Adsorption of 17α-ethynyl estradiol and β-estradiol on graphene oxide surface: An experimental and computational study

Priyakshree Borthakur a,b, Purna K. Boruah a,b, Manash R. Das a,b,⁎ Natallia Kulik c, Babak Minofar c,d,⁎⁎

a Materials Sciences and Technology Division, CSIR-North East Institute of Science and Technology, Jorhat 785006, Assam, India
b Academy of Scientific and Innovative Research, CSIR-NEIST Campus, India
c Institute of Microbiology, Academy of Sciences of the Czech Republic, Zamek 136, 37333 Nove Hrady, Czech Republic
d Faculty of Science, University of South Bohemia, Braníčkova 1760, 37005 České Budějovice, Czech Republic

⁎ Correspondence to: M. R. Das, Advanced Materials Group, Materials Sciences and Technology Division, CSIR-North East Institute of Science and Technology, Jorhat 785006, Assam, India.
⁎⁎ Correspondence to: B. Minofar, Center for Nanobiology and Structural Biology, Institute of Microbiology, Academy of Sciences of the Czech Republic and Faculty of Science, University of South Bohemia, České Budějovice, Czech Republic.
E-mail addresses: mrdas@neist.res.in (M.R. Das), minofar@nh.cas.cz (B. Minofar).

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A B S T R A C T
Adsorption of endocrine disrupting chemicals (EDCs) such as 17α-ethynyl estradiol and β-estradiol on sp² hybridized graphene oxide (GO) sheets as an efficient adsorbent was carried out. The effect of different experimental parameters such as the concentration of adsorbent and adsorbate as well as pH of the medium were investigated. It was observed that both 17α-ethynyl estradiol and β-estradiol molecules interact with the aromatic skeleton of graphene oxide ring by hydrogen bonding and electrostatic interactions between the oxygen containing functional groups of GO and —OH groups of micropollutant molecules in addition to π-π interactions between the π-electrons of graphene oxide and the aromatic rings of the micropollutant molecules. It was found that the adsorption was facilitated in acidic medium and maximum adsorption efficiency of GO was found to be 98.46% and 97.19% for 17α-ethynyl estradiol and β-estradiol, respectively at pH 3 within 50 min. Classical molecular dynamics (MD) simulations were performed to analyze the adsorption process in the molecular level to support the experimental findings. The results obtained from the computational study show good agreement with the experimental findings.

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1. Introduction

Over the last few decades, increase in urbanization and industrialization pose the exposure of pharmaceutical micropollutants into the environment which becomes a serious environmental issue. Pharmaceutical compounds which are usually used in veterinary and human medicines can enter the environment through direct disposal of unused medicines in wastewater or excretion from humans and animals body [1,2]. Among the different pharmaceutical substances, the substances which can affect the endocrine system are called endocrine disrupting chemicals (EDCs), and they can lead serious environmental and health problems [3]. Among the different EDCs, 17α-ethynyl estradiol and β-estradiol are widely distributed almost in surface water, waste water, ground water, as well as drinking water and are considered as significant endocrine disruptors [4–9]. 17α-ethynyl estradiol is used as an artificial pharmaceutical like ovulation inhibitor and β-estradiol is used as a reproductive hormone [10,11]. In recent years, these EDCs have been found in wastewater effluent discharged from different manmade artificial sources. Therefore, removal of these pharmaceutical pollutants from the wastewater effluents has become an important issue. Researchers have put attention on different removal techniques for the treatment of these pharmaceutical waste water effluents. Different treatment methodologies including nano-filtration, advanced oxidation processes, reverse osmosis and adsorption techniques are widely used to remove these contaminants from wastewater [12,13]. Among the different techniques, adsorption is the eco-friendly, cost-effective, easy removal technique which is widely used in the removal of pollutant molecules using a selective, low cost, effective adsorbent materials.

