Using polymer coated nanoparticles for adsorption of micropollutants from water

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\textbf{GRAPHICAL ABSTRACT}

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\textbf{ABSTRACT}

In this study, polyvinylpyrrolidone (PVP)-coated magnetite nanoparticles were synthesized to adsorb six emerging contaminants (Tonalide, Bisphenol-A, Triclosan, Metolachlor, Ketoprofen and Estriol) from aqueous solutions. The PVP-coated NPs were characterized by dynamic light scattering (DLS) measurements, thermal analysis, and X-ray diffraction. Results indicated that PVP-coated NPs were successfully used as a separable adsorbent for removing the micropollutants from water. Adsorption results were modeled using Langmuir and Freundlich isotherms, which showed a better fit of data to the Langmuir model. The adsorbent showed good adsorption performance in which Bisphenol-A and Ketoprofen were the most effectively removed micropollutants, with 98 and 95% removal using only 0.1 mg of the adsorbent within 15 min of contact time, respectively. Kinetic studies were performed using the pseudo-second-order model to compare the performance of PVP-coated NPs with granular activated carbon (GAC) revealing the superiority of PVP-coated NPs over GAC. Thermodynamic parameters of the adsorption of the micropollutants onto the adsorbate showed the adsorption process was endothermic and spontaneous. Adsorbate regeneration studies were performed with methanol, ethanol, and the UV/H\textsubscript{2}O\textsubscript{2} process in five regeneration cycles. Methanol treatment ensured the highest level of regeneration.

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1. Introduction

Nowadays, it is becoming difficult to find unpolluted water resources for drinking purposes. Water resource contamination can emanate from natural sources and/or anthropogenic activities [1,2]. Industrial development and population growth have imposed thousands of synthetic organic compounds to aquatic fresh ecosystems [3]. Micropollutants, such as pesticides, pharmaceuticals, industrial chemicals, and hormones are present at very low concentrations, and can raise significant toxicological concerns for aquatic ecosystems, and thereby human health [4,5]. Independent of source, a large degree of the micropollutants have been found in water resources because they are not bio-degradable [6]. The persistent nature of these compounds means that if released into nature the contaminants will stay in the soil for a long time before reaching the groundwater. Even if they reach the wastewater treatment plant, they are likely to be released with wastewater effluent to surface water bodies [7,8].

Recently researchers have focused on using adsorption techniques to remove these emerging contaminants from water bodies [9–11]. Activated carbon has been studied widely and showed promising removal efficiency as it has high porosity and internal surface area. However, regeneration of saturated activated carbon is energy demanding (requiring heating to 500–900 °C), and does not fully restore the removal performance [12]. In addition, the probability of releasing carbon dust during the treatment process causes some restrictions over its application in some cases [13,14].

There are also limitations over application of other adsorbents like zeolite, and carbon nanotubes (CNTs) [15,16]. Saturated absorbents have to be removed by separation methods such as filtration or centrifugation in order to achieve a free absorbent solution that facilitates regeneration of the absorbent. Applying these costly methods puts constraints on using these absorbents in industrial sites [17].

Given the restrictions of current adsorption methods for removing organic micropollutants, novel solutions are being actively sought [18–20]. Polymer-modified iron or iron oxide nanoparticles have been intensively studied for applications in soil and groundwater treatment for various kinds of contaminants including micropollutants [21–27]. Phenrat [24] used a novel electromagnetically enhanced treatment concept for in situ remediation of a source zone of chlorinated dense non-aqueous phase liquid (DNAPL), causing groundwater contamination. Their results showed acceleration in the degradation of the DNAPLs by using polystyrene sulfonate (PSS)-modified zero valent iron NPs in combination with a low frequency AC electromagnetic field. In another study, Bauerlein et al. [10], studied the removal of some ionic organic compounds by both activated carbon and charged polymeric materials. Their results showed that sorption of all charged compounds to oppositely charged polymers was stronger than to activated carbon, especially for the double-charged cation metformin.

