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An Asymmetric Electrochemical System with Complementary Tunability in Hydrophobicity for Selective Separations of Organics

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S *Supporting Information*

ABSTRACT: Conducting polymers modified with redox-active moieties or amphiphilic surfactants are promising adsorbent materials for the separation of neutral organic species from water. We develop an asymmetric system combining a polyvinylferrocene−polypyrrole hybrid (PVF−PPy) and an amphiphilic surfactant dioctyl sulfosuccinate (AOT)-doped polypyrrole (PPy(AOT)) that have complementary hydrophobicity tunability in response to electrochemical modulations. Both materials are hydrophobic in their respective neutral states, exhibiting high affinities toward organics. Upon application of a mild potential to oxidize PVF−PPy and reduce PPy(AOT), these polymers can be simultaneously rendered hydrophilic, thereby driving desorption of organics and regeneration of the materials. The asymmetric system can be used in a cyclic fashion, through repeated electrical shorting of the two electrodes to program the capture of organics from a large volume of feed solution, and application of a potential (above 0.9 V) to stimulate the release of the adsorbed organics into a small volume of desorption solution. The asymmetric configuration has multiple benefits, including suppression of water parasitic reactions, high energetic efficiency, and selectivity for target organic species. Therefore, the electrode system has the potential to reduce the energy consumption in the mitigation of organic contaminants over conventional methods, with the additional ability to recover valuable organic products, opening up new possibilities for addressing the water−energy nexus.
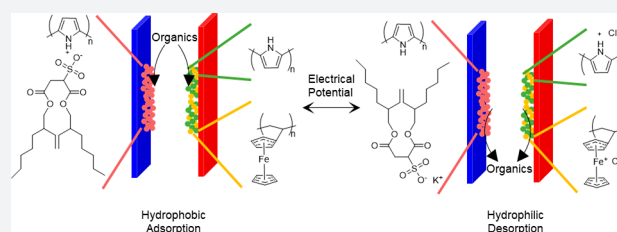
1. INTRODUCTION

Chemical separations processes are energy-intensive and are responsible for 10−15% of the world's total energy consumption, with distillation, evaporation, and other conventional technologies accounting for more than 80% of this energy expenditure.[1] Improved separation efficiencies can be achieved through more recent technologies such as reverse osmosis, nanofiltration, and capacitive deionization, which are particularly effective for removing charged ions from water.[1−3] The separation of nonionic organic species in processes such as wastewater treatment and pharmaceutical product purification is also of importance. Indeed, water pollution by neutral organic contaminants, such as industrial chemicals, pesticides, pharmaceuticals, and personal care products, is an emerging issue globally, and their presence at low concentrations (in the range of μg L^{-1} to mg L^{-1} at the point of discharge or from treatment facilities) complicates the separation processes.[4−11] Among different chemical separation technologies, air stripping, pervaporation, biological treatment, and carbon adsorption are more suitable for organics at low concentrations,[12] with adsorption by activated carbon being the most efficient and widely adopted.[13]

Current wastewater or drinking water treatment plants are not specifically equipped for eliminating neutral organic contaminants[6,9] which can therefore pass through domestic and industrial wastewater discharges and end up in the aquatic environment. Many neutral organic contaminants have proven to have ecotoxicological effects on aquatic life, animals, and even human beings, that include short-term and long-term toxicity, endocrine disrupting effects, and antibiotic resistance of microorganisms.[5−7] Similar to wastewater treatment, purification of pharmaceutical compounds involves a wide array of organic compounds and is essential for ensuring the quality of medications. Removal of neutral organic species by adsorbents such as activated carbon (AC) is a common practice, but sorbent regeneration through thermal processes, pH adjustment, or solvent extraction is often challenging or costly.[14] Therefore, AC regeneration is usually done in centralized treatment facilities, adding transportation cost to the operations.[15] Electrical energy is inexpensive and widely available and can be more efficient compared to the aforementioned alternative ways to regenerate adsorbents.[16] Adsorbents that can be regenerated by electricity present a practical and scalable point-of-use solution for separating neutral organic compounds from aqueous solutions.

Several electrochemical methods have been developed for the separation of organic compounds: Electrocoagulation consumes iron or aluminum to generate coagulants and can have disadvantages with respect to sustainability and cost of metal electrodes.[17] Electrochemical regeneration of activated carbons applies a current to desorb and destroy adsorbed
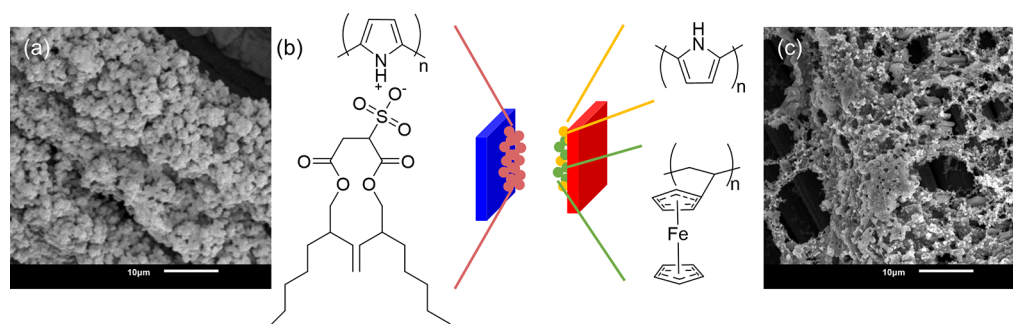
Figure 1. Scanning electron microscopy (SEM) images of (a) PPy(AOT) and (c) PVF—PPy. (b) Schematic of the asymmetric system.

organics, but the relatively high current (10−100 mA) and long charging period (5−40 h) may be prohibitive for industrial applications.[18] A cyclical electrochemical stage process proposed by Jemaa et al. that uses complexing agents dissolved in a contacting phase to transfer organic species from a feed phase to a receiving phase is promising because the complexation between the organics and the agents is reversible and can be modulated by electrochemical redox reactions.[16] To recycle the complexing agents and avoid contamination of the feed and stripping solutions, the contacting phase must be immiscible with these solutions, in which the agents should also be insoluble.

