Development of Two New Efficient Means of Wastewater Treatment

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Summary

Wastewater accumulation is a daunting issue. This global concern stimulates scientists to search for more effective ways of treating wastewater and preserving natural resources. In this study, we have augmented current treatment efficiencies and general effectiveness by creating two new methods. Using hollow fiber membrane (HFM) based liquid-liquid extraction technology in water treatment, we have demonstrated that this technique is more efficient than the current available methods at extracting organic components into the organic phase inside the HFM. Meanwhile, we have used polymeric resins to absorb both neutral and charged organic components in wastewater. Both newly developed methods have the potential to be industrialized for combating the human-caused wastewater contamination issue with increased vigor and efficiency.

Introduction

Wastewater pollution is one of the most pressing, deleterious global issues. In fact, over two billion tons of human and animal excrement end up in Earth's waterways daily. In light of a recent United Nations report revealing that the global population will increase by about 14% (from 7 billion to 8 billion) by 2025, this astronomical rate of waste deposition in our waterways will have increased significantly (1-2). Inadequate wastewater treatment and management allow contaminated water to accumulate and diminish the limited water resources necessary for human consumption (which includes but is not limited to the following: agriculture, cleaning, and hydrating the world's population). One of the most prominent victims and perpetrators of this problem is southeast China, where high rates of industrialization and insufficient water treatment jeopardize China's environment, human health, and agriculture. Sixteen of the twenty most polluted cities in the world are located in this region, wherein 300 million struggle for access to clean drinking water (3). This crisis warrants greater attention and requires greater efforts to alleviate this issue through more efficient and cost-effective methods of water treatment.

A survey in 2012 revealed that half of the water being treated in China's 4,000 water treatment plants fails to meet national standards of safe tap water quality (4). Out of these 4,000 treatment plants, 1,000 of them were deemed unacceptable in their treatment methods to produce safe tap water. Out of the 60 million tons of tap water churned out daily, 30 million tons are damaging to human health due to an excessive amount of harmful bacteria from human and animal wastes, as well as the presence of heavy metals.

Tracing the Path of Water

It is important to understand where this water pollution crisis stems from to effectively alleviate its harmful effects. The various problems that arise from untreated wastewater result from different sources of the contamination. Generally, wastewater in China results from the following three sources: agricultural waste from irrigation and farming, municipal waste from humans and animals, and industrial chemicals/run-off wastes. Mirroring a substantial rate of ongoing urban development and industrialization in China starting in the late 20th century, water treatment methods have not been able to catch up with the volume of toxic metals and hazardous substances being released from industrial plants (3). In addition, a plethora of human and animal wastes accumulate in the waterways due to inefficient urban drainage and sewage systems. Wastewater pollution also stems from China's agricultural use. Water shortages and competition result in farmers using untreated municipal water for irrigation and drinking, a treatment that damages soil and crops. The combination of urban and farming wastes find waterways and accumulate in valuable bodies of water, such as the Chaohu Lake. Chaohu, which is one of the five largest freshwater lakes in China, is a vital resource for the region encompassing it. Commercial fishing and irrigation for farmers require this lake to be clean. However, due to the rapid growth of cities and increase in competition for water resources, Chaohu Lake has been marred by an unnaturally high amount of nutrients, toxic metals, and municipal waste. This has resulted in human health impacts to those living around the vast lake, as well as environmental concerns. Given these problems, an efficacious water treatment system focusing on the