Iron oxide nanoparticles (NPs) are attractive for their magnetism and low toxicity characteristics [28]. The former provides easily magnetic separation of NPs from aqueous solutions. Phenrat et al. [29] showed low toxicity of magnetite in comparison to nanoscale zerovalent iron. In addition, they showed that the addition of a polymer can reduce toxicity even more on mammalian cells (BV2 and N27) due to surface modification. The surface coating can probably change the interaction of the particles with the cell membranes.

If the developed adsorbent is able to remove contaminants but cannot be regenerated, it thus will become a contaminant. Regenerating techniques like using organic solvents, inorganic solvents, and redox agents have been developed. In this study two organic solvents and one redox agent were studied to regenerate the saturated PVP-NPs. Composite magnetic materials have been produced by thermal decomposition and used for separation purposes. However, synthesis methods mainly need organic solvents and high temperatures, which make industrial applications difficult [30].

In this study, a simple and inexpensive hydrothermal method was used to produce polyvinylpyrrolidone (PVP)-coated magnetite nanoparticles to adsorb a variety of organic micropollutants from the aqueous phase. This method needs no organic solvents, requires lower energy input, and ambient atmospheric environments. It has been previously shown that PVP-coated NPs are stable in environmental systems [30]. After production of PVP-coated NPs, characteristics of the absorbent, its removal efficiency, and thermodynamic parameters for Tonalide, Bisphenol-A, Triclosan, Metolachlor, Estriol and Ketoprofen were studied.

2. Materials and methods

2.1. Reagents and chemicals

Ferrous chloride (FeCl₂·4H₂O, 99%), ferric chloride (FeCl₃·6H₂O, 99%), ammonium hydroxide (25%), sodium hydroxide (NaOH), sulfuric acid (98%), hydrogen peroxide (30%), ethanol, and methanol were obtained from Merck (Germany) and used as received. Polyvinylpyrrolidone (PVP) (> 95%), Potassium persulfate (KPS), sodium bisulfite (> 95%), Suwannee River Fulvic Acid (SRFA), granular activated carbon (GAC), and organic micropollutants (Tonalide, Bisphenol-A, Triclosan, Metolachlor, Ketoprofen and Estriol) were purchased from Sigma-Aldrich (USA). Ultrapure water (Millipore, USA) was used for nanoparticle preparation and kinetic studies.

2.2. Synthesis of nanoparticles

Magnetic nanoparticles were synthesized using a hydrothermal method [31]. PVP, ferric chloride, and ferrous chloride were used as precursors, and ammonium hydroxide was used as a precipitation agent. First, 0.50 mmol of PVP was added to 10.0 mL of ultrapure water and was stirred at 90 °C for 2 h. Then, 2 mmol of Ferric chloride and 6 mmol of ferrous chloride were added to the solution and stirred at 90 °C for 2 h. Then, 10.0 mL of ammonium hydroxide was added into the solution dropwise under continuous stirring. After adding ammonium hydroxide, the color of the mixture turned black and was mixed at 90 °C for 2 h. The precipitates were rinsed twice with ultrapure water, separated with a magnet and sonicated to disperse in water.