To work around the stringent solubility requirements of this electrochemical separation process, we immobilized the mass separation agents on conductive solid substrates to form adsorbents responsive to electrochemical modulations. The benefits are 2-fold: first, electrons are transferred directly from the electrodes to the immobilized adsorbents, in contrast to the approach taken by Jemaa et al., in which the complexing agents needed to migrate to be within the vicinity of the electrode for redox reactions to take place; second, the solid electrodes can be contacted with the feed or receiving phase in a swing process akin to that used in traditional adsorption operations, but with voltage swings rather than changes in temperature, pressure, or solution conditions. Electrodes functionalized with redox-active materials have been developed to remove ionic species and charged biomacromolecules from aqueous solutions in a reversible manner,[3,19−23] and we have shown recently that electrically conductive materials with immobilized redox-responsive moieties can be applied also to the separation of neutral organic species from solution.[2,24] We used polypyrrole (PPy) deposited on carbon substrates as the adsorbent and adopted two different approaches to modulate its hydrophobicity and hence affinity toward organic solutes in water: incorporation of a polyvinylferrocene (PVF) redox-responsive polymer in the PPy electrode coating[2] and doping of the PPy with the amphiphilic surfactant dioctyl sulfosuccinate (AOT).[24] We refer here to the two types of material as PVF—PPy and PPy(AOT), respectively. Building on the previous efforts on material design, we explore the synergistic properties of PVF—PPy and PPy(AOT) in electrochemically mediated separations of organics by pairing them as opposing electrodes in an asymmetric electrochemical cell.

As in the electrosorption of ionic species by redox-active materials, the trade-off between energy cost and extent of separation warrants careful choice of electrochemical cell configurations, electrode material, and process parameters to achieve the most efficient separation.[2,3] Since PVF—PPy is

more hydrophobic when reduced, and hydrophilic when oxidized, while PPy(AOT) behaves in the opposite manner, i.e., is more hydrophilic when reduced and more hydrophobic when oxidized, the PVF—PPy and PPy(AOT) electrodes form an attractive pair for an asymmetric system to work in tandem. With no voltage applied to the cell, both electrodes are relatively hydrophobic and able to adsorb neutral organic molecules, but when an appropriate electrical potential is applied to the cell to charge both electrodes, the organics will desorb from the loaded electrodes. Reactivation of the two electrodes to prepare them for the next adsorption cycle is spontaneous on simple shorting of the two electrodes. With only the desorption step costing energy, the asymmetric system has the potential to achieve high energetic efficiency. The asymmetric electrode system for capturing organic compounds from water can be used in conjunction with degradation methods, such as electrochemical advanced oxidation processes, to transform toxic organic compounds to less harmful forms or useful compounds.[25]

In this work, we first demonstrate experimentally that the asymmetric system can be used reversibly to remove model organic species from water, with limited decay in capacity over a number of cycles and an ability to suppress parasitic reactions in water. We then analyze the energetic efficiency and economic viability of electrochemically mediated separations of organics relative to conventional adsorption by activated carbons regenerated by thermal desorption or solvent extraction. We finally show the generality and selectivity of the PPy-based asymmetric system in the context of a separation that is of direct relevance to pharmaceutical purification.

2. RESULTS AND DISCUSSION

The functional materials in an asymmetric system for electrochemically mediated separations need to exhibit three properties: (1) electrical conductivity to respond to applied potentials, (2) different affinities toward organic species depending on the applied electrochemical modulation, and (3) high surface area for interactions with organic species to foster a high adsorption capacity. Therefore, we functionalized polypyrrole, a common intrinsically conducting polymer, coated on carbon fibers to serve as an underlying conductive network, with two approaches, involving ferrocene moieties and amphiphilic AOT surfactants, to modulate the affinities of the materials toward organic species.[2,24] The PVF—PPy hybrids and doped PPy(AOT) were synthesized using electropolymerization techniques. The resulting polymer films coated on commercial carbon cloth substrates possessed the desired highly porous morphology (Figure 1a,c). An

asymmetric system was assembled with a PVF−PPy positive electrode and a PPy(AOT) negative electrode (Figure 1b).

2.1. Asymmetric PPy-Based System. It is important to balance the charges of the positive and negative electrodes constituting the asymmetric system. One common approach is to adjust the mass of the functional materials on the two electrodes such that the capacitances are equalized.[26] We therefore first estimated the specific capacitances (C) of the PVF−PPy and PPy(AOT) electrodes using three-electrode cyclic voltammetry (CV) profiles according to the following equation (Figure S1):[27]

$$C = \frac{\int I \, dV}{2\Delta Vmv} \tag{1}$$

where I is the current (A), ΔV is the applied potential window (V), m is the mass of the polymer on the electrode, and v is the potential scan rate (V s^{-1}). The specific capacitance of PPy(AOT) is approximately twice that of PVF−PPy at low scan rates (49.5 versus 22.8 F g^{-1}). Therefore, we adjusted the electropolymerization reaction times such that the mass loading ratio of the PVF−PPy to PPy(AOT) was approximately 2:1.

The electrochemical behavior of the asymmetric system with PVF−PPy and PPy(AOT) electrodes of balanced charges was investigated by cyclic voltammetry (CV) in a two-electrode configuration. We monitored the CV responses of the full cell by setting a potential window of 1.2 V and recorded the responses of the individual electrodes versus a Ag/AgCl reference electrode (Figure 2). The paired Faradaic reactions on the two electrodes are the oxidation and reduction, respectively, of the ferrocene moieties in PVF−PPy hybrids,[28] and potassium insertion and repulsion accompanied by reorientation of the surfactant dopants in PPy(AOT).[29] The latter happens because the AOT doping anions are largely immobilized within the polymer during the oxidative polymerization due to their size and, hence, rely on cation (potassium in this case) exchange with the solution to maintain the electroneutrality of the PPy film during electrochemical modulation.[30]