Graphene, a single layer novel star material made up of sp² hybridized carbon atoms, has attracted growing attention because of its structural characteristic, remarkable optical, mechanical, chemical, thermal and electrical properties and has potential applications in different fields like energy storage devices, polymer composites, fuel cells, transparent conductors, environment remediation etc. [14–17]. Sun et al. studied the adsorption of 17β-estradiol and bisphenol A using graphene oxide (GO) and reduced graphene oxide (rGO) as adsorbent. They also investigated the effect of different minerals including goethite, kaolin, montmorillonite and found that these minerals had an inhibitory effect on the adsorption process [18]. Due to the high
specific surface area, availability of different functional groups, and the possibility of formation of π-π interaction between the aromatic ring of GO and those of EDCs make it a relevant adsorbent for the removal of 17α-ethynyl estradiol and β-estradiol from the wastewater [19–21]. In the present study, our objective is to investigate the different adsorption parameters for the adsorption of two EDCs (17α-ethynyl estradiol and β-estradiol, Fig. 1) on GO sheets through both experimental and computational study. Moreover, the effect of different experimental parameters including pH of the medium, adsorbent concentration, adsorbate concentration on the adsorption process has been also studied.

2. Experimental sections

2.1. Materials

Graphite powder (<20 μm, Sigma-Aldrich), potassium permanganate (>99%, E Merck, India), sulfuric acid (AR grade; Qualigens, India), H₂O₂ (30%; Qualigens), hydrochloric acid (AR grade, Qualigens, India), NaOH (99%; Qualigens), 17α-ethynyl estradiol (98%, Sigma Aldrich), β-estradiol (98%, Sigma Aldrich).

2.2. Synthesis and characterization of graphene oxide

The adsorbent material GO was synthesized adopting Hummers and Offemann method. The details synthesis method and the characterization technique are discussed in our previous study [22,23].

2.3. Preparation of micro-pollutant solution

20 ppm (20 mg/L) stock solution of each micro pollutant namely 17α-ethynyl estradiol and β-estradiol were prepared by accurately weighted 2 mg molecules in 100 mL distilled water. For adsorption study, different solutions of micropollutant molecules have been prepared by dilution of stock solution with distilled water.

2.4. Adsorption study of micro-pollutant molecules on graphene oxide sheets

Initially, for adsorption study, calibration curves were prepared by analysing the UV absorbance at wavelength of λ_{max} = 282 nm for 17α-ethynyl estradiol and at λ_{max} = 283 nm for β-estradiol. For adsorption experiment, 8 mg/L micropollutant solution was added to a suspension of GO with concentration 0.4 g/L at pH 5. The pH of the reaction mixture was adjusted with the help of a pH meter (Systronics, μ-pH system 362, India) by adding 0.1 N HCl and NaOH solutions. The entire volume of the reaction mixture was adjusted up to 50 mL using distilled water and allowed to stir for 2 h at 25 °C. 5 mL of the reaction mixture was collected at a fixed time interval and immediately frozen in an ice bath and the adsorbent was separated from the reaction mixture by centrifugation. The residual concentration of the micropollutant present in the reaction mixture was analysed with the help of UV–vis spectrophotometer (SPECORD 200, Analytik Zena) compared with standard calibration curve at the wavelength of λ_{max} = 282 nm for 17α-ethynyl estradiol and at λ_{max} = 283 nm for β-estradiol, respectively. The removal efficiency of GO towards micropollutant was evaluated by using the following standard equation.

\[
\% \text{Adsorption} = \left\{1 - \frac{C_t}{C_0}\right\} \times 100
\]  

where, C₀ and Cₜ are the concentration at initial time and at time ‘t’ respectively.

