Oil Decontamination

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Hydrogel-Assisted Transfer of Graphene Oxides into Nonpolar Organic Media for Oil Decontamination

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Abstract: *In this work, graphene oxide (GO)-loaded agarose hydrogel was transferred into oil such as hexadecane via stepwise solvent exchange with no chemical modification of the GO hydrophilic surface and the agarose network. After transfer, the GOs, loaded in the agarose network, could effectively and efficiently adsorb lipophilic dyes in oil via hydrogen bonding between the polar groups of the GOs and the dyes. The maximum adsorption capacity was 355.9 mg g^{-1} for Nile red for instance, which is substantially larger than that of pristine agarose hydrogel and hydrophilic GO powder. The dye concentration for effective adsorption can be as low as 0.5 ppm. Thus, the present work demonstrates the promising potential of using hydrophilic adsorbents for efficient removal of polar impurities from oil.*

A trace amount of polar impurities in oil can lead to big issues in many technical applications. Take engine fuels, for instance: it is known that the presence of aromatics and polar organic sulfur or nitrogen compounds in engine fuels significantly deteriorates the combustion performance, which further has adverse environmental and health impacts.[1] The presence of toxic impurities such as aflatoxins in eatable oil even at concentration of ppm (μg mL^{-1}) may cause serious food safety issues.[2] Since their unacceptable concentration in oil is of the order of ppm in most cases, polar impurities are hardly removed by means of conventional oil purification processes such as distillation.[3] Ultrafiltration or nanofiltration techniques have been developed for efficient oil decontamination, the applicability of which, however, is limited by high cost incurred in membrane manufacture and recycling and pressure-driven filtration operation.[4] On the other hand, the separation selectivity of membrane filtration may not be favorable for the generic purpose of oil decontamination.[5] Herein we demonstrate a simple strategy for efficient oil decontamination via adsorption of polar organic contaminants by hydrophilic graphene oxides (GOs) in nonpolar organic media with the help of hydrogel as amphibious dispersing agent.

Adsorption is a fairly cost-effective method for water purification and widely applied in many industrial processes and our daily life.[6] Activated carbon is one of conventionally used adsorbents.[7] Recently, GOs emerge as excellent adsorbents, since they have exceedingly large surface areas arising from to the (quasi-)monolayered feature and a large number of polar groups decorated on the surfaces and the edges in particular.[8] Despite the success in water purification, however, GOs and other currently available adsorbents are hardly applied for removal of polar organic impurities in oil. The obvious technical dilemma is that a number of polar groups on the surfaces of adsorbents are necessitated for effective adsorption of polar impurities, including metal ions and polar organic molecules, but these surface polar groups make the adsorbents hardly dispersed in nonpolar organic media.[9] The dispersability of the hydrophilic adsorbents in oil can be improved by surface hydrophobization, but the transformation of the surface polar groups to the nonpolar ones is obviously not favorable for effective adsorption. Up to date, it is still an experimental challenge to directly transfer hydrophilic particles into oil without sacrifice of their polar groups. We recently demonstrated reversible exchange of water in hydrogel with water-immiscible organic solvents, which enabled reversible phase transfer and encapsulation of nanoparticles with the aid of hydrogel.[10] Encouraged by this success, here we generated GO-loaded agarose hydrogel and then transferred the resulting composite hydrogel into nonpolar organic media such as hexadecane via stepwise solvent exchange. Since the GOs, loaded in the agarose network, were hardly changed during solvent exchange, their polar surfaces remained in direct contact with the nonpolar, organic surrounding and thus capable of effectively and efficiently adsorbing polar organic molecules at the concentration as low as 0.5 ppm.