The two adsorbent materials exhibited differences in hydrophobicity depending on the electrochemical signals. For PVF−PPy, when the applied potential (E) is lower than the formal potential of ferrocene (E^0 = 0.34 V versus Ag/AgCl), the PVF−PPy adsorbent is hydrophobic; most ferrocene moieties are reduced, and organics can be taken up by reduced PVF−PPy. For $E \gg E^0$, the PVF−PPy adsorbent becomes relatively hydrophilic; most ferrocene moieties are oxidized and positively charged, and therefore water molecules interact more favorably with the adsorbent and displace neutral organic species previously adsorbed on the polymer.[2] In contrast, for PPy(AOT), when the applied potential (E) is higher than the formal potential of potassium insertion and repulsion (E^0 = −0.21 V versus Ag/AgCl), the polymer is hydrophobic, since the positively charged PPy backbone attracts the negatively charged sulfonate groups of AOT such that the hydrophobic tails of the surfactant rearrange to be on the surface of the material. When $E \ll E^0$, PPy(AOT) is more hydrophilic as the relatively neutral PPy backbone induces AOT anions to reorient themselves such that the hydrophobic tails move closer to the polymer chains; the sulfonate groups are exposed on the surface.[24]
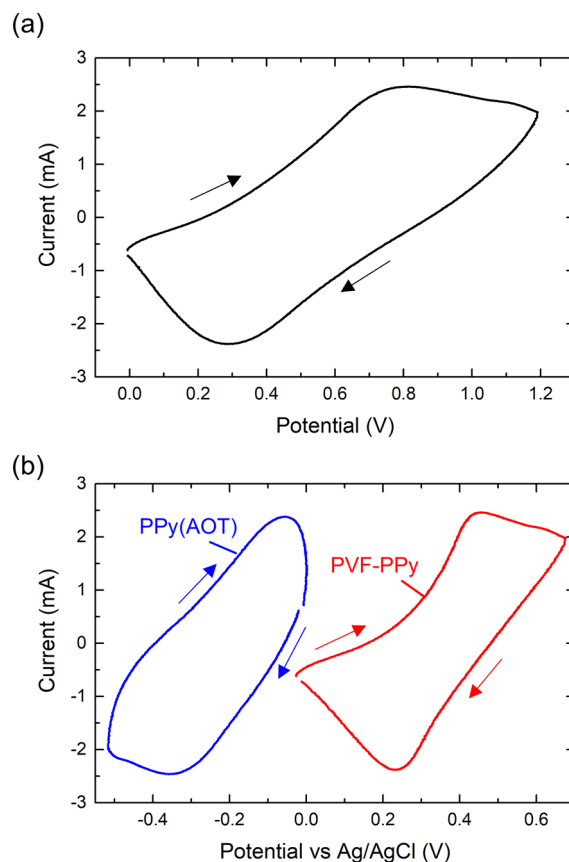
(a)

(b)

Figure 2. Cyclic voltammograms of (a) the full cell and (b) the individual electrodes in the PVF−PPy//PPy(AOT) asymmetric system in a two-electrode configuration (scan rates 10 mV s^{-1}). The arrows indicate the direction of voltage scans for the whole cell and the individual electrodes.

The Nernst equation describes the impact of applied potential on the relative amounts (R) of the oxidized to reduced moieties on the polymers (i.e., a measure of the relative hydrophilicity of the ferrocene-containing electrodes and of the hydrophobicity of the AOT-doped PPy coating):

$$E = E^0 + \left(\frac{k_B T}{e}\right) \ln(R) \tag{2}$$

where k_B is the Boltzmann constant, T the temperature, and e the elementary charge. Therefore, by adjusting the potential, we can modulate the affinities of the two PPy-based polymers for organics.

The CV profile of the full PVF−PPy//PPy(AOT) system shows a pair of redox peaks around 0.55 V (Figure 2a). This suggests that a potential drop across the two electrodes of greater than 0.55 V should be applied to render both materials hydrophilic to release adsorbed compounds. Subsequently, we can apply a potential below 0.55 V or simply short the two dual-functionalized electrodes (0 V) to reoxidize PPy(AOT) and reduce PVF−PPy, thereby reactivating the materials for further adsorption in their hydrophobic states.

2.2. Electrochemically Mediated Separations of Organics. The adsorption capability of the asymmetric system is demonstrated with a common azo dye compound widely used in the textile industry, Sudan Orange G (SOG), as a model contaminant. The equilibrium adsorption of SOG by

the PVF−PPy//PPy(AOT) asymmetric system can be fitted well by the Freundlich adsorption isotherm[31]

$$Q_e = kC_e^{1/n} \tag{3}$$

where the Freundlich exponent $1/n$, an indication of the extent to which adsorption is favored, increases as $1/n$ approaches zero (Figure 3a). While the Freundlich and Langmuir models both provide good fits for the batch adsorption data based on R^2 (Section S2, Supporting Information), the Freundlich isotherm was selected for this study because it is commonly applied to the adsorption of organic molecules on activated

carbons or molecular sieves, and its parameters capture differences in surface heterogeneity of adsorbents (prefactor) and cooperative adsorption (exponent).[13] When the asymmetric system is charged at a high potential of 1.2 V, $1/n$ takes on a value close to unity (1.01); i.e., the isotherm is almost linear, following Henry's Law. For the shorted asymmetric system in which PPy(AOT) is oxidized and PVF−PPy reduced, the fitted $1/n$ value was 0.54, consistent with the fact that the oxidized PPy(AOT) and reduced PVF−PPy have higher affinities for SOG in their hydrophobic states.[2,24]

The Freundlich isotherm parameters $\ln(k)$ and $1/n$ correlate linearly with the applied potential (Figure 3b), reflecting the changes in hydrophilicity of the adsorbent with charging of the electrodes; the linearity arises because the electrochemical cell exhibited capacitance-like features such that, for a fixed charging time of 10 min, the total number of charges exchanged (and hence hydrophilicity) increased linearly with the applied potential, as shown in the inset in Figure 3b. Moreover, Figure 3c shows that the Freundlich equation parameters are themselves correlated linearly, as has been observed by others for the adsorption of a wide range of organic compounds from aqueous solution onto activated carbons.[32,33] This behavior can be interpreted in terms of the Polanyi adsorption theory on the adsorption of organic compounds from an aqueous solution to a heterogeneous surface.[32,34−36] Polanyi defined the adsorption potential (ϵ_s) as the energy required to remove the molecule from a saturated solution to a point outside the attractive force field of the adsorbent

$$\epsilon_s = RT \ln\left(\frac{C_s}{C_e}\right) \tag{4}$$

where C_s and C_e are, respectively, the solubility limit and bulk equilibrium concentrations of the solutes in the liquid phase. Dubinin related the volume of solutes adsorbed on 1 g of adsorbent to the adsorption potential via the equation

$$W = W_0 \exp\left(-\frac{a}{V_s}\epsilon_s\right) \tag{5}$$

where W_0 is the limiting volume per gram of the adsorbent available for adsorption, a is a parameter characteristic of the adsorbent and independent of adsorbates, and V_s is the molar volume of solutes.[32,35−37] With $Q_e = \rho W$, where ρ is the solute density, and with ϵ_s given by eq 5, the mass of solute on the polymer can be written as

$$Q_e = \rho W_0 \left(\frac{C_e}{C_s}\right)^{aRT/V_s} \tag{6}$$

which is of the form given in eq 3, and from which the fitting parameters of the Freundlich equations can be identified as