### Table 1

**Molecular description of the tested micropollutants.**

<table>
<thead>
<tr>
<th>Compound Relevance</th>
<th>Tonalide Musk compound</th>
<th>Bisphenol-A Plastic component</th>
<th>Triclosan Antibacterial and antifungal agent</th>
<th>Metolachlor Leading pesticide</th>
<th>Ketoprofen Anti-Inflammatory drug</th>
<th>Estriol One of the estrogen hormones</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical formula</td>
<td>C₁₈H₁₈O₂</td>
<td>C₁₈H₁₈O₂</td>
<td>C₁₈H₁₈Cl₂</td>
<td>C₁₈H₂ClNO₂</td>
<td>C₁₈H₁O₂</td>
<td>C₁₈H₈O₁</td>
</tr>
<tr>
<td>Molecular weight (g/mol)</td>
<td>258.4</td>
<td>228.29</td>
<td>289.53</td>
<td>283.8</td>
<td>254.28</td>
<td>288.39</td>
</tr>
<tr>
<td>Solubility (mg/L)</td>
<td>1.8</td>
<td>192</td>
<td>10</td>
<td>530</td>
<td>51</td>
<td>119</td>
</tr>
<tr>
<td>Log Kow</td>
<td>5.9–6.3</td>
<td>2.2–3.4</td>
<td>4.76</td>
<td>3.13</td>
<td>2.99</td>
<td>2.45</td>
</tr>
<tr>
<td>Log Koc</td>
<td>3.80–4.80</td>
<td>2.06–3.59</td>
<td>3.38–4.20</td>
<td>1.34–3.36</td>
<td>2.12</td>
<td>3.08</td>
</tr>
</tbody>
</table>
2.3. Analysis methods

Micropollutant concentrations were measured by gas chromatography–mass spectrometry (GC/MS) equipped with a fused capillary column (TRB-5, 60 m, 0.32 mm ID) [5,32,33]. The apparatus was operated in the internal ionization mode. A 30 m × 0.25 mm, df = 0.25 µm capillary column SGE (Ringwood, Australia) was used under the following conditions: electron energy = 60 eV; transfer-line temperature = 200 °C; scan speed = 1000 Hz [4,8]. Table 1 describes the chemical characteristics and relevance of the tested emerging micropollutants. These compounds were selected from different industry. Total organic carbon (TOC) was measured with a Shimadzu TOC analyzer (5000A, Shimadzu Corp., Japan).

The structure of magnetic nanoparticles was analyzed using Cu Ka (k = 0.1542 nm) radiation from an X-ray Diffractometer (Scintag XDS-2000 θ/θ powder diffractometer). The XRD scattering was observed over a range of 10–80° with step sizes of 0.03–0.05°, and count times between 20 and 55 s. The average crystallite size was calculated according to the full width at the half-maximum height (FWHM) of the (311) plane using Scherrer (Eq. (1)) [34]:

\[
\tau = \frac{k \gamma}{\beta \cos \theta}
\]

(1)

where τ is the mean size of crystalline domain, k is a dimensionless shape factor (0.89 for magnetite), λ is the X-ray wavelength (1.54059 Å), β is the line broadening at half the maximum intensity (FWHM) after subtracting the instrumental broadening, and θ is Bragg’s angle. By assuming a spherical shape for nanoparticles and using the following equation (Eq. (2)), particle size (d) can be calculated [35]:

\[
d = \frac{4}{3} \tau
\]

(2)

DLS measurements were performed with a Malvern Zetasizer NanoSizor particle analyzer with a solid-state He–Ne laser at a scattering angle of 1731 at 25 °C (pH 6–8) [36]. For this analysis, all samples were diluted to approximately 0.1 mg/mL. Then, samples were filtered through a Whatman Anotop alumina membrane (pore size of 220 nm). The experiments were performed at NaCl concentrations of 0.001 and 0.16 mol/L at pH 7. All samples were analyzed directly after filtration every three minutes over a one hour period. The average DLS measurements were determined from ten replicates. Zeta potential measurements were also done with a Malvern Zetasizer Nanosizer at 25 °C. Zeta potential measurements were performed by dispersing the sonicated samples (with 10 min of sonication) at a concentration of 0.1 mg/mL. The ionic strength was adjusted to 0.001 mol/L NaCl. The pH was initially adjusted to 2.0 and zeta potential was measured by increasing the pH to 12 using sodium hydroxide solution. The average zeta potential and DLS measurements were determined from ten replicates. Thermal analysis was conducted by using a thermogravimetric analyzer (TGA) (Netzsch TG209, Germany) at a heating rate of 10 °C per minute under constant nitrogen flow [16].