Agarose hydrogel was obtained via cooling the hot (80 °C) aqueous solution of agarose below the gelation temperature (36 °C); the agarose content was 15 mg g^{-1}. Hydrogel is a hydrophilic polymer network highly swollen by water, so it is conventionally used in aqueous media. In the current work, counter-intuitively, the agarose hydrogel will be used in oil. As depicted in Figure 1 a, the resulting agarose hydrogel is incubated firstly in ethanol, which enables ethanol substitution for water in the hydrogel network thanks to the miscibility of ethanol with water. By taking the advantage of ethanol being miscible with many organic solvents, the similar incubation treatment enables replacement of the ethanol, soaked in the agarose hydrogel, by hexadecane or other nonpolar organic solvents. After solvent exchange, the agarose hydrogel is incubated in the hexadecane solution of Nile Red (NR) (Figure 1 b). NR was chosen as model polar organic impurity (Scheme S1 in the Supporting Information), since it is hardly soluble in water but highly in many polar and nonpolar organic solvents with the adsorption and fluores-

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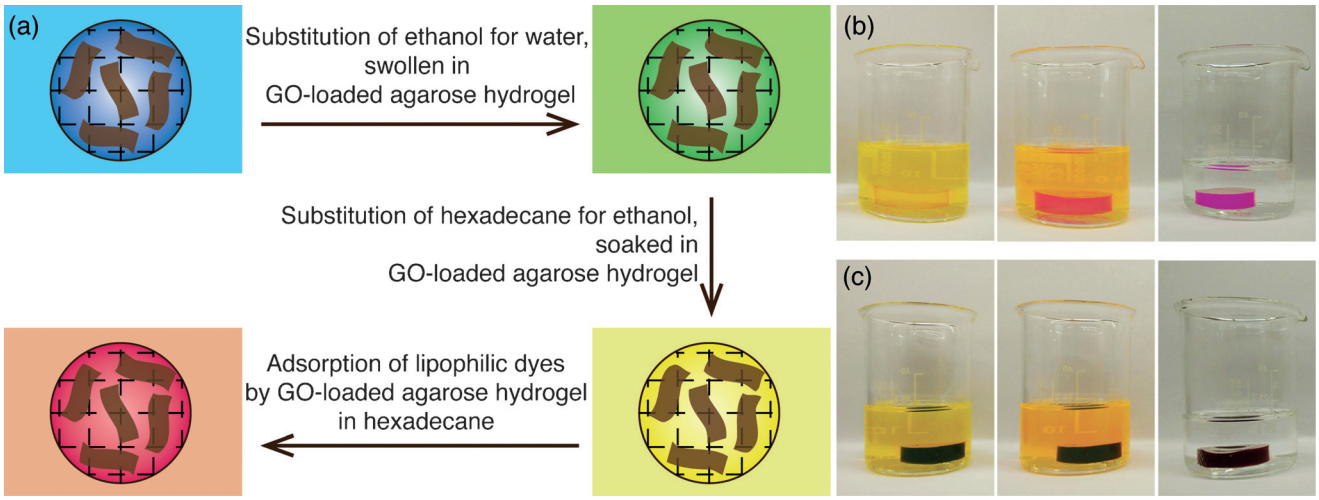

Figure 1. a) Transfer of GO-loaded agarose hydrogel beads from water to hexadecane via stepwise solvent exchange using ethanol as intermediate and adsorption of lipophilic dye by the composite hydrogel beads in hexadecane. b,c) Photographs of the agarose hydrogel blocks loaded without (b) and with GOs (c) taken after they are placed in the NR solutions in hexadecane (left panels), incubated for 2 h (middle panels), and transferred back to pure hexadecane (right panels). The NR concentration in hexadecane is 10 mg L^{-1}. The agarose content is 15 mg g^{-1} and the GO content 0.2 mg g^{-1} in the hydrogel blocks.

cence color strongly sensitive to the solvent polarity.[11] Figure 1b shows that upon incubation in the hexadecane solution of NR, the edge of the agarose hydrogel block is noticeably pink. While the hydrogel bulk displays a yellow color, which is almost identical to that of the hexadecane solution of NR (Figure S1a). This is indicative of that the hydrogel bulk is uniformly soaked by hexadecane and NR molecules can freely diffuse through the hydrogel bulk. After 2 h incubation, the whole hydrogel block becomes uniformly pink, which is close to the color of the ethanol solution of NR (Figure S1b). This suggests effective adsorption of NR molecules into the agarose network, as the agarose network provides NR the environment more polar than hexadecane. However, the maximal adsorption uptake of pristine agarose hydrogel is fairly low, 0.27 mg g^{-1} (Figure 2a). This can be rationalized by the fact that when agarose hydrogel is transferred into hexadecane, the surface hydroxyl groups of the hydrogel network orient themselves inwards to avoid contacting with hexadecane (Figure S2), thus largely reducing the number of the hydroxyl groups available for adsorption of NR molecules.