$$k = \rho W_0 C_s^{-aRT/V_s} \tag{7}$$

and

$$\frac{1}{n} = \frac{aRT}{V_s} \tag{8}$$

Therefore

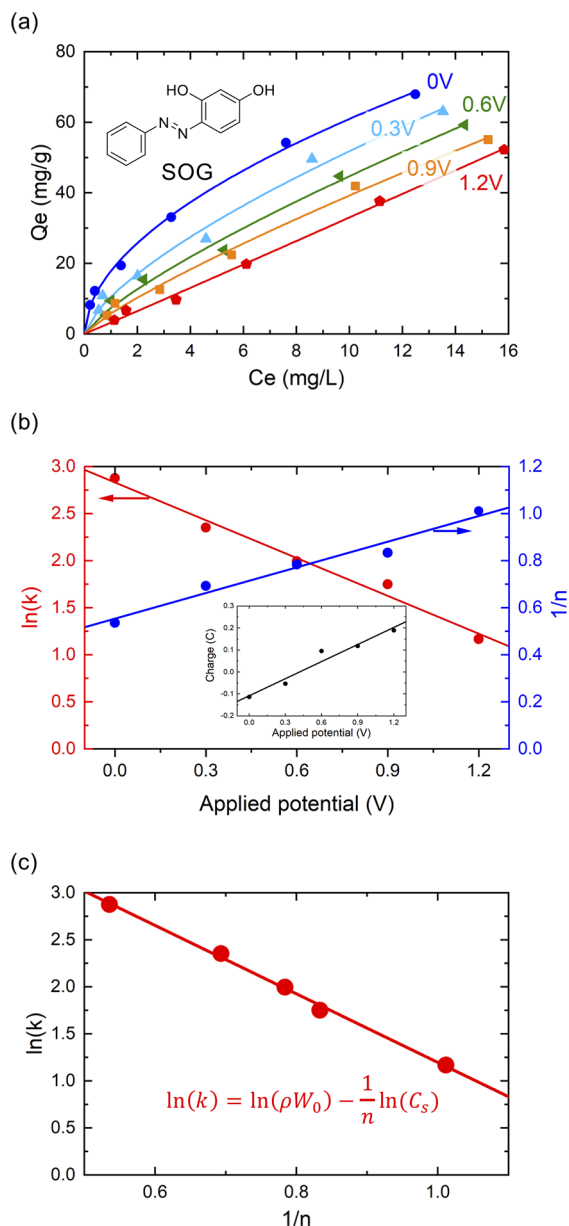$$\ln(k) = \ln(\rho W_0) - \frac{1}{n}\ln(C_s) \tag{9}$$

Figure 3. (a) Adsorption isotherms for Sudan Orange dye on the PVF−PPy//PPy(AOT) asymmetric system modulated by various applied potentials as fitted with the Freundlich equation. (b) Linear dependence of the fitting parameters of the Freundlich equation on applied potentials/charges. The R^2 values for $\ln(k)$ and $1/n$ vs applied potential, and charges vs applied potential were 0.983, 0.967, and 0.951, respectively. (c) Linear correlation between the two Freundlich parameters obtained at different potentials ($R^2 = 0.997$).

The intercept in eq 9 reflects the limiting capacity of the adsorbent, which should be independent of solute for solutes of similar density.[32,35−37] The value of ρW_0 estimated for our system is 130 mg g^{-1}, which is of similar magnitude to the value of 227 mg g^{-1} obtained by Abe et al. for a wide range of organic compounds on activated carbon.[32]

The disparity in hydrophobicity and hence affinity for organics under different charging conditions allows for the simultaneous reversibility of sorption by the two adsorbents that is crucial for a swing separation process. The electroswing separation is more effective for the separation of solutes present at low concentrations where the availability of the sites for adsorption is modulated by electrochemical stimuli.

2.3. Cyclic Adsorption. As was previously shown with individual PVF−PPy and PPy(AOT) polymers, the potential-dependent affinity permits the use of electrochemical means to program adsorption and desorption, thereby enabling the loading and regeneration of the sorbent materials.[2,24] Figure 4a
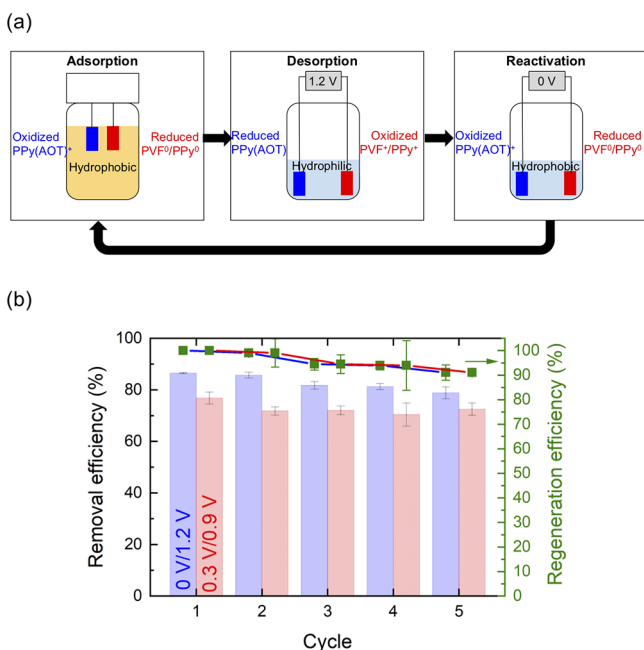
(a)

(b)

Figure 4. (a) Schematic illustration of the cyclic adsorption process. (b) Removal (left y axis and bars) and regeneration (right y axis and squares) efficiencies of the PVF−PPy//PPy(AOT) asymmetric system discharged/charged at 0 V/1.2 V and 0.3 V/0.9 V over five consecutive adsorption/desorption cycles.

depicts the application of a PVF−PPy//PPy(AOT) asymmetric electrochemical cell for removing organics from water. The electrode pair is immersed in the feed solution, and after reaching equilibrium, the system can be charged for 10 min, for example at 1.2 V, to render both polymers hydrophilic and to drive the desorption of the organics. Subsequently, the system can be discharged at 0 V for 10 min to return the polymers to their hydrophobic states for adsorption in the next cycle. The electrochemical characterization of the electrode cell has suggested that the half-cell potential of the asymmetric system is 0.55 V (Figure 2a), and therefore we may also charge and discharge at less extreme potentials, for example, at 0.9 and 0.3 V, respectively.