The mechanism for adsorption of EDCs onto GO surface was analysed through the Fourier transform infrared (FT-IR) spectra using IR Affinity, Shimadzu, Japan FT-IR spectrophotometer equipped with a Shimadzu DRS-8000 DRIFT accessory and IR solution software with 4 cm⁻¹ spectral resolution. After adsorption of EDCs, GO was characterized by XRD analysis recorded using Rigaku X-ray diffractometer (Model: ULTIMA IV, Rigaku, Japan) with a scanning rate of 4° min⁻¹ and 2θ value ranging from 5–100° using Cu Kα (λ = 1.54056 Å) as the X-ray source and operates at a generator voltage of 40 kV and current of 40 mA, respectively. The surface morphology of GO after adsorption of EDCs was analysed by field emission scanning electron microscopy (FESEM) using ZEISS Gemini scanning electron microscope (Germany) operated at an accelerating voltage of 9–7 kV.

2.5. Computational details

In order to investigate the nature of the interaction of micropollutants namely 17α-ethynyl estradiol and β-estradiol with the surface of GO in molecular level, classical molecular dynamics (MD) simulation has been performed. MD simulations have been performed in the solutions of GO with micropollutants in different protonation states as both 17α-ethynyl estradiol and β-estradiol can be deprotonated in the solution. The aim of the computational study is to support experimental findings and understand the nature of interaction in the adsorption process.

For performing MD simulations, structures of 17α-ethynyl estradiol and β-estradiol have been built and their geometry optimized by ab initio geometry optimization using the Gaussian 09 package [24] by employing the B3LYP/cc-pVDZ method. To calculate the partial charges of micropollutants, optimized geometries of molecules and ions have been used for restrained electrostatic potential (RESP) fitting scheme [25] by Antechamber program [26].

Parameters of GO were taken from our previous work [27]. In order to solvate GO molecule, micropollutant molecules and ions in the cubic box with water, Packmol package has been used which solvates molecules in random manner in the box [28,29]. Ions and molecules of micropollutants were parametrized by applying the General Amber Force Field (GAFF) model [30], and SPC/E model [31] of water was applied. First steepest descent minimization procedure was applied for all systems to remove all unexpected and unfavourable contacts due to random solvation of molecules, ions and water molecules in the

Fig. 1. Structure of micropollutants viz. 17α-ethynyl estradiol and β-estradiol.
box then equilibration for 500 ps with NVT (canonical ensemble) and then 500 ps NPT (isothermal–isobaric ensemble) restrained simulations. For constraining the bonds, linear constraint solver (LINCS) algorithm [32] was used for all bonds containing hydrogen atoms and the short-range non-bonded interactions were set to zero with the cut-off distance of 1.2 nm. Particle mesh Ewald method procedure was used for calculation of long-range electrostatic interaction [33]. All particles of the system were assigned to initial velocities which were taken consistent with Maxwell–Boltzmann distribution at 300 K. To maintain constant temperature and pressure for all simulated systems, V-rescale coupling algorithm was used [34] with the time constant of 0.1 ps. All production runs were run in NPT ensemble for 50 ns at 300 K with a time step of 2 fs for all simulations. For analysis of data, coordinates, velocities, and energies were saved every 10 ps for all MD simulations. All simulations were performed employing Gromacs 5.0 program package [35–37]. Visual Molecular Dynamics (VMD) program was used for visualizations of the trajectories and preparation of snapshots [38].

3. Results and discussions

3.1. Removal of 17α-ethynyl estradiol and β-estradiol using GO sheets

In order to investigate the practicability of GO sheets towards removal of EDCs, the adsorption study was carried out under different experimental conditions. It was found that the adsorption capacity of EDCs onto GO surface enhanced with increase in time. The adsorption of EDCs onto the GO surface occurs due to the π-π interactions between the EDCs and delocalized π electrons of the un-oxidized aromatic region of GO sheet.

