Composite Poly[2-(Dimethylamino)ethyl Methacrylate-*co*-Ethylene Dimethacrylate/Graphene Oxide Adsorbent for Highly Efficient Removal of Estrone from Water

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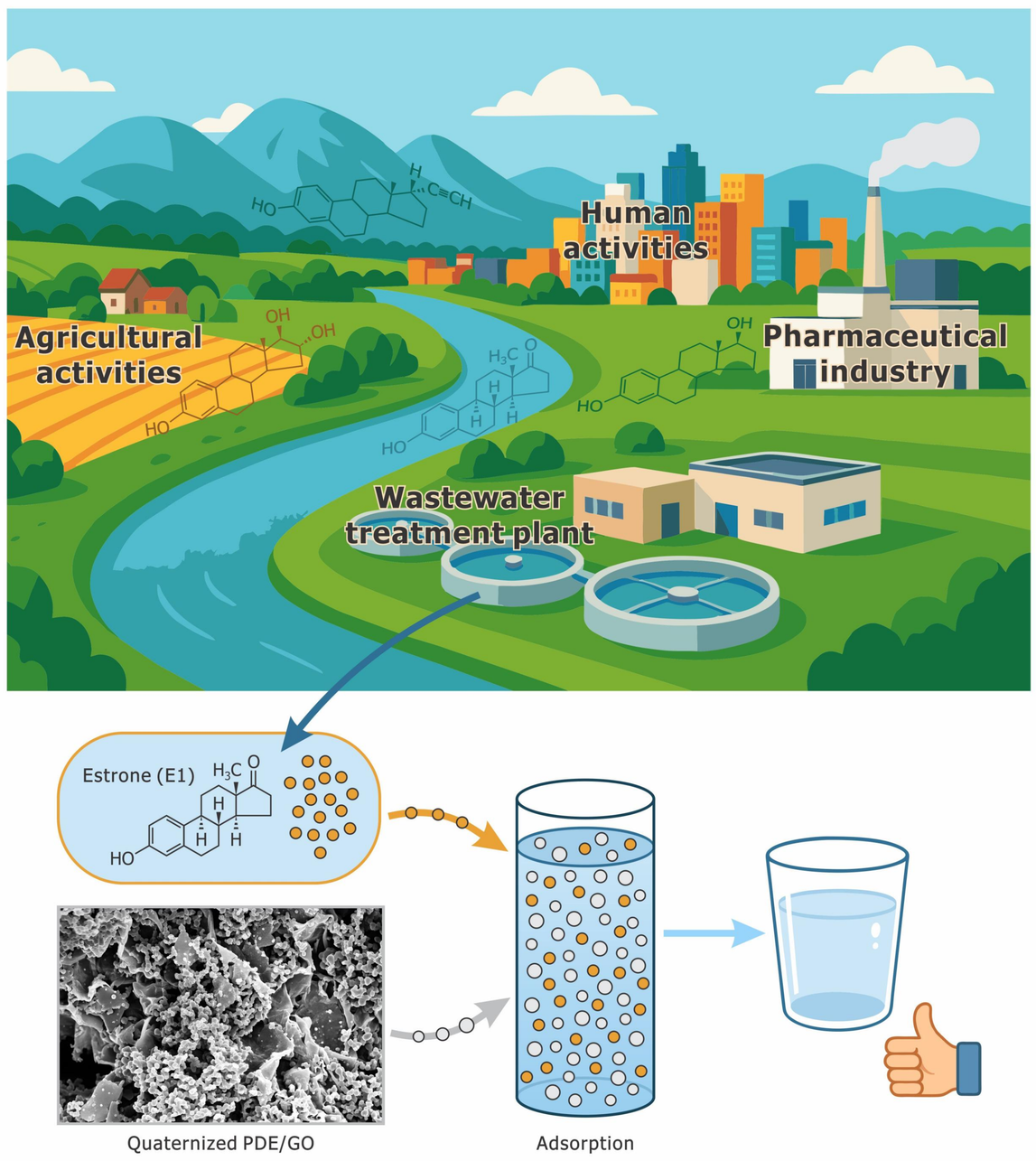