2.4. Experimental procedure

Adsorption experiments were performed in a 50-mL sealed glass vial. NPs were added to the solution containing 50.0 µg/L of each micropollutant at a pH value of 7.0. Sonication was used for five minutes before conducting the experiments to separate attached nanoparticles (NPs). The pH was adjusted with dilution of NaOH and HCl solutions. Vials were agitated at 150 rpm using a rotary shaker. Containers were wrapped with aluminum foil to minimize photolysis.

After conducting the adsorption experiments, nanoparticles were separated with a 1.5 × 0.75 × 0.5 inch neodymium magnet (Grade N 52, K & J Magnetics Inc.) for 30 min. To analyze the samples, solutions were collected in 5.0 mL aliquots and sent immediately for analysis. To consider the effect of initial sonication and reduce the chance of analytical uncertainties, a stock sample was maintained with the same experimental conditions except the adsorption process [10]. Results were reported by comparing the final concentration of micropollutants in the stock sample to the experimental samples. All experiments were conducted at least three times and the mean values reported.

The isotherms were obtained as follows. PVP-coated NPs (0.1 mg) and the different concentrations of micropollutant were added in a 50 mL sealed glass vial. The micropollutant concentration range was 25–250 µg/L. The vial was shaken at different temperatures (298, 308, and 318 K) for 20 min and the precipitation was separated magnetically.

Some studies have shown incomplete adsorption of micropollutants in natural samples. To investigate the effect of DOM on adsorption of micropollutants, the adsorption removal efficiencies for both PVP-coated NPs and GAC were compared with distilled water and SRFA-added water samples (DOM = 8 mg C/L).

Regeneration experiments were done in a volume of 100 mL. For UV/H2O2 regenerating experiments a solution containing 20 mg/L of hydrogen peroxide was mixed with 2 mg of saturated NPs in a 500 mL four-neck cylindrical quartz reactor for 30 min. The reactor was placed on a rotary shaker with rotary speed being the same as the adsorption experiments (150 rpm). UV irradiation was provided with one 30 W low-pressure UV mercury lamp placed in the center of the reactor. The residual H2O2 was neutralized with sodium bisulfite [37].

For methanol and ethanol regenerating experiments, all experimental conditions were the same as those with UV/H2O2, except UV irradiation and existence of hydrogen peroxide in which were replaced either by methanol (20 mg/L) or ethanol (20 mg/L). The regenerated adsorbents were reacted again with micropollutant solution to study the recycling rate. The regeneration tests were repeated 5 times.

3. Results and discussions

3.1. Characterizations of PVP-coated nanoparticles

Fig. 1a shows the size distribution of synthesized nanoparticles using DLS. The hydrodynamic diameter measured by DLS was 106.2 ± 3.6 nm with an average polydispersity index (Pdi) of 0.25. According to the DLS results, NPs are well-dispersed and monodispersed enough for the DSL technique to be valid, since the Pdi Value was less than 0.7 indicating that the sample did not have a broad size distribution and was suitable for the dynamic light scattering technique [36].

The XRD pattern of the PVP-coated iron oxide NPs is shown in Fig. 1b which shows that the dominant phase of NPs is magnetite (Fe3O4), though maghemite was also detected. The calculated lattice parameter α was 8.3889 Å. Since the lattice of maghemite and magnetite are 8.3515 Å (JCPDS 39-1346) and 8.3960 Å (JCPDS 19-629), respectively, the main crystalline phase could be identified as magnetite [19,38]. Using Eqs. (1) and (2), the average crystal size of 14.3 nm and particle size of 19.7 nm were calculated.

The TGA curve for PVP-coated iron oxide nanoparticles is depicted in Fig. 2. The initial weight loss before 240 °C could be due to the desorption of adsorbed water and/or surface hydroxyls. It can be seen that the sample weight significantly decreased around 300 °C. This can be ascribed to the formation of iron oxides and the decomposition of amorphous iron hydroxides. The major weight loss took place around 372 °C which could be due to the decomposition of the coated PVP layer as such a loss did not occur in the uncoated sample [38]. Subsequently, the micropollutant removal capacity of PVP-coated iron oxide NPs was studied.