We explored the reusability of both materials by conducting adsorption and desorption of SOG using the asymmetric

system for five consecutive cycles. Figure 4b shows the evolution over the course of five cycles of pollutant removal efficiency (left y axis), defined as the percentage of contaminants removed from the feed, and regeneration efficiency (RE, right y axis) defined as the fraction of contaminants removed in a later cycle relative to those removed in the first cycle. The charge/discharge cycle at more extreme potentials (1.2 and 0 V versus 0.9 and 0.3 V) allows roughly 10% more organics to be removed in each cycle. Moreover, most of the adsorption capacity of the asymmetric system can be recovered through electrochemical modulations, indicated by RE greater than 91% over the five cycles for either pair of applied potentials. The video in the Supporting Information shows the ability to stimulate the desorption of dyes into the desorption solution upon application of a potential of 0.9 V.

Since the electrochemically mediated separation process is not thermodynamically spontaneous, it requires electrochemical energy to charge the system to drive desorption, the amount of which is dependent on the potentials applied. Therefore, we need to determine the optimum pair of applied potentials by considering the trade-off between energy expenditure (more extreme potentials) and separation extent (more contaminant removal), as discussed below.

2.4. Suppression of Parasitic Reactions. A major challenge for electrochemical devices operating in an aqueous environment is the narrow stable operating voltage window afforded by water. Water splitting can cause loss of energy to side reactions and pH fluctuations that may impact the adsorption capacity. The thermodynamic potential for water electrolysis is only 1.23 V, beyond which undesired parasitic reactions will occur:[38−40]

$$2H^+ + 2e^- \rightarrow H_2(g)$$
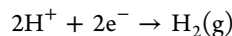
under acidic conditions, or

$$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^- \tag{10}$$
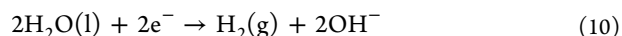
under basic conditions, at the cathode, and

$$2H_2O(l) \rightarrow O_2(g) + 4H^+ + 4e^- \tag{11}$$
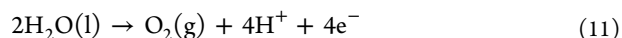
at the anode, where eqs 10 and 11 are the hydrogen evolution (HER) and oxygen evolution (OER) reactions, respectively. In addition to the effects of the whole-cell potential, a side reaction can occur if the potential window of an individual cathode or anode reaches its respective stability limit.[41] The equilibrium potential of eq 10 varies as a function of pH in water:

$$E = E^0 + \frac{k_B T}{2e} \ln \frac{a_{H^+}^2 a_{e^-}^2}{a_{H_2}} = -0.06 \text{ pH} \tag{12}$$

where $E^0 = 0$ V is the standard reduction potential of the HER (SHE), and a_{H^+}, a_{e^-}, and a_{H_2} are the activities of the reactants and reaction products. For example, with an initial pH of 6.94 in an aqueous solution, the HER can take place when the potential on the cathode reaches −0.42 V versus SHE or −0.60 V versus Ag/AgCl.

Cells in which the anode is functionalized with PVF-containing materials are prone to the HER side reaction when the anode is paired with various types of materials on the cathode, including platinum (Pt), carbon nanotubes, or chemically identical PVF-based material in the neutral state.[3]

In the desorption step of an electrochemically mediated separation, an electrode functionalized with PVF–PPy is oxidized to render the polymer hydrophilic. If the negative electrode is Pt, the HER with H^+ consumption or OH^- production can occur to a significant extent.

Table 1 shows the final solution phase pH after potentials are applied to electrochemical cells consisting of a PVF–PPy

Table 1. Final Solution Phase pH after Different Applied Potentials Were Applied to Electrochemical Cells Assembled with Electrodes Coated with Different PPy-Based Polymers or Platinum (Pt), Allowing the Deduction of Loss of Charge Towards Water Splitting Based on an Initial pH of 6.94

positive electrode	negative electrode	potential (V)	final pH	% charge toward water splitting
PVF–PPy	PPy(AOT)	0.0	6.97	0.00
PVF–PPy	PPy(AOT)	0.3	7.13	0.04
PVF–PPy	PPy(AOT)	0.9	7.29	0.04
PVF–PPy	PPy(AOT)	1.2	7.30	0.03
PVF–PPy	Pt	0.7	10.41	42.0
Pt	PPy(AOT)	0.5	5.48	0.81

positive electrode and a PPy(AOT) counter electrode, or of the two PPy-based materials independently paired with Pt. Even when a constant 1.2 V was applied to the asymmetric PVF–PPy//PPy(AOT) system for 10 min, where the relative potentials on PVF–PPy and PPy(AOT) were approximately 0.7 and −0.5 V versus Ag/AgCl, respectively (Section S1, Supporting Information), the pH increase (from an initial pH of 6.94) for the asymmetric system is quite limited because the Faradaic reaction occurring during the reduction of the PPy(AOT) electrode accommodates electrons from the oxidation of the PVF–PPy in lieu of the HER that would otherwise occur. Without a dual-functionalized asymmetric system, water splitting reactions occur to provide the necessary electrons to complement the redox reactions of PVF–PPy or PPy(AOT). The fast kinetics of the HER on Pt allows the regeneration of the PVF–PPy electrode at 0.7 V versus Ag/AgCl in a PVF–PPy//Pt system to proceed without retardation, and with an increase in the solution phase pH from nearly neutral (6.94) to 10.41. Similarly, with Pt as the counter electrode to PPy(AOT), the OER occurs to provide electrons for the reduction of PPy(AOT) at −0.5 V versus Ag/AgCl, with a resultant decrease in the pH to 5.48. The asymmetric electrochemical cell configuration is clearly successful in preventing pH fluctuations during the electroswing operation (Figure 5a).

The other benefit of suppressing parasitic reactions is that the Faradaic efficiency of the electrochemical modulations is enhanced. Figure 5b shows the loss of charges to water splitting reactions in the PVF–PPy//Pt, PVF–PPy//PPy(AOT), and Pt//PPy(AOT) systems, where the positive charge refers to the production of hydroxide, and negative magnitude represents the proton generation. The dual-functionalized asymmetric system PPy(AOT) counter electrode allows over 99% of the charges to be utilized in electrochemical modulation of the polymers whereas almost 42% of charges are lost to OH^- production when PVF–PPy is paired with Pt. The dramatic reduction in HER enhances current efficiencies by eliminating parasitic water splitting reactions.
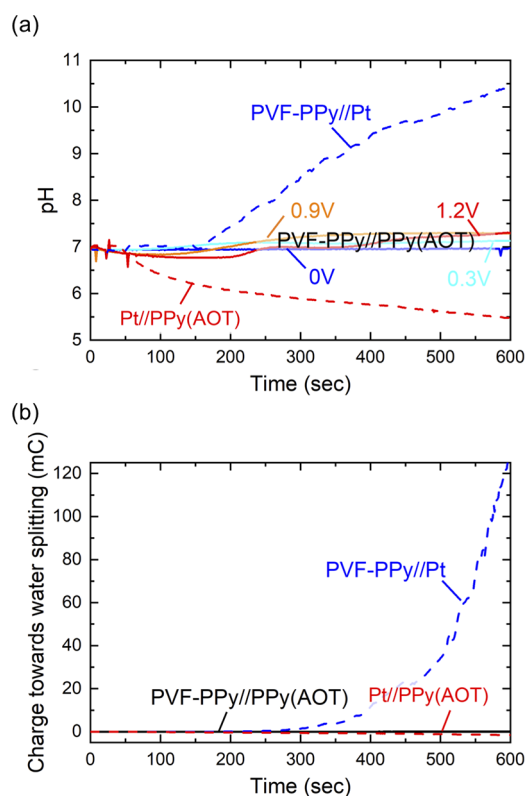