3.2. Effect of adsorbent and adsorbate concentration

The effect of the amount of GO concentration on the adsorption of EDCs was studied by changing the concentration of GO keeping other parameters constant i.e.; concentration of EDCs was 8 mg/L and at pH 5, the GO concentration was varied from 0.1 g/L to 0.5 g/L. Maximum adsorption efficiency was found to be 96.37% for 17α-ethyl estradiol and 95.31% for β-estradiol at GO concentration of 0.4 g/L at pH 5. At GO concentration above 0.4 g/L adsorption efficiency was decreased (Fig. 2a). At higher concentration, GO undergoes agglomeration and thus the active adsorption sites decreases and adsorption efficiency is also decreased. The adsorption efficiency of 17α-ethyl estradiol was found to be more efficient than that of β-estradiol. This is because of the fact that in addition to π-π interaction between the aromatic ring of 17α-ethyl estradiol and GO, 17α-ethyl estradiol can also bind through π-π interaction between π electrons of ==CH group of micropollutant and the π-electrons of GO surface which is absent in β-estradiol.

The concentration of micropollutant also affects the adsorption efficiency of GO surface. To investigate the effect of adsorbate concentration on adsorption onto GO surface, adsorption experiment was carried out by varying the micropollutant concentration from 6 mg/L to 14 mg/L at a fixed GO concentration of 0.4 g/L and at pH 5. It was observed that with an increase in adsorbate concentration, the adsorption efficiency was decreased. It is due to the fact that at a higher concentration, more pollutant molecules adsorb on the GO surface and thus block

![Fig. 2. Adsorption efficiency of EDCs (a) at different GO concentration (EDCs concentration 8 mg/L; pH 5); (b) at different concentration of 17α-ethyl estradiol (EE2) and (c) at different concentration of β-estradiol (E2) (GO concentration = 0.4 g/L and pH 5).](image-url)
the active sites of the adsorbent surface and decreases the adsorption efficiency. The variation of adsorption efficiency for 17α-ethynyl estradiol and β-estradiol at different concentration is depicted in Fig. 2b and c.

3.3. Effect of pH

The effect of initial pH on the adsorption of EDCs on GO surface was investigated by stirring the mixture containing 8 mg/L of EDCs solution, 0.4 g/L GO at different pH namely (pH 3, 5, 7, 9, 11) of the reaction medium. Fig. 3, shows that in acidic medium, the adsorption efficiency increases. Both 17α-ethynyl estradiol and β-estradiol molecules undergo π-π interactions between the π-electrons of GO and the aromatic rings of the micropollutant molecules. Moreover, hydrogen bonding interactions and electrostatic interactions take place between the π-containing functional groups of GO and —OH groups of 17α-ethynyl estradiol and β-estradiol molecules [39, 40]. It is mentioned in our previous study that at lower pH, the surface charge (zeta potential) value of GO tends to be positive than those in alkaline medium [27]. On the other hand, in alkaline medium (higher pH), GO surface becomes more negative because of the ionization of surface functional groups by the reaction with OH− ions of the solution. Both 17α-ethynyl estradiol and β-estradiol are considered as weak organic acids with their dissociation constant (pKa ≈ 10). Therefore, both the EDCs (17α-ethynyl estradiol and β-estradiol molecules) can exist either as neutral molecule or ionic form within the pH range 3–11. With increase of pH of the medium, EDCs exist in anionic form due to ionization of the —OH groups present in the molecule. Therefore, the electrostatic repulsion between the anionic form of EDCs and negatively charged GO surface becomes predominant and thus the adsorption is decreased. In lower pH, interactions between the EDC molecules and GO surface become more feasible and hence adsorption efficiency is increased. Maximum adsorption efficiency of GO was found to be 98.46% and 97.19% for 17α-ethynyl estradiol and β-estradiol, respectively at pH 3 within 50 min. The variation of adsorption efficiency for 17α-ethynyl estradiol and β-estradiol at different pH is shown in Fig. 3.