The average zeta potential was 11.5 ± 0.4 mV indicating the sorption of PVP shifts the slip plane out of the surface of the particle and to the effect of adsorbed non-charged polymeric layer as suggested by Ohshima’s soft particle analysis which decreases the apparent electro-photoret mobility [29].
3.2. The effect of dosage and contact time

Adsorbent dosage and contact time play significant roles in the adsorption removal of the micropollutants. By Increasing contact time and dosage more chance will be given to the absorbents to adsorb pollutants. On the other hand, either over-dosage of adsorbent or excessive contact time increases the operational costs. Therefore, it is indispensable to optimize the adsorbent dose and contact time.

In order to evaluate the adsorptive capacity of the polymer coated nanoparticles, the removal of each micropollutant was studied with different dosages of NPs. Fig. 3(a) shows the effect of adsorbent concentration on the micropollutant removal. The experiments were performed at pH 7.5 and the detention time was 20 min. The adsorption efficiency was improved when adsorbent
with the interface concentration. At this point almost all of the adsorbate concentration was removed. The concentrations of all micropollutants were sharply reduced in the first 10 min of contact time. Concentration reduction continued gradually after 10 min. Bisphenol-A and Ketoprofen were the most effectively removed micropolllutants, with 98 and 95% removal, respectively, using only 0.1 mg of the adsorbent within 15 min. This could be due to their chemical structures, physiochemical properties, as well as the specific surface properties of the adsorbent. Micropolllutants with high polar bonds tend to be adsorbed more easily. As Bisphenol-A, Triclosan, Ketoprofen, and Estriol have O–H bond(s) in their chemical structure that can easily bind to PVP [39]. The next significant factor that can affect adsorption capacity could be molecular weight because Bisphenol-A and Ketoprofen had less molecular weight than Triclosan and Estriol.

The change of adsorption capacity with increasing reaction time can be attributed to the following stages [16,28] conceptualized in Fig. 4. First, the instantaneous adsorption of micropolllutants occurred within a short period of time. This step can be attributed to interactive forces between the micropolllutant molecules and the surface of the adsorbent. Second, as the contact time increased, a gradual achievement of the equilibrium was observed, since most of the active sites on the surface of the adsorbent were occupied by the micropolllutants. In addition, physisorption was the main adsorptive action for which physical bonding of the micropolllutant molecules occurs on the surface of the adsorbent. This takes place due to Van der Waals forces. Finally, the adsorption equilibrium between micropolllutant molecules and PVP-coated NPs was attained.

To study the amount of each micropolllutant adsorbed by PVP-coated NPs and GAC at equilibrium condition, the pseudo-second-order model was used to explain the adsorption kinetics, which is expressed in Eq. (3) [40]:

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{t}{q_e}$$  \hspace{1cm} (3)

where $k$ (mg/min/µg) is the second-order rate constant, $q_e$ (µg/µg) is the adsorption capacity at any time $t$ (min), and $q_e$ (µg/µg) is the adsorption capacity at equilibrium.

The results of adsorption kinetics are tabulated in Table 2. In addition, the kinetic removal curves of the tested micropolllutants are presented in Fig. S1. According to the results, all correlation of coefficients were greater than 0.99. The corresponding linear regressions were obtained for the values of $q_e$ and $k$ from Eq. (3). For experiments with PVP-coated NPs, the value of $q_e$ (18.2 µg/µg) for Tonalide was lower than the other micropolllutants. This could be attributed to the difference in molecular structure of the target micropolllutants. The $k$ value for Bisphenol-A adsorbed by PVP-coated NPs was 15 times greater than that of the GAC experiments. This indicates a high adsorption capacity of PVP-coated NPs. This is probably due to the availability of more readily-accessible binding sites (located at the outer surface of the adsorbent) on the PVP-NPs compared to GAC. Alsbaiee et al. [9], also showed rapid adsorption of a variety of organic micropolllutants with higher adsorption rate constants than those of activated carbon.