Despite its low adsorption capacity, the success of the pristine agarose hydrogel in adsorption of NR in hexadecane encouraged us to load effective adsorbents, GOs, into the agarose hydrogel to enhance the adsorption efficiency. GOs were chosen because their honeycomb lattice structures is very rigid and their polar groups are directly bound on the surfaces and edges, which prevent the orientation of the polar group upon contact with oil. If the structures of adsorbents are flexible or the polar groups are bound on adsorbents via relatively long spacers, the orientation of these polar groups would be unavoidable in oil. GO-loaded agarose hydrogel was produced by cooling the hot aqueous dispersions of GO/agarose mixtures to room temperature; the agarose content was 15 mg g^{-1} and the GO content 0.2 mg g^{-1}. The GO loading was evidenced by the black color of the resulting composite hydrogel, but the GOs were hardly visualized due to their ultrathin feature (Figure S3). Following the solvent exchange procedure depicted in Figure 1a, the GO-loaded agarose hydrogel can be transferred into hexadecane. After 2 h incubation with the NR solution in hexadecane, the color of the composite hydrogel is changed from black to purple (Figure 1c), indicative of the NR uptake. To facilitate the adsorption of GO-loaded agarose hydrogel toward NR, the composite hydrogel beads with sizes of 2–4 mm were produced by dropwise adding the hot aqueous dispersions of GO/agarose mixtures into liquid nitrogen. When the resulting composite hydrogel beads are incubated in the hexadecane solution of NR at the concentration of 10 mg mL^{-1} for 4 h, the NR solution becomes colorless while the composite hydrogel beads become uniformly fluorescent (insets in Figure 2a), underlining efficient removal of NR molecules from hexadecane. Figure 2a shows that the NR adsorption uptake by GO-loaded agarose hydrogel beads is 175.7 mg g^{-1}, which is 650 times larger than that of pristine agarose hydrogel beads (0.27 mg g^{-1}). In comparison, when hydrophilic GO powder is directly dispersed into the NR solution in hexadecane, their adsorption uptake is just 2.4 mg g^{-1}, which is 73 times smaller than that of GO-loaded agarose hydrogel. The poor dispersability of hydrophilic GO powder in hexadecane account for the low adsorption efficiency. Note that according to the NR adsorption uptake of GO-loaded agarose hydrogel beads (175.7 mg g^{-1}) and the GO concentration in the hydrogel (0.2 mg g^{-1}), the NR concentration in the whole hydrogel is estimated as 35 μg mL^{-1}, which is much larger than the NR solubility in water (< 1 μg mL^{-1}).[11] Thus, one can rule out the contribution of the NR solubility in the residual amount of water, residing in the agarose network, to the adsorption uptake of the composite hydrogel beads. As-prepared GO-loaded agarose hydrogel beads were also utilized for adsorption of another lipophilic dye, Oil Red O (ORO) (Scheme S1). The adsorption uptake of GOs-loaded agarose