Figure 5. (a) pH evolution during charging of the PVF–PPy(AOT)//Pt, Pt//PPy(AOT), and PVF–PPy//PPy(AOT) systems. (b) Amount of charge (mC) going toward water splitting OH^- production and the HER in the course of modulating the PVF–PPy//PPy(AOT) asymmetric system and either PVF–PPy or PPy(AOT) paired with a Pt counter electrode.

2.5. Energetic Efficiency. Adsorption has proven to be an effective unit operation for the removal of organics from wastewater.[5,6,11,13,42] The ability to regenerate the adsorbent efficiently is important to avoid merely transferring contaminants from the liquid phase to the solids for disposal, and to enable reuse of the sorbent.[43] To assess the practicality of the PPy-based asymmetric system, we evaluate the economic viability and environmental impact of electrochemically mediated separations using the PPy-based system under different applied potentials and compare them with those of conventional activated carbons used extensively for the mitigation of organic contaminants, and which are regenerated by thermal desorption or solvent extraction.[44,45] As with the comparison between capacitive deionization and reverse osmosis in desalination,[46] we use the concept of specific energy consumption (SE), defined as energy consumption per gram of organic contaminants removed, to evaluate the energetic efficiencies of alternative adsorbents and regeneration strategies:

$$SE = \frac{E}{Q_e RE} \tag{13}$$

where E is the energy consumed per gram of adsorbent during the regeneration step (J g^{-1} adsorbent), Q_e is the adsorption capacity (g contaminant g^{-1} adsorbent), and RE is the regeneration efficiency.

Thermal regeneration of activated carbons typically involves heating the saturated AC to remove the retained adsorbate.

The intensive heating may cause changes in the carbonaceous structure of, or mass losses in, the adsorbent, or charred residues may be left behind on the AC, all of which contribute to the loss of activity in the regenerated AC.[44] To estimate the energy consumption during the thermal regeneration of activated carbons, we calculate the heat requirements according to[47,48]

$$Q = nC_p(T_R - T_0) \tag{14}$$

where n is the total purge gas used (mol of purge gas per gram of activated carbons), C_p is the heat capacity of the purge gas, and T_R and T_0 are the regeneration and reference temperatures, respectively.

Activated carbons can also be regenerated through extraction of adsorbates with organic solvents, followed by removal of any retained solvent. Although this method may prevent mass losses or damage to the porous structure of AC, the use of a solvent can incur high economic costs or raise toxicity concerns.[45] Poey et al. have shown that thermal regeneration is more cost-competitive than solvent regeneration and becomes increasingly more so at higher throughput.[49] Solvent regeneration may take days of soaking of the AC, and the high cost of solvent and capital requirements for solvent regeneration may be prohibitive for industrial-scale applications. We therefore focus on benchmarking thermal regeneration of AC for comparison with the electrochemical regeneration operations.

For the PVF−PPy//PPy(AOT) asymmetric system, the energy consumption for the electrochemical regeneration is obtained from the electrical energy involved in the discharge process at the defined applied potentials:

$$E = \frac{qE_{app}}{m} \tag{15}$$

where q is the total charge transferred between the electrodes at the cell potential E_{app} applied to the PVF−PPy//PPy(AOT) system, and m is the total mass of polymers on the electrodes. Further details are given in the Supporting Information, Section S3.

Table 2 lists the key parameters and compares the energetic efficiencies of the activated carbons and the PPy-based system

Table 2. Comparison of the Energy Efficiencies for Activated Carbons Regenerated by Thermal Desorption, and PVF−PPy//PPy(AOT) Regenerated Electrochemically

	activated carbons	PVF−PPy//PPy(AOT)	
metric	thermal	0−1.2 V	0.3−0.9 V
energy consumption (J g⁻¹ adsorbent)	235	27	12
specific energy consumption (SE) (J g⁻¹ contaminant)	1474	2395	1258

with their respective regeneration methods. The PVF−PPy//PPy(AOT) asymmetric system, when regenerated at 0.9 V and reactivated at 0.3 V, is more efficient than when electrochemical modulations at 1.2 V/0 V are used, and than the thermal regeneration of activated carbons. The SEs of the thermally regenerated activated carbons for organic compounds and the PVF−PPy//PPy(AOT) system are quite similar in magnitude. An additional sensitivity analysis on the relative efficiencies of thermal regeneration of activated carbons and the electrochemical regeneration of the PVF−

PPy//PPy(AOT) systems is given in the Supporting Information, Section S3.

Capital cost and material costs are also important factors for determining the economic viability of these alternative technologies. The high-temperature operations demand deployment of stainless-steel equipment, incurring high capital costs, and require large-scale centralized facilities to achieve economy of scale.[42] For the PPy-based asymmetric system, the manufacturing cost of the novel materials on a large scale are yet to be determined.

On the basis of this analysis, we conclude that the PVF−PPy//PPy(AOT) cell regenerated at 0.9 V and subsequently reactivated by charging the system at 0.3 V which is competitive in terms of specific energy consumption (SE) among the cases considered here. The SE values for the electrochemically regenerated PVF−PPy//PPy(AOT) are conservative and can be enhanced if the energy in the reactivation (shorting) step can be recovered and stored for subsequent desorption processes. Moreover, the adsorption capacity of the PVF−PPy//PPy(AOT) used in the calculation is obtained from the cyclic experiment where the system was exposed to very dilute solutions containing Sudan Orange G and is only ∼1/5 of the maximum value measured. These considerations warrant further investigation of the electrochemically mediated separation technology and adsorbent materials to improve their robustness and economic viability.