### 3.3. Adsorption isotherms

Adsorption isotherms are valuable curves describing the phenomenon leading the retention or release of a substance from the aqueous to the solid phase at a constant temperature and pH. Langmuir and Freundlich adsorption isotherms were used for modeling adsorption data. The Langmuir isotherm assumes homogeneous adsorption, in which all sites have equal adsorption capacity. The Langmuir adsorption isotherm can be expressed by Eq. (4):
where $C_e$ is the equilibrium concentration in the liquid phase (µg/L), $q_e$ is the amount of adsorbate adsorbed on the adsorbent at equilibrium conditions (µg/mg), $q_m$ is the maximum theoretical adsorption capacity of the adsorbent (µg/mg), and $K_d$ is the adsorption equilibrium constant (L/µg).

An equilibrium parameter or a dimensionless constant of separation factor ($R_L$) can also be expressed as a critical characteristic of the Langmuir isotherm, which is defined as Eq. (5) [41]:

$$R_L = \frac{1}{1 + \frac{C_d}{C_0}}$$

where $C_d$ is the initial concentration of micropollutants and $R_L$ indicates the shape of the isotherm; values between 0 and 1 indicate favorable adsorption, whereas $R_L = 0$, $R_L = 1$, and $R_L > 1$, indicate irreversible, linear, and unfavorable, adsorption isotherms, respectively [42].

On the other hand, the Freundlich adsorption isotherm assumes that there are many types of binding sites which have different free energy of sorption values, and there are a large amount of sorbent sites. This isotherm expresses the diversity of free energies related to the adsorbate by the heterogeneous adsorption [43].

The Freundlich adsorption isotherm can be expressed by Eq. (5) [43]:

$$q_e = K_a C_e^{1/n}$$

where $K_a$ (µg/mg) (L/µg)^{(1/n)} is the adsorption coefficient of the Freundlich isotherm and $1/n$ is the Freundlich intensity parameter. If the value of $1/n$ is lower than 1, it indicates a normal Langmuir isotherm. The amount of micropollutant adsorbed per unit adsorbent ($q_e$) (µg/mg) was evaluated by dividing the amount adsorbed by the concentration of PVP-coated NPs.

The linearized form of the Freundlich model is shown below [44,45] in Eq. (6):

$$\log(q_e) = \log(k) + \frac{1}{n} \log(C)$$

The adsorption isotherms of Tonalide and Bisphenol-A for both Langmuir and Freundlich isotherms are depicted in Fig. 5(a) and (b), respectively. Adsorption isotherm plots for other tested micropollutants can be found in Figs. S2 and S3. Results showed that the adsorption data for all micropollutants were well fitted to the Langmuir model (R^2 > 0.99). Therefore, a monolayer of the micropollutants was formed on the surface of PVP-coated NPs.

Corresponding adsorption parameters for all tested micropollutants are listed in Table 3. According to the results, $R_L$ values for Langmuir isotherm were between 0 and 1 and the value of $1/n$ for Freundlich isotherm was smaller than 1, which indicate favorable adsorption. The maximum adsorption capacities ($q_m$) by the Langmuir model were achieved for Bisphenol-A and Ketoprofen as 90.91 and 83.33 µg/mg, respectively. These two compounds have smaller molecular size in comparison to the other studied compounds. The smaller molecular size can help more molecules to be adsorbed on the surface of the adsorbent.

The large adsorption capacity of PVP-coated NPs can be ascribed to the strong adsorption affinity of the adsorbent towards the target micropollutants, which emanated from unique surface characteristics.

Table 4 lists the maximum theoretical adsorption capacity ($q_m$) and the correlation coefficients ($R^2$) at three different temperatures (298, 308 and 318 K). All the $R^2$ values were above 0.94, indicating that Langmuir isotherm had acceptable agreement with the experimental data. Results indicated that when the temperature increased, $q_m$ values increased. This could be probably due to the interactive forces between adsorbate and adsorbent that control the process. Therefore, it can be concluded that the adsorption of the micropollutants on PVP-coated NPs is an endothermic process.