3.4. Mechanism of adsorption

To understand the adsorption mechanism of micropollutant molecules on GO surface, DRIFT spectra of 17α-ethynyl estradiol and β-estradiol were recorded before and after adsorption on GO surface (Fig. 4). It is seen from the DRIFT spectra of 17α-ethynyl estradiol that, the band at 3300 cm−1 appears due to the —OH stretching vibration. The band at 2922 cm−1 resembles to the asymmetric stretching vibration of —CH2 groups. The vibrational bands appear at 1598 cm−1 ascribed the aromatic C=C bond stretching vibration. Similarly, for β-estradiol the adsorption band appears at 3218 cm−1 corresponds to the —OH stretching vibration. The band at 2938 cm−1 appears due to the —CH2 asymmetric stretching. The bands at around 1600 cm−1 and 1477 cm−1 appear due to the stretching vibration of aromatic C=C bonds and band at 1239 cm−1 is attributed to the C—O bond vibration. After adsorption of EDCs molecules on GO surface, the displacement of the aromatic C=C bond stretching vibration indicates the π-π interactions between the aromatic ring of GO and the EDC molecules. Moreover, there is a decrease in intensity of the absorbance peak at 1730 cm−1 of GO attributed to the electrostatic interactions between GO surface and EDCs. The shifting of the peak due to —OH stretching also indicates the electrostatic interaction between adsorbate and adsorbent molecules [41, 42].

3.5. Characterization of GO after adsorption of EDCs

After performing the adsorption experiments, the GO sheets were characterized by XRD and FESEM analysis to reveal the crystallinity change and morphology changes of GO during the adsorption. For that, the GO was repeatedly washed with water followed by acetone and dried at 60 °C for 4 h. The XRD pattern of GO before and after adsorption of EDCs are shown in Fig. 5. It is observed in Fig. 5a that, after adsorption of EDC molecules on GO surface, the peaks at around 2θ = 10° become broad and an additional peak at around 2θ = 25° appears which confirms the fractional reduction of GO due to the electrostatic interactions between GO and EDC molecules which results in the dissociation of oxygen containing functional groups present on GO surface [42]. Similarly, FESEM analysis was carried out for GO before and after adsorption of the EDCs molecules on its surface as shown in Fig. 5b and c. The FESEM images show that the morphology of GO sheets after adsorption of EDC molecules remains unchanged. Similar GO sheets were clearly observed before and after adsorption of EDC molecules.

3.6. Computational results and discussion

MD simulations have been used to investigate the dynamics of the adsorption process of different EDCs at the surface of GO and to reveal the adsorption mechanism of EDCs at GO surface in molecular level. The micropollutants and GO modelled in different ionization states (neutral and ionic forms) to understand the effect of pH on adsorption process and reveal the role of both weak and strong interactions on the mechanism of adsorption. Analysis of MD trajectories showed that adsorption of 17α-ethynyl estradiol and β-estradiol on GO surface depends on interaction time, concentration and charge of EDCs and pH of the medium.

The time dependence of adsorption of micropollutant molecules and ions at the surface of GO in acidic condition is shown in Fig. 6. At low pH 17α-ethynyl estradiol molecules were adsorbed faster than β-estradiol (Fig. 6A and B) but at the end of the simulations both neutral and ionic
forms of micropollutant were adsorbed at the surface of GO. To be seen in Fig. 6A that the $\beta$-estradiol ion was not adsorbed to the surface in 50 ns of simulation time thus this simulation was extended to longer time and in $\sim$100 ns simulation time the $\beta$-estradiol molecule was adsorbed on the surface of GO.

The organization of two $\beta$-estradiol molecules adsorbed on the surface of GO surface is shown in Fig. 7. $\beta$-estradiol molecule could be oriented towards GO surface in two modes as it is shown as mol1 and mol2. In both orientations, phenyl ring of $\beta$-estradiol forms $\pi-\pi$ stacking interaction with GO while other hydrogen atoms close to GO forms weaker interactions. The distance from the first molecule (mol1) to the surface of GO is slightly longer than for second molecule (mol2) due to the presence of methyl group at the position of C18 [43,44].