2.6. Selective Separation of Organic Pharmaceutical Compounds. We have previously shown the robustness of the two polypyrrole-based adsorbent materials in the adsorption and release of organic species, including pharmaceuticals such as propranolol hydrochloride (PP) and carcinogenic aromatics such as bisphenol A.[2,24] Many separation scenarios involve mixtures of organic compounds to remove impurities or recover valuable molecules.[3] For example, in the manufacture of PP, a β-adrenergic blocking agent widely used to treat hypertension and angina pectoris, many intermediate products emerge from the multistep synthesis pathway and, hence, need to be removed to be compliant with the regulatory requirement that the relative concentrations of individual impurities be below 0.2%.[50] We explored the ability of the PVF−PPy//PPy(AOT) system to separate a mixture of propranolol hydrochloride (PP) and one of the impurities found in the synthesis mixture, unreacted 1-naphthol (1-NO), which participates in an alkylation reaction with epichlorohydrin, the first reaction in the pathway to produce PP.[51]

We first compared the individual propensities of PP and 1-NO to adsorb on the PVF−PPy and PPy(AOT) electrodes by measuring their equilibrium distribution coefficients in single component solutions.

$$K_d = \frac{Q_e}{C_e} \tag{16}$$

Here, Q_e (mg g⁻¹) is the mass of the adsorbed organic compound (PP or 1-NO) per gram of polymer, and C_e (mg L⁻¹) is the concentration of the respective compound in the liquid phase. As shown in Figure 6a, the K_d values for 1-NO are higher than those for PP at the corresponding potentials, suggesting that higher selectivity for 1-NO impurities over PP will be afforded by the asymmetric system. The separation factor (α) defined as the ratio of the distribution coefficients for 1-NO and PP
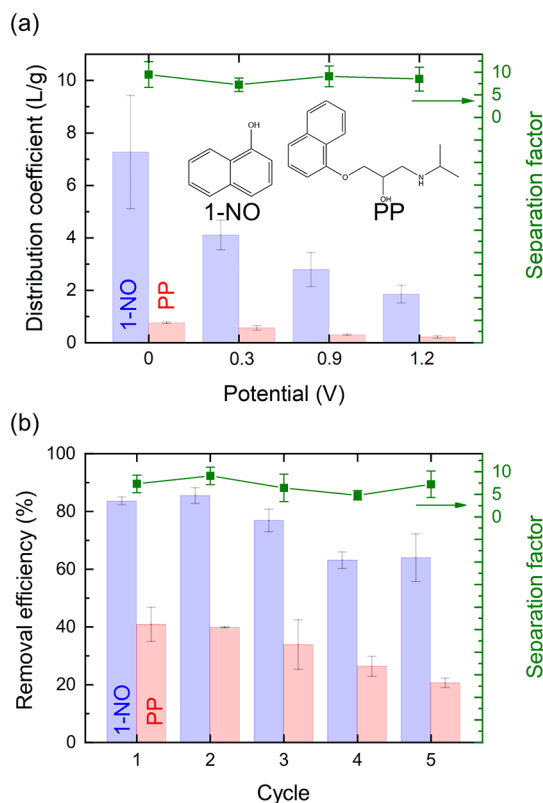
Figure 6. (a) Equilibrium distribution coefficients K_d for 1-NO and PP between the PVF–PPy// PPy(AOT) electrodes and the aqueous solutions containing a single component when the asymmetric system is subjected to different potentials prior to the adsorption (left y axis and bars). The resulting separation coefficients deduced from ratios of the measured K_d values (right y axis and squares). (b) Removal efficiencies (left y axis and bars) and separation factors (right y axis and squares) for five consecutive cycles of separations of a PP and 1-NO mixture.

$$\alpha = \frac{K_{d,\text{1-NO}}}{K_{d,\text{PP}}} \tag{17}$$

is on average 8.5 for the different applied potentials (Figure 6a).

We tested the selectivity and reusability of the PVF–PPy// PPy(AOT) asymmetric system by conducting five consecutive separations of a binary mixture of 30.6 mg L^{-1} PP and 3.6 mg L^{-1} 1-NO, a concentration ratio which simulates that of a typical product–impurity mixture. Figure 6b shows that up to 85% of 1-NO can be removed while only roughly 40% of PP is taken up in the first cycle. Moreover, the removal efficiency of PP suffers a greater loss compared to that of 1-NO in subsequent cycles. The observed separation factor when the binary mixture of PP and 1-NO (Figure 6b) is challenged is on average 7.0, slightly lower than that deduced from the ratio of K_d values measured with a single component present in the solution, likely due to the competitive binding of PP and 1-NO onto PVF–PPy//PPy(AOT). The interplay between different organics and their impact on the selectivity, capacity, and reversibility of the electrochemically regenerable adsorbent warrant further investigation but are beyond the scope of this paper.

2.7. Stability of the PPy-Based Polymers. We have demonstrated that the asymmetric system can maintain over 91% of the initial capacity over five consecutive adsorption/ desorption cycles. Past studies have shown that the PVF–PPy and PPy(AOT) materials can sustain greater than 50 cycles of electrochemical charging/discharging.[2,24] One potential source of instability is the leaching of the AOT dopants due to a decrease in electrostatic interaction when PPy(AOT) is reduced. If AOT anions leached into the desorption solution they would become new contaminants as well as cause a decrease in the ability to modulate the hydrophobicity of the PPy polymer. An AOT surfactant of the monomer form is less toxic than that at higher concentrations (3 mM or 96 ppm sulfur) at which micelles are formed, according to an *in vitro* study of AOT stabilized silver nanoparticles.[52] Due to the geometry of AOT, however, it is difficult for AOT surfactants alone to form micelles in water.

We investigated the leaching of AOT dopants by monitoring the sulfur content in the desorption solution using an inductively coupled plasma optical emission spectrometer (ICP-OES) with a detection limit down to 0.1 ppm. We were unable to detect any sulfur content in the desorption solution after applying 1.2 V to the asymmetric system, the highest potential considered in this study (Section S4, Supporting Information), suggesting stability of the materials suitable for the application.

The robustness of the polymer-coated electrodes may be further challenged by the presence of larger organic matter (e.g., humic acids) in the aqueous streams. Additional research is required to determine the likelihood of fouling on the two dissimilar polypyrrole-based adsorbents. Alternatively, organic matter can be removed using membrane-based technologies prior to application of the asymmetric system for the targeting of organic molecules in solution.

