
<td>294.12</td>
<td>$K_F$ (mg/g)</td>
</tr>
<tr>
<td>$K_L$ (L/mg)</td>
<td>0.3617</td>
<td>$n$</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.7428</td>
<td>$R^2$</td>
</tr>
</tbody>
</table>
onto the TU-P(AN-co-AA). The value of \( n > 1 \) indicated favourable adsorption of PNP onto the TU-P(AN-co-AA) polymer (Kaman et al. 2017). Hence, the adsorption process took place at heterogeneous adsorbent surfaces and multilayer adsorption occurred.

**Adsorption kinetics study**

To determine the adsorption mechanism of PNP uptake by TU-P(AN-co-AA) and possible rate-controlling steps, pseudo-first-order, pseudo-second-order and intraparticle diffusion kinetic models were used to test the experimental data. The linearized forms of the kinetic models employed are shown in Equations (7)–(9) (Lagergren 1898; Weber & Morris 1963; Ho 2006).

\[
\log \left( \frac{q_t - q_i}{q_e - q_i} \right) = \log \left( \frac{q_e}{q_i} \right) - k_1 t / 2.303
\]

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} \left( \frac{1}{q_e} t \right)
\]

\[
q_t = k_{id} t^{1/2} + C
\]

where \( q_t \) represents the amount of adsorbate per mass unit of adsorbent in at any time \( t \) (mg/g) and \( k_1 \) (min\(^{-1}\)), \( k_2 \) (g/mg min) and \( k_{id} \) (mg/g min\(^{1.5}\)) represent the rate constant of first-order adsorption, second-order adsorption and intraparticle diffusion, respectively. \( C \) (mg/g) is the intercept that relates to the thickness of boundary layer.

Figure S7 (Supplementary Information) shows the graphs of pseudo-first-order, pseudo-second-order and intraparticle diffusion kinetic models. The kinetic parameters and correlation factor of the kinetic models employed are given in Table 4. From Table 4, the calculated adsorption capacity, \( q_{e,cal} \) from the pseudo-first-order model showed major inconsistency with the experimental adsorption capacity, \( q_{e,exp} \) and the R\(^2\) values were far from unity. This indicated that the pseudo-first-order kinetic model was not suitable to explain the adsorption interaction of PNP molecules with the adsorbent. By contrast, the values of \( q_{e,cal} \) determined from the pseudo-second-order kinetic model showed good agreement with the \( q_{e,exp} \) and the R\(^2\) values are the highest among the kinetic models tested. This indicated that the pseudo-second-order kinetic model can best describe the adsorption process. Multiple lines that do not pass through the origin can be seen in the graph of the intraparticle diffusion model. This indicated the occurrence of two or more rate-determining adsorption steps in the adsorption of PNP onto the TU-P(AN-co-AA) (Inyinbor et al. 2016). Hence, the pseudo-second-order kinetic model is the most suitable model for describing the adsorption process of PNP onto TU-P(AN-co-AA) and both chemical adsorption and intraparticle diffusion were involved in the removal of PNP by TU-P(AN-co-AA).

**Thermodynamic study**

The effect of temperature (298 K–328 K) on the adsorption performance of PNP by TU-P(AN-co-AA) was investigated (Figures S6 and S8, Supplementary Information). The thermodynamic parameters, including Gibbs free energy of adsorption, \( \Delta G^0 \) (kJ/mol), enthalpy change, \( \Delta H^0 \) (kJ/mol) and entropy change, \( \Delta S^0 \) (J/mol K), were determined using thermodynamic

<table>
<thead>
<tr>
<th>Models</th>
<th>Parameters</th>
<th>( q_{e,exp} ) (mg/g)</th>
<th>( q_{e,cal} ) (mg/g)</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pseudo-first-order</td>
<td>( k_1 ) (min(^{-1}))</td>
<td>0.0682</td>
<td>49.570</td>
<td>6.2864</td>
</tr>
<tr>
<td>Pseudo-second-order</td>
<td>( k_2 ) (g/mg min)</td>
<td>0.0189</td>
<td>49.570</td>
<td>50.251</td>
</tr>
<tr>
<td>Intraparticle diffusion</td>
<td>( k_{id} ) (mg/g min(^{1.5}))</td>
<td>3.2968</td>
<td>C (mg/g)</td>
<td>24.920</td>
</tr>
</tbody>
</table>
Equations (10)–(12) (Shen et al. 2015; Dolaksiz et al. 2018).

\[ \Delta G^o = \Delta H^o - T \Delta S^o \]  
\[ \ln k_d = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \]  
\[ k_d = \frac{q_e}{C_e} \]

where \( T \) is the temperature (K), \( k_d \) is the equilibrium coefficient and \( R \) is the ideal gas constant (8.314 J/mol K). From the Van ‘t Hoff plot of \( \ln k_d \) vs \( 1/T \) shown in Figure S8 (Supplementary Information), the values of \( \Delta H^o \) and \( \Delta S^o \) can be determined from the gradient slope and the intercept of the plot, respectively. The thermodynamic parameters determined from the equations are shown in Table 5. The negative values of \( \Delta G^o \) suggested that the adsorption process was exothermic and spontaneous (Asif Tahir et al. 2016). The positive value of \( \Delta S^o \) indicated that the adsorption process of PNP onto the surface of TU-P(AN-co-AA) involved dissociative mechanisms, where temperature increases would cause negative effects on the adsorption performance (Saha & Chowdhury 2011).