17$\alpha$-Ethynyl estradiol as well could be adsorbed with methyl at C18 carbon towards GO surface or towards water. The preferred adsorbed orientation of 17$\alpha$-ethynyl estradiol is similar to second molecules of $\beta$-estradiol (mol2), when methyl group at C18 is oriented towards the solution. In the case of 17$\alpha$-ethynyl estradiol there is additional interaction of GO with $-\text{C}==\text{C}-\text{H}$ group.

As an interesting point to note is the relative stability of attraction and cooperation between micropollutant molecules at the surface. Adsorbed molecules at the surface of GO do not leave the surface, in other words no desorption to the solution is observed during 100 ns of simulation time. It can be concluded that complexes of micropollutants with GO are stable and adsorption of one molecule at the surface of GO increases the probability and affinity of the surface for another molecule to be adsorbed.

By increasing the pH of the solution, the total number of micropollutant molecules adsorbed to the surface of GO decreases; which is due to electrostatic repulsion between negatively charged GO with negatively charged micropollutants, which supports experimental findings (see Fig. 9B, D).

With the increase of concentration of micropollutants the numbers of adsorbed molecules at the surface of GO increases which also supports experimental evidences. MD simulations showed that the number of adsorbed molecules at the surface of GO reaches a saturation value. When the adsorbed molecules at the surface of GO form the first adsorption layer therefore, saturated GO surface could not attract more molecules to the surface, however more
molecules are adsorbed by formation of cluster of micropollutant molecules with formation of second adsorption layer as shown in Fig. 8.

To show the observed phenomena quantitatively from MD trajectories, radial distribution function (RDF) has been applied. In the simulation of acidic condition with 10 molecules of 17α-ethynyl estradiol 9 molecules form the first adsorption layer and last remaining molecule made the adsorption second layer (blue peak in Fig. 9A and increase of total number of adsorbed molecules in Fig. 9B).

There is an interesting difference in the dynamics of charged β-estradiol and 17α-ethynyl estradiol at high and low pH values in which adsorption of charged micropollutants is less favourable at low pH values while at high pH values charged molecules absorbed better than neutral species (Fig. 9 C, D). Two forces cause this phenomena a) electrostatic repulsion between negatively charged groups on GO and negatively charged micropollutant molecules b) hydrophobic clusters formation of micropollutant molecules at the surface.

Formation of the second and third adsorption layers (RDF and cumulative number in Fig. 9) of micropollutant is related to the hydrophobic property of EDCs molecules which allow them to make stable aggregate in water that is observed in MD simulation (Fig. 8).

Formation of second and third layers of micropollutants at the surface of GO sheets affected by solvent accessible surface of GO to form hydrophobic cluster of micropollutants. The hydrophobic clustering appears at the surface of GO and in a bulk solution and becomes

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**Fig. 6.** The distance of the centre of mass of micropollutant molecules and ions to the surface of GO molecule during MD simulations in acidic solution. A) β-estradiol (E2) and B) 17α-ethynyl estradiol (EE2).

**Fig. 7.** Top view (A) and side view (B) of the molecules of GO and β-estradiol (E2) after 50 ns from MD simulation in acidic condition. (C) and (D) are snapshots from simulation of GO in basic conditions with 10 neutral 17α-ethynyl estradiol (EE2) molecules. Hydrophobic cluster of neutral molecules is formed in the beginning of simulation. At 50 ns of simulation time (C) it can be observed that the cluster of hydrophobic molecules is close to the surface of GO, however just after 100 ns simulation time hydrophobic cluster of micropollutant molecules aggregates at the surface of GO. (Color code: C, Cyan; O, red; H, white; Na, blue.) (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
predominant with the increase of the concentration of micropollutants in the solution. Analysis of MD simulations showed that the neutral molecules of β-estradiol and 17α-ethynyl estradiol have higher affinity for cluster formation. Cluster formation nicely explains the difference between absorption of neutral and ionic 17α-ethynyl estradiol in basic condition (Fig. 7): when cluster of neutral 17α-ethynyl estradiol molecules not adsorbed at the surface of GO thus the number of adsorbed neutral molecules becomes lower than charged ions and do not form clusters therefore available for surface adsorption. By increasing the MD simulation time, adsorption of hydrophobic clusters by GO due to dynamics of such cluster become more favourable. (Figs. 9D and 7C, D).