Thermodynamic parameters such as the change in free energy ($\Delta G^\circ$), enthalpy ($\Delta H^\circ$), and entropy ($\Delta S^\circ$) were calculated for the adsorption of micropollutants using the following equations [12]:

$$K_c = \frac{C_\infty}{C_s}$$

$$\Delta G^\circ = -RT \ln(K_c)$$

$$\ln(K_c) = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}$$

where $K_c$ is equilibrium constant, $C_\infty$ and $C_s$ are the concentrations of micropollutants adsorbed by the adsorbent (µg/L) and remained in the aqueous phase at equilibrium (µg/L) respectively. R is the universal gas constant (8.314 J/mol K), and T is temperature (K). $\Delta H^\circ$ and $\Delta S^\circ$ can be calculated from the slope and intercept of ln $K_c$ vs. 1/T (Van’t Hoff plot (Fig. 6)). Van’t Hoff plots for adsorption of other tested micropollutants are shown in Figs. S4 and S5. The thermodynamic parameters are summarized in Table 5. Positive values of $\Delta H^\circ$ showed endothermic adsorption processes for all micropollutants. In addition, positive values of $\Delta S^\circ$ indicated the affinity of the tested micropollutants and increasing randomness at the liquid-solid interface during the adsorption process. Negative values of $\Delta G^\circ$ indicated spontaneous adsorption and the degree of spontaneity increased with increasing temperature.

### 3.4. The effect of dissolved organic matter (DOM)

Micropollutants usually exist with DOM in water bodies [46]. Therefore, the possible competition between micropollutants and DOM should be considered when performing an adsorption experiment.

<table>
<thead>
<tr>
<th>Compound</th>
<th>T (K)</th>
<th>$q_m$ (µg/mg)</th>
<th>R^2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tonalide</td>
<td>298</td>
<td>107.19</td>
<td>0.9766</td>
</tr>
<tr>
<td></td>
<td>308</td>
<td>95.36</td>
<td>0.9684</td>
</tr>
<tr>
<td></td>
<td>318</td>
<td>84.68</td>
<td>0.9742</td>
</tr>
<tr>
<td>Bisphenol-A</td>
<td>298</td>
<td>129.65</td>
<td>0.9764</td>
</tr>
<tr>
<td></td>
<td>308</td>
<td>107.19</td>
<td>0.9610</td>
</tr>
<tr>
<td></td>
<td>318</td>
<td>92.69</td>
<td>0.9536</td>
</tr>
<tr>
<td>Triclosan</td>
<td>298</td>
<td>82.39</td>
<td>0.9661</td>
</tr>
<tr>
<td></td>
<td>308</td>
<td>68.28</td>
<td>0.9566</td>
</tr>
<tr>
<td></td>
<td>318</td>
<td>56.17</td>
<td>0.9724</td>
</tr>
<tr>
<td>Metolachlor</td>
<td>298</td>
<td>79.69</td>
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<td>308</td>
<td>76.47</td>
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<tr>
<td></td>
<td>318</td>
<td>70.61</td>
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Further experiments showed that 5.5 mg/L of PVP-coated NPs concentration was the optimal concentration when SRFA was added to the sample. This increase in the adsorbate concentration was indispensable due to the fact that the SRFA acts as a competitor for PVP-coated NPs meaning that a higher adsorbate concentration is required to remove the same amount of target micropollutants.