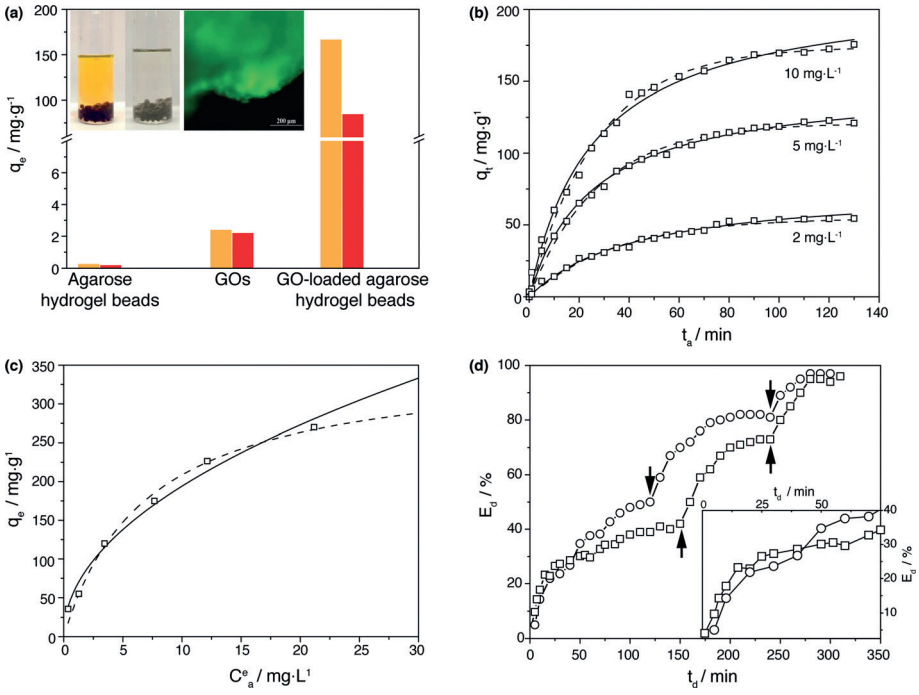

Figure 2. a) Summary of the equilibrium adsorption uptake of NR (orange columns) and ORO (red columns) by agarose hydrogel beads, GO powder, and GO-loaded agarose hydrogel beads. The adsorbents are incubated in 10 mL of the dye solution in hexadecane for 4 h and the initial dye concentration is 10 mg L^{-1}. In the hydrogel beads, the agarose content is 15 mg g^{-1} and the GO content is 0.2 mg g^{-1}. Left inset shows that the composite beads are placed in the NR solution in hexadecane (left panel) and incubated for 4 h (right panel). Right inset shows that the composite beads become uniformly fluorescent after the NR adsorption. b) Plots of the adsorption uptake (q_t) of NR by GO-loaded agarose hydrogel beads versus adsorption time (t_a). The composite beads are incubated in 10 mL of the NR solution in hexadecane for adsorption and the initial NR concentration of the organic dyes is varied from 2 to 5 and 10 mg L^{-1}. The adsorption kinetics profiles (open squares) are fitted by pseudo-first-order (dashed curves) and pseudo-second-order models (solid curves), respectively. c) Adsorption isotherms of NR (open squares) by the composite hydrogel beads, which are fitted by Langmuir (dashed curves) and Freundlich models (solid curves), respectively. d) Plots of the NR desorption efficiency (E_d) versus desorption time (t_d). The initial NR concentration in hexadecane is 10 mg L^{-1} for adsorption. To release the adsorbed NR molecules, the composite hydrogel beads are consecutively incubated in fresh ethanol. The black arrows in Figures indicate the time when the composite hydrogel beads are bought into fresh ethanol.

hydrogel beads is 77.6 mg g^{-1}, which is larger than that of pristine agarose hydrogel beads (0.22 mg g^{-1}) by 350 times and that of GOs (2.2 mg g^{-1}) by 35 times (Figure 2a).

Figure 2b and Figure S4a show the adsorption kinetics of GO-loaded agarose hydrogel beads towards NR and ORO, respectively, in hexadecane. The pseudo-second-order model fits the adsorption kinetics better than the pseudo-first-order model, as confirmed by the coefficient of determination (r^2) listed in Table S1. This suggests that chemisorption is the rate-determining step for the dye adsorption by GOs in hexadecane.[12] The hydrogen bonding between the nonionic polar groups of lipophilic dyes and GOs, as depicted in Schemes S1 and S2, should be the driving force for adsorption of the dyes by the GOs loaded in agarose network (see Figure 3). Figure 2c and Figure S4b show the adsorption isotherm of GO-loaded agarose hydrogel beads towards NR and ORO, respectively, in hexadecane. Table 1 suggests that Langmuir model fits the adsorption isotherms better than Freundlich model; the poor fitting based on Freundlich model is indicated by the $1/n$ value of <1.[13] The fitting results confirm homogeneous monolayer adsorption of lipophilic dyes by the GOs, loaded in the agarose network. In terms of adsorption kinetics and isotherm, therefore, the adsorption in oil proceeds in a way fairly similar to that in water. Table 1 indicates that the maximum adsorption capacity (q_m) of GO-loaded agarose hydrogel beads towards NR and ORO is calculated to 355.9 mg g^{-1} and 179.1 mg g^{-1}, respectively. Here we found that the GOs-loaded agarose hydrogel beads were able to effectively adsorb NR in hexadecane at the NR concentration as low as 0.5 μg mL^{-1} (Figure S5), while NR adsorption was hardly observed at the concentration of 0.3 μg mL^{-1}. The minimal concentration (0.5 μg mL^{-1}) of NR in hexadecane for effective adsorption is 100 times smaller than the NR solubility in alkane solvents (e.g. 68 μg mL^{-1} in heptane[11]), thus underlining strong interaction (hydrogen bonding) of the polar groups of the GOs, loaded in agarose network, with the polar groups of the NR molecules in oil.