3. CONCLUSION

We have designed an asymmetric system consisting of PPy(AOT) and PVF–PPy polymers for electrochemically mediated separations of organics from water, exploiting their complementary tunabilities in hydrophobicity. We demonstrated reusability of the system for 5 cycles. The asymmetric system showed improvements in suppressing parasitic water splitting reactions to maintain solution pH and to reduce loss of electrical energy to side reactions. In energetic efficiency terms, the electrochemically mediated separation technology using the PVF–PPy//PPy(AOT) system is competitive in comparison with thermally regenerated activated carbons. The system also shows selectivity for certain organics present in mixtures, suggesting potential applications in pharmaceutical and other such purifications. The ease of implementation of the PVF–PPy//PPy(AOT) system, only requiring mild electrical energy for regeneration which can potentially be derived from renewable sources, permits electrochemically mediated separations to be performed both in industrial settings and at distributed or remote locations.

4. EXPERIMENTAL SECTION

4.1. Electrochemical Synthesis and Characterizations of Polymers. The two types of polypyrrole-based electrodes were prepared through reported electropolymerization methods[2,24,28] on a PARSTAT MC 2000 potentiostat with an auxiliary electrometer (Princeton Applied Research) in a three-electrode configuration. The working, counter, and reference electrodes were carbon fiber cloth (ElectroChem Inc.), a platinum wire (BASi), and Ag/AgCl (3 M NaCl), respectively.

For PPy(AOT), the electropolymerization bath contained 0.3 M pyrrole (Millipore Sigma), 0.3 mg mL^{-1} bipyrrole (Toronto Research Chemicals), and 0.1 M sodium dioctyl sulfosuccinate (Millipore Sigma).[24] A constant current density of 2.5 mA cm^{-2} was applied for 5 min to yield a polymer loading of 2.85 ± 0.08 mg cm^{-2}.[24] For PVF−PPy, the bath contained 2 mg mL^{-1} PVF (molecular weight 50 000 g mol^{-1}, Polysciences), 0.2 M pyrrole, and 0.1 M tetrabutylammonia perchlorate (Millipore Sigma) in chloroform.[24] A constant current potential of 0.7 V was applied for 10 min to yield a polymer loading of 5.68 ± 0.47 mg cm^{-2}. Cyclic voltammetry (CV) measurements were done in 0.1 M potassium chloride (KCl) aqueous solution.

4.2. Separation of Organic Solutes. Adsorption studies were performed at ambient temperature in 20 mL scintillation vials continuously shaken at 150 rpm to increase mixing. The concentrations of the model contaminant Sudan Orange G and pharmaceutical synthesis compounds propranolol hydrochloride (PP) and 1-naphthol (1-NO) (Millipore Sigma) in the aqueous phase (C_e) were measured by a Cary 60 ultraviolet−visible (UV−vis) spectroscope. The mass of solute adsorbed to PPy(AOT)- and PVF−PPy-coated electrodes was determined as $Q_e = \frac{(C_0 - C_e)\text{Vol}}{m}$, where Q_e (mg g^{-1} polymer) is the solute adsorbed per gram of polymer, C_0 (mg L^{-1}) and C_e (mg L^{-1}) are the initial and final solute concentrations in the solution phase, respectively, m (g) is the mass of the particular type of polymer on the carbon fiber cloth substrate, and Vol (L) is the volume of solution. The Freundlich isotherm equation was fitted to the batch adsorption data. We assembled the two electrodes into the PVF−PPy//PPy(AOT) asymmetric system for adsorption studies, rendered both materials hydrophobic by discharging at 0 or 0.3 V, waited until equilibrium was reached, and then regenerated the system by applying a positive potential (0.9 or 1.2 V) for 10 min in 5 mL of 0.1 M KCl solution. The adsorption process was monitored for up to 24 h, and equilibrium was typically reached with 10 h. To reuse the electrodes in subsequent cycles of adsorption, the polymer was reactivated for adsorption by applying 0 or 0.3 V for 10 min in the same 0.1 M KCl desorption solution. Concentrations of PP and 1-NO in the binary mixture were determined using high-performance liquid chromatography (HPLC) equipped with a flame-ionization detector (FID) (Agilent) and a ZORBAX Extend 80 Å C18 (4.6 × 50 mm, 5 μm) analytical column (2.1 mm × 50 mm, particle size 3.5 μm). Samples for the HPLC analysis were prepared by adding 20 μL of N-benzylmethylamine as internal standards to 1 mL of solutions. Samples of 5 μL were injected and eluted using a gradient pump delivering 1 mL min^{-1} of a water and acetonitrile mobile phase, each containing 0.1 vol % formic acid. OpenLab CDS software was used to determine the area under the peaks in the chromatograms and to carry out baseline correction. All results reported are based on the average of three replicates.

4.3. pH Monitoring. To assess the impact of parasitic reactions due to water electrolysis, pH was monitored *in situ* during electrochemical modulation of the hydrophobicity of the materials through potential swings. A custom LabView program and the Orion ROSS Combination Semimicro pH electrode were used to collect the pH data. The evolution of OH$^-$ was directly computed from pH fluctuations and subsequently converted to the charges lost to hydrogen or oxygen evolution reactions, respectively.

4.4. Assessment of AOT Leaching. To assess the leaching of AOT during desorption, an inductively coupled plasma optical emission spectrometer (ICP-OES Optima 8000, PerkinElmer) equipped with a GemTip cross-flow II nebulizer and a Ryton HF-resistant Scott-type spray chamber was used to determine the sulfur content in the desorption solution. Standard solutions for creating the sulfur calibration curve (Figure S3 in the Supporting Information) were prepared by sequential dilution of a stock solution (Millipore Sigma 1000 mg L^{-1} S in H$_2$O). The operating conditions for the ICP-OES analysis were as follows: wavelength, 180.669 nm; radio frequency power, 1500 W; principal plasma gas flow-rate, 10.0 L min^{-1}; auxiliary gas flow-rate, 0.2 L min^{-1}; and nebulizer gas flow-rate, 0.7 L min^{-1}.

4.5. Safety Statement. No unexpected or unusually high safety hazards were encountered.

■ ASSOCIATED CONTENT

ⓢ Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscentsci.9b00379.

> Details of electrochemical characterizations, fitting of isotherm models, analysis of energetic efficiency, and ICP-OES calibration (PDF)
> Desorption of Sudan Orange G from the PVF−PPy//PPy(AOT) asymmetric system to a 5 mL 0.1 M KCl solution without any potentials applied in the first 10 min and with 0.9 V applied for another 10 minuets, and the video is sped up to 20 times faster (MP4)

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The manuscript was written with contributions by all authors.

Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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