INTRODUCTION

Steroid estrogens (SEs) as a class of endocrine-disrupting compounds are one of the **major micropollutants in environment with toxicological effect on ecosystem and living creatures at very low concentrations (~ 10 ng/L)**. Natural SEs, such as estrone (E1), 17β-estradiol (E2), estriol (E3), 17α-ethynyl estradiol (EE2) are characterized with higher harmful estrogenic potency on reproductive, neuro-endocrine, cardiovascular systems and they may induce immunotoxicity, genotoxicity, carcinogenity, endocrine disruption. SEs including natural and synthetic estrogens are usually used in pharmaceuticals, food, personal care products, and pesticides and due to widespread use cause serious contamination of wastewater **discharged into various water resources even after processing in wastewater treatment plants**. Besides, animal and human excretions also contain SEs that represent another important source of water environment contamination. **Based on the literature, SEs have been detected in effluents from wastewater treatment plants at concentrations ranging from 0.1 to 196 ng/L. Therefore, there is an urgent need to develop effective treatment technology for the removal of SEs at trace levels from water and waterwaste. Especially, the removal of E1 is crucial due to its widespread presence in water bodies worldwide and its inclusion on the priority lists of the United States, the European Union, and Australia.** Conventional treatment technologies include adsorptive removal, coagulation, membrane filtration, photocatalysis, ozonation, chlorination, and biodegradation. **However, an efficiency of these treatment processes is limited and processed water still contains residual contaminants with concentration µg/L or even ng/L.**

This work presents **the development of quaternized composite** poly[2-(dimethylamino)ethyl methacrylate-*co*-ethylenedimethacrylate/graphene oxide (PDE/GO) **adsorbent** that **quickly and effectively removes E1 from water at its very low concentration.** PDE and composite PDE/GO adsorbents were prepared by precipitation polymerization in a H_2O/ethanol mixture and then they were quaternized using iodomethane (Figures 1a-c). We evaluated the effectiveness of quaternized PDE/GO, quaternized PDE, and GO in removing E1 from water at E1 initial concentration of 200 µg/L, at 25 °C and a pH range of 5 to 9, using 2 mg/mL of each adsorbent during 120 minutes. While GO (Table 1) and quaternized PDE adsorbents (Table 2) demonstrated a removal efficacy of 40-60%, **the quaternized composite PDE/GO adsorbent exhibited remarkable 100% removal of E1 within 5 minutes across all tested pH levels (Table 3)**, attributed to the synergistic effect of the composite PDE/GO particles. All analyses were performed in triplicate.

EXPERIMENTAL & RESULTS

- **PDE (Figure 1a) and composite PDE/GO adsorbents were prepared by precipitation polymerization in H_2O/EtOH mixture, initiated with potassium persulfate, 80 °C, 24 h, 400 rpm**
- **Quaternization of the adsorbents (2.2 g; Figure 1b and 1c) using an excess of iodomethane (20 ml), ambient temperature, 24 h, magnetic stirring**
- **The presence and quantity of quaternary ammonium cations in PDE and composite PDE/GO adsorbents were studied with NMR (Figures 2-4), quternization 50 %**
- **Specific surface areas:**
  - ***GO = 0.07 m^2/g***
  - ***quaternized PDE = 6.91 m^2/g***
  - ***quaternized PDE/GO = 30.45 m^2g***

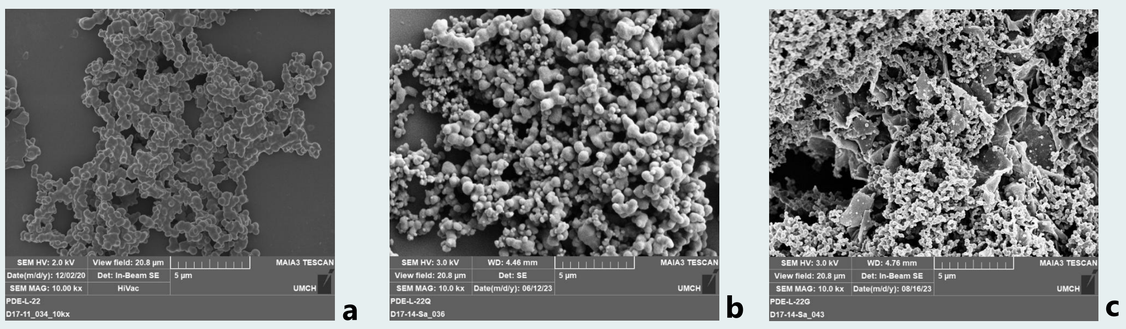

Figure 1. SEM micrographs of PDE particles (a), quaternized PDE adsorbent (b) and quaternized composite PDE/GO adsorbent (c).

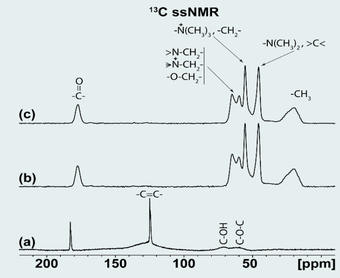

Figure 2. Experimental spin-echo ^{13}C MAS NMR spectrum of GO (a) and ^{13}C CP/MAS NMR spectra of quaternized PDE adsorbent (b) and quaternized PDE/GO adsorbent (c). The samples were recorded at 20 kHz spinning speed under MAS on 16.4 T NMR spectrometer.

Table 1. E1 adsorption form water using GO. E1 initial concentration was 200 µg/L, experimental temperature 25 °C, pH range 5 to 9, adsorbent concentration was 2 mg/mL, adsortion time 120 minutes. HPLC analysis of eluents: HPLC Shimadzu Prominence, LC column LiChroCART® 250-4.6 (RP-18e 5 µm), mobile phase 70% MeOH, 30% H_2O, 0.1% HCOOH, flow rate 1 mL/min, volume injection 20 µL, fluorescence detector (ex. 280 nm, em. 310 nm). All adsorption and HPLC analyses were performed in triplicate.

	pH 5			pH 6			pH 7			pH 8			pH 9		
Time (min)	***Amount adsorbed (µg)***	***Standard deviation***	***Efficacy (%)***	***Amount adsorbed (µg)***	***Standard deviation***	***Efficacy (%)***	***Amount adsorbed (µg)***	***Standard deviation***	***Efficacy (%)***	***Amount adsorbed (µg)***	***Standard deviation***	***Efficacy (%)***	***Amount adsorbed (µg)***	***Standard deviation***	***Efficacy (%)***
1	84.9	12	42.5	69	3	34.6	91.8	6.5	45.9	62	12.3	31.2	88	4.5	44.2
5	56	7.1	43	76	4.1	38.1	71.4	4.6	35.7	39	3.4	19.6	87	4.4	43.5
15	101.4	2.6	50.7	71	4.4	35.7	58.3	11.8	29.1	38	10.4	19	105	17.4	52.4
30	82.2	8.4	41.1	85	17.1	42.7	67.2	1.4	33.6	41	7.9	20.3	73	4.9	36.7
45	86	13.7	43	94	13.6	46.9	66.3	13.3	33.2	35	5.2	17.3	80	5.9	39.8
60	70.9	4.4	35.4	64	0.4	31.8	69.7	1.3	34.9	39	1.2	19.3	81	1.4	40.7
120	76.5	10.5	38.3	54	3.3	27	63	5.7	31.5	34	5.3	17.2	69	10.1	34.4

Table 2. E1 adsorption form water using quaternized PDE adsorbent. E1 initial concentration was 200 µg/L, experimental temperature 25 °C, pH range 5 to 9, adsorbent concentration was 2 mg/mL, adsortion time 120 minutes. HPLC analysis of eluents: HPLC Shimadzu Prominence, LC column LiChroCART® 250-4.6 (RP-18e 5 µm), mobile phase 70% MeOH, 30% H_2O, 0.1% HCOOH, flow rate 1 mL/min, volume injection 20 µL, fluorescence detector (ex. 280 nm, em. 310 nm). All adsorption and HPLC analyses were performed in triplicate.

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1	93	9	46.5	105.6	3.3	52.8	141.3	9.7	70.6	124.9	2.7	62.5	118.1	6.1	59.1
5	107.7	12.2	53.8	105.6	1.4	52.8	123.6	12.6	61.8	125.8	6.2	62.9	123.2	7	61.6
15	120.5	1.7	60.3	118.6	1.4	59.3	120.5	13.6	60.3	118	1.6	59	130.9	6.4	65.5
30	117.4	5	58.7	116	5.5	58	124.2	6	62.1	121.3	1.9	60.7	128.4	2.4	64.2
45	109.8	4.1	54.9	132.3	4.4	66.1	124.9	14.1	62.4	138.2	4.1	69.1	135.2	17.1	67.6
60	110.1	3	55	136.8	13.5	68.4	132.4	3.1	66.2	132.3	10.4	66.1	133.7	3.2	66.8
120	122	3	61	149.9	8.1	74.9	131.4	5.7	65.7	123.1	5.2	61.6	142.9	5.5	71.5

Table 3. E1 adsorption form water using quaternized composite PDE/GO adsorbent. E1 initial concentration was 200 µg/L, experimental temperature 25 °C, pH range 5 to 9, adsorbent concentration was 2 mg/mL, adsortion time 120 minutes. HPLC analysis of eluents: HPLC Shimadzu Prominence, LC column LiChroCART® 250-4.6 (RP-18e 5 µm), mobile phase 70% MeOH, 30% H_2O, 0.1% HCOOH, flow rate 1 mL/min, volume injection 20 µL, fluorescence detector (ex. 280 nm, em. 310 nm). All adsorption and HPLC analyses were performed in triplicate.

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1	200	0	100	200	0	100	200	0	100	200	0	100	200	0	100
5	200	0	100	200	0	100	200	0	100	200	0	100	200	0	100
15	200	0	100	200	0	100	200	0	100	200	0	100	200	0	100
30	200	0	100	200	0	100	200	0	100	200	0	100	200	0	100
45	200	0	100	200	0	100	200	0	100	200	0	100	200	0	100
60	200	0	100	200	0	100	200	0	100	200	0	100	200	0	100
120	200	0	100	200	0	100	200	0	100	200	0	100	200	0	100

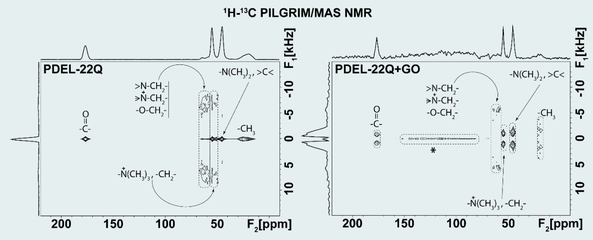

Figure 3. Experimental ^{1}H-^{13}C PILGRIM NMR spectra of neat PDEL-22Q polymer matrix (left hand spectrum) and PDEL-22Q+GO composite (right-hand spectrum). The samples were recorded at 12.5 kHz under MAS on 11.7 T spectrometer. The central signal marked by asteris (*) is an artefact caused by baseline distorsion.

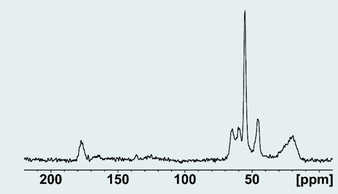

Figure 4. Experimental ^{13}C MAS NMR spectrum of PDE-L-22Q sample recorded at 20 kHz spinning speed under MAS on 16.4 T NMR spectrometer. Repetition delay 10 s and SPINAL 64 decoupling sequence were used for 5120 accumulations.

CONCLUSIONS

- SEs are one of the major micropollutants in environment with toxicological effect at very low concentrations
- We developed the quaternized composite PDE/GO adsorbent
- Quaternized composite PDE/GO adsorbent exhibited remarkable 100% removal of E1 from water within 5 minutes in pH range from 5 to 9

ACKNOWLEDGEMENT

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