Comparison of sorption capacity with other developed adsorbents

Adsorption capacity is central to the large-scale application of each adsorptive material. The maximum adsorbent capacity is always estimated based on equilibrium data from an adsorption isotherm. The maximum TU-P(AN-co-AA) capacity for the PNP entrapment from liquid phase was compared with various adsorbents in the literature, and values of adsorption

<table>
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<tr>
<th>Table 5</th>
<th>Thermodynamic parameters for PNP adsorption onto TU-P(AN-co-AA)</th>
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</thead>
<tbody>
<tr>
<td>Temperature ( T ) (K)</td>
<td>( k_d )</td>
</tr>
<tr>
<td>298</td>
<td>41.324</td>
</tr>
<tr>
<td>308</td>
<td>38.544</td>
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<tr>
<td>318</td>
<td>37.121</td>
</tr>
<tr>
<td>328</td>
<td>34.139</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 6</th>
<th>Comparison of PNP sequestration using various adsorbents</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adsorbent</td>
<td>Sorption capacity (mg/g)</td>
</tr>
<tr>
<td>Montmorillonite–graphene oxide composite (MGC)</td>
<td>60.28</td>
</tr>
<tr>
<td>Nanographite oxide</td>
<td>268.50</td>
</tr>
<tr>
<td>Cauliflower leaf activated carbon</td>
<td>37.74</td>
</tr>
<tr>
<td>( \beta )-cyclodextrin silica gel</td>
<td>41.50</td>
</tr>
<tr>
<td>Nanozeolite</td>
<td>156.70</td>
</tr>
<tr>
<td>Silver(I) trizolate metal organic framework</td>
<td>143.50</td>
</tr>
<tr>
<td>Char ash</td>
<td>11.63</td>
</tr>
<tr>
<td>Aminopropyl-modified mesoporous MCM-48</td>
<td>107.53</td>
</tr>
<tr>
<td>Lantana camara</td>
<td>91.07</td>
</tr>
<tr>
<td>Surface molecularly imprinted polymers (SMIPs)</td>
<td>157.30</td>
</tr>
<tr>
<td>TU-P(AN-co-AA)</td>
<td>294.12</td>
</tr>
</tbody>
</table>
capacities are shown in Table 6. The comparisons revealed that the monolayer adsorption capacity of the functionalized poly-meric material towards PNP was high compared to other adsorbents reported.

Regeneration study
The ability of an adsorbent to be recycled or regenerated is considered to be one of the crucial criteria to determine the feasibility of an adsorbent to be implemented into practical uses. The solvent desorption method was conducted by adding the saturated TU-P(AN-co-AA) adsorbent to a mixed solution of ethanol/deionized water at ratio of 4:1 and agitated for 3 hours. The experimental results are shown in Figure S9 (Supplementary Information), from which it is clear that the adsorption performance of the regenerated TU-P(AN-co-AA) adsorbent after four cycles of adsorption/desorption process was still more than 95% of the original adsorption performance. This suggests that the synthesized TU-P(AN-co-AA) polymeric adsorbent can be regenerated for multiple uses in removal of PNP from aqueous solution.

CONCLUSIONS
In this study, poly(acrylonitrile-co-acrylic acid) polymer was prepared by the redox polymerization method, modified with thiourea and its adsorption performance on the removal of PNP from aqueous solution was investigated in batch mode. The equilibrium data had showed good agreement with the Freundlich adsorption isotherm model, with a Langmuir maximum monolayer adsorption capacity of 294.12 mg/g. The kinetic data was best described by the pseudo-second-order kinetic model and the thermodynamics study showed that the adsorption process of PNP onto TU-P(AN-co-AA) was an exothermic process and spontaneous. The regeneration study also proved that the synthesized polymeric adsorbent could be regenerated with ethanol/deionized water mixture as the eluent and reused for PNP removal from aqueous solution. The experimental findings suggested that the synthesized TU-P(AN-co-AA) polymeric adsorbent is a potential adsorbent in PNP sequestration from polluted water sources and can be reused with no significant decline in adsorption capacity.

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DATA AVAILABILITY STATEMENT
All relevant data are included in the paper or its Supplementary Information.

REFERENCES


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