The strong interaction is also confirmed by the difficulty in dye desorption from the GO-loaded agarose hydrogel beads (Figures 2d and S6). To release the adsorbed lipophilic dyes, we incubated GO-loaded agarose hydrogel beads in ethanol. Ethanol was chosen because it is an excellent solvent for the lipophilic dyes used, NR and ORO, and it is able to form hydrogen bonds with the GOs and the agarose networks in the composite hydrogel beads, which are favorable for release of the dyes from the composite hydrogel beads. Figure 2d shows that after NR adsorption, the incubation of the composite hydrogel beads in ethanol can cause the quick release of the adsorbed NR molecules and the desorption efficiency reaches 30% within 25 min, while the

Table 1: Summary of the fitting results of the adsorption isotherms of NR and ORO by GO-loaded agarose hydrogel beads based on Langmuir and Freundlich models.

Dye	Langmuir model			Freundlich model		
	q_m [mg g^{-1}]	k_L [L mg^{-1}]	r^2	K_F [mg g$^{1-1/n}$ g^{-1} L$^{1/n}$]	$1/n$ [g L^{-1}]	r^2
NR	355.9	0.142	0.988	62.4	0.49	0.977
ORO	179.1	0.090	0.901	25.1	0.50	0.914

equilibrium desorption is established after 2 h incubation with the desorption efficiency of ca. 40%; further prolonging the incubation time cannot improve the dye desorption. The burst release fashion suggests that the NR desorption from GO-loaded agarose hydrogel beads is driven by the dissolution of the adsorbed NR molecules in ethanol. Since the solubility of NRs in ethanol is of the order of 1 mg mL^{-1}, the poor desorption efficiency underlines the strong interaction between the polar groups of the NR molecules and GOs to suppress the NR dissolution. The release of the adsorbed NR molecules can be resumed only by incubation of the composite hydrogel beads in fresh ethanol; the desorption efficiency reaches ca. 96% after 3 times repetition of incubation of the composite hydrogel beads in fresh ethanol. Note that the regenerated GO-loaded agarose hydrogel beads can be reused for dye adsorption. Figure 2d also reveals that the desorption efficiency of the adsorbed NR molecules can reach ca. 50% when the GO-loaded agarose hydrogel beads are incubated in water/ethanol mixtures for 2 h. The strong hydration of the GOs, loaded in the agarose beads, in water/ethanol mixtures should account for the improved desorption efficiency. As highlighted in the inset in Figure 2d, however, the NR desorption efficiency during the first 25 min incubation of the composite hydrogel beads in water/ethanol mixtures is noticeably smaller than that in pure ethanol. This is in agreement with the fact that the solubility of NR in pure ethanol is larger than in water/ethanol mixtures, thus highlighting the NR desorption is a dissolution-driven process. Here we found that although the solubility of ORO in ethanol is comparable to or better than that of NR, ca. 90% of the adsorbed ORO molecules were released only after 4 times repetition of incubation of GO-loaded agarose hydrogel beads in fresh ethanol (Figure S6). This suggests that the interaction between the polar groups of the ORO and the GOs is stronger than that between the polar groups of the NR and the GOs (see below).