Fig. 7 showed the average adsorption removal efficiencies of micropollutants in the distilled water and surface water for both PVP-coated NPs and GAC. According to the results, GAC was more affected by the addition of DOM to the water sample. However, PVP-coated NPs showed a great performance for the same conditions. It took 25 min for PVP-coated NPs to reach equilibrium while the equilibrium time for GAC was 55 min. The significant decrease in the removal of micropollutants might be caused by the competitive inhibition of DOM with micropollutants on GAC. This result implies that the inhibition of adsorption in the SRFA water samples is due to competition of hydrophobic adsorption interaction of SRFA with micropollutants on the surface of GAC to occupy adsorption sites.

Table 5
Thermodynamic parameters for the adsorption of tested micropollutants onto PVP-coated NPs.

<table>
<thead>
<tr>
<th>Compound</th>
<th>ΔH° (kJ/mol)</th>
<th>ΔS° (J/mol K)</th>
<th>ΔG° (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>298 K</td>
<td>308 K</td>
<td>318 K</td>
</tr>
<tr>
<td>Tonalide</td>
<td>158.22</td>
<td>48.56</td>
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<td></td>
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<td>−2.17</td>
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<tr>
<td></td>
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<td></td>
<td>−4.00</td>
</tr>
<tr>
<td>Bisphenol-A</td>
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<td>117.56</td>
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<tr>
<td>Ketoprofen</td>
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</table>

Adsorbent regeneration is critical to ensure its sustainability [47]. In this study three regeneration methods were studied. Fig. 8 compares all regeneration methods to regenerate the removal capacity of the adsorbent for five consecutive cycles. This figure reports the average removal efficiency of micropollutants that are based on the micropollutants concentrations in the solution. Tables S1–S3 in the supplementary materials show the removal efficiency of all micropollutants for each regeneration method. According to the results the average removal efficiency for the methanol method was almost the same for all five cycles, while ethanol’s desorption efficiency decreased slightly. This showed that methanol could effectively detach the micropollutants from the surface of the adsorbent due to lower molecular weight, since ethanol (MW = 46) > methanol (MW = 32). This could be due to the fact that smaller molecules can penetrate more easily into the micropores of the adsorbent and displaces the adsorbate more effectively.

Because alcohols have a hydroxyl group in their structures, organic micropollutants are more soluble in them. For example, Filippa et al. [48] found the solubility of Ketrophen in water, ethanol, and methanol to be $6.27 \times 10^{-4}$, 1.85 and 1.75 mol/L, respectively. Therefore, methanol and ethanol are able to easily desorb the studied micropollutants.

On the other hand, the regeneration performance of the UV/H$_2$O$_2$ process was tested as a system that does not have any waste at the end of the regeneration process [49]. This system is recognized as one of the more effective advanced oxidation processes (AOPs) that is able to remove a wide range of contaminants [4,50]. Organic pollutants adsorbed onto the adsorbent surface can be mineralized into harmless compounds such as carbon dioxide and water. It can be seen from Fig. 8 that
the adsorption efficiency decreased when the UV/H₂O₂ treatment was applied. The main reason could be the non-selective nature of UV/H₂O₂ process to degrade oxidizable substances. In fact, this system can degrade adsorbed micropollutants and the surface of the coated polymer at the same time. Therefore, the regenerated adsorbent has probably less effective adsorption sites for the next cycles.

4. Conclusions

In this study, PVP-coated NP was successfully produced using a new method and its characterizations were evaluated by different techniques. The adsorbent was successfully used for removing micropollutants from aqueous solutions. The adsorbent dosage, contact time, temperature, and dissolved organic matter competitor had a significant effect on the adsorption performance of PVP-coated NPs. The maximum adsorption capacities of Bisphenol-A and Ketoprofen on the adsorbent were determined to be 61.70 and 80.05 μg/mg, respectively. Results of isotherm modeling indicated that the Langmuir model was well fitted to the experimental data. In addition, the pseudo second order model was used to describe the adsorption kinetics. The thermodynamic parameters of all tested micropollutant adsorption onto the PVP-coated NPs showed that the adsorption process was endothermic and spontaneous. Methanol regeneration studies showed that PVP-coated NPs could be recycled and used for at least five cycles.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.colsurfa.2017.08.008.

References