Decrease of adsorption at higher pH is related to increase of the electrostatic repulsion between negatively charged carboxyl groups of GO and negatively charged micropollutants molecules. Solvated positive Na⁺ counter ions form a layer on both sides of the GO.

MD simulation revealed that in acidic media with 10 neutral molecules of β-estradiol, micropollutant molecules make a good arranged structured adsorption layer around GO surface (Fig. 8). Sodium ions do not form organized layer around GO in acidic condition but adsorbed to the carboxyl groups of GO to make strong contact ion pair.

Formation of Na⁺ layer improves binding of micropollutant ions to the surface of GO however, it decreases the space for binding of neutral molecules to the surface of GO. Also, formation of organized Na⁺ layer influences the adsorption of 17α-ethynyl estradiol differently than β-estradiol to the surface of GO, leading to improve adsorption of β-estradiol in higher pH values for better ability of 17α-ethynyl estradiol to make well organized pattern.

4. Conclusions

In the present study, adsorption of EDCs (17α-ethynyl estradiol and β-estradiol) on GO sheets was carried out. The adsorption process of EDCs on GO has been monitored by different factors such as initial concentration of adsorbent and adsorbate molecules, initial pH of the medium. We observed that both 17α-ethynyl estradiol and β-estradiol molecules interact with the aromatic skeleton of GO ring by both hydrogen bonding interactions and electrostatic interactions between the oxygen containing functional groups of GO and —OH groups of micropollutant molecules in addition to π-π interactions between the π-electrons of positively charged GO surface and the aromatic rings of the micropollutant molecules. The interactions between the EDCs molecules and GO surface is more feasible in an acidic condition due to more π-π interactions between the π-electrons of positively charged GO surface and the aromatic rings of the micropollutant molecules. Maximum adsorption efficiency of GO was found to be 98.46% and 97.19% for 17α-ethynyl estradiol and β-estradiol, respectively at pH 3 within 50 min. In case of 17α-ethynyl estradiol, in addition to π-π interaction between the aromatic ring of 17α-ethynyl estradiol and GO, π-π
bonding interaction between π electrons of –CH group of micropollutants and the π-electrons of GO surface may occur which enhances the adsorption efficiency of 17α-ethyl estradiol (EE2) in compare to adsorption efficiency of β-estradiol. To support the experimental findings, classical molecular dynamics (MD) simulation has been performed and radial distribution function (RDF) was calculated from trajectories. MD simulation showed that adsorbed molecules at the surface of GO do not leave the surface, therefore no desorption to the solution is observed during 100 ns of simulation time. Micropollutant molecules can form stable complexes through bonding with GO and adsorption of one molecule at the surface of GO increases the probability and affinity of the surface towards the adsorption of another molecule. From the above experimental results, it can be concluded that adsorption of pollutant molecules on GO surface is considerably affected by the surface properties of the adsorbent which is influenced by the pH of the medium.

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![Fig. 9. RDF and cumulative number of molecules in different conditions, calculated for systems containing 10 micropollutant molecules over one GO molecule. First peak corresponds to adsorbed molecules at the surface of GO. In general β-estradiol (E2) molecules are to the surface of GO than 17α-ethyl estradiol (EE2). Peaks close to the first peaks (within ~0.2 nm) correspond to improper orientation of attracted residues, while further peaks appear due to formation of second (blue on A and red on C) and third (red on C) layers of micropollutant molecules. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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