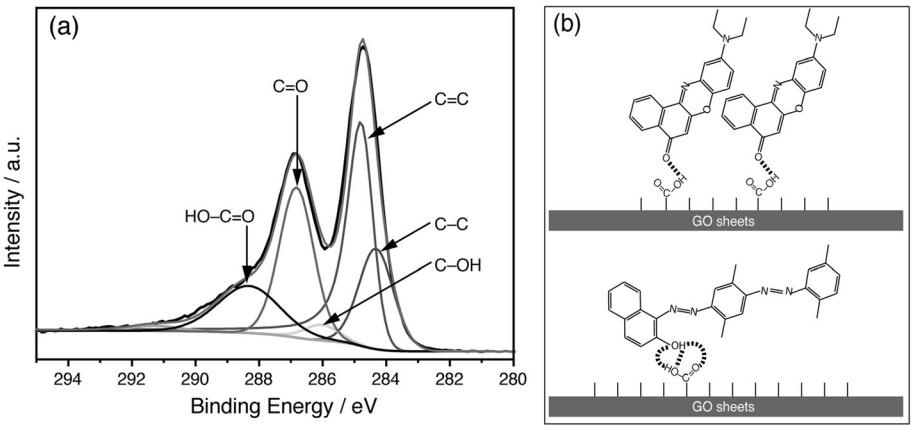

Figure 3. a) High-resolution XPS spectrum of the GOs used in the present work, in which the C 1s signal is deconvoluted into the peaks of C=C, C–C, C=O, COOH, and C–OH groups, indicated by black arrows. b) Adsorption of NR (upper panel) and ORO (lower panel) on the GO sheet via hydrogen bonding between their polar groups, highlighted by dashed lines.

For better understanding of the adsorption performance of GO-loaded agarose hydrogel towards lipophilic dyes in oil, the molecular nature of the used GOs were quantitatively assessed by X-ray photoelectron spectroscopy (XPS). After de-convolution of the carbon 1s signal of the GOs, Figure 3a reveals three strong peaks assigned to C=C at 284.8 eV, C–C at 284.3 eV and C=O at 286.8 eV, a noticeable peak assigned of O-C=O at 288.3 eV and a very week peak assigned C-OH at 286.0 eV. Accordingly, one can estimate 28.7% of the GO carbon atoms in the form of carbonyl group (C=O), 16.2% in the form of the carboxyl group (COOH), 3.0% in the form of the hydroxyl group (OH). Since the polar groups of NR and ORO are mainly of proton acceptor type (Scheme S1), they can effectively form hydrogen bonds only with the proton donor groups of GOs. For the sake of simplification, here only the hydrogen bonding of the GO COOH groups with the dye polar groups are considered as the COOH groups are the dominant proton donor groups of the GOs according to the XPS data (Figure 3a) and they are known to reside preferentially at the edges of GOs (Scheme S2),[14] which benefits the adsorption of dye molecules even taking into consideration the unavoidable fact that the used GOs probably are the particles comprising several GO monolayers stacked. Hence the utilization efficiency (ζ_u)of the COOH groups of GOs for dye adsorption can be estimated by $\zeta_u = n_{dye}/n_{COOH}$. The molar amount of the COOH groups (n_{COOH}) is estimated to be 11.48 mmol for 1 g of GOs according to the molar fraction (16.2%) calculated from the XPS data (Figure 3a).[15] The molar amount of dyes (n_{dye}), adsorbed by 1 g of GOs, loaded in agarose network, is estimated to be 1.12 mmol and 0.44 mmol for NR and ORO, respectively, according to the q_m values listed in Table 1. As a result, ζ_u is 9.8% for NR adsorption and 3.8% for ORO adsorption, respectively.

Both NR and ORO are bulky molecules as compared with the C=C bonds of GOs (1.42 Å). On the basis of the molecular nature (Schemes S1), one NR molecule adsorb onto (the edge of) one GO sheet via hydrogen bonding of its quinone or tertiary amine group mainly with one COOH group on the GO edge (Figure 3b). In this configuration, the length occupied per NR molecule on the GO edge is 5.76 Å according to the NR molecular structure (Scheme S1), which is equivalent to 4 C=C lengths. As such, when one NR molecule is adsorbed onto the COOH group of one GO sheet, it blocks 3 nearest neighbors of the COOH group, so the maximal utilization efficiency (ζ_u^m) of the GO polar groups for NR adsorption is ca. 25.0% (1/4). In the case of ORO adsorption, it occurs via hydrogen bonding of ORO OH groups with the COOH groups of GOs (Figure 3b). As a result, the length occupied per ORO molecule on the GO edge is 15.6 Å according to the ORO molecule structure (Scheme S1), which is equivalent to 11 C=C lengths. Hence the ζ_u^m of the GO polar groups for ORO adsorption is ca. 9.1% (1/11). The difference in ζ_u^m is reflected by the fact that

the adsorption uptake of ORO by GO-loaded agarose hydrogel is smaller than that of NR, listed in Table 1. Within GO-loaded agarose hydrogel, on the other hand, some of the COOH groups of the GOs may form hydrogen bonds with the OH groups of the agarose network. Further, the agglomeration of the GOs loaded in the agarose network is unavoidable via hydrogen binding between the polar groups of neighboring GO sheets especially during solvent exchange from water to oil; hydrogen bonding is expected stronger in oil than in water. Hence only a fraction (f_a) of the COOH groups of the GOs, loaded in agarose network, are responsible for adsorption of lipophilic dyes in oil. The effective value of the maximal utilization efficiency of the GO COOH groups for dye adsorption is $f_a\zeta_u^m$. Taken together, the adsorption efficiency (ξ_a) of the GO COOH groups towards lipophilic dyes can be estimated by $\xi_a = \zeta_u/f_a\zeta_u^m$. By assuming f_a =0.5 for the sake of simplification, ξ_a is 78.0% for NR adsorption and 84.2% for ORO adsorption.

The values of ξ_a may be underestimated, since unavoidable agarose wrapping of the GOs and agglomeration of the GOs in the composite hydrogel may be severe and make f_a smaller than 50%. However, our rationalization indicates the reasonably high values of ξ_a, thus underlining high effective utilization of the free polar groups of GOs for adsorption of lipophilic dyes in oil. Further, our rationalization also suggests that the hydrogen bonding between ORO and GO is stronger than that between NR and GO. This is supported by the fact that the OH groups of ORO act as both proton acceptors and donors while the quinone or tertiary amine groups of NR act only as proton acceptors. This is also supported by the fact that ORO is more difficult to desorb from GO-loaded agarose hydrogel than NR (Figure 2d). Here the effect of f_a was observed as the GO concentration effect of GO-loaded agarose hydrogel on the adsorption uptake of lipophilic dyes (Figure S7). The adsorption uptake of the dyes decreased when the GO concentration decreased from 0.2 mg mL^{-1} to 0.1 mg mL^{-1}. The increase of the GO loading to 0.5 mg mL^{-1} caused considerable reduction in the adsorption uptake of the dyes, which could be due to agglomeration of the GOs in the agarose network at high concentration, thus resulting in reduction in f_a.

In conclusion, we successfully demonstrate that GO-loaded agarose hydrogel can effectively and efficiently adsorb lipophilic dyes in oil after being transferred from water into oil via stepwise solvent exchange. The successful adsorption of dyes in oil relies on the fact that the polar groups of the GOs, loaded in the agarose network, remain in direct contact with oil and capable of interacting with lipophilic dyes via hydrogen bonding. GO-loaded agarose hydrogel beads show maximum adsorption capacity of 355.9 mg g^{-1} and 179.1 mg g^{-1}, respectively, towards of NR and ORO, which is substantially higher than that of pristine hydrogel or hydrophilic GO powder. The minimal dye concentration is 0.5 ppm for effective adsorption. Thanks to its manufacture and operation ease, the present adsorption-based strategy can be readily extended to a diversity of hydrogels and inorganic or organic nanostructured adsorbents with better adsorption efficiency and especially selectivity, thus holding immense promise in technical applications for large-scale oil decontamination such as desulfurization of engine fuel.

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[15] According to Figure 3a, the molecular weight of the GOs used here is $0.52\times12+0.48\times16+0.19\times1=14.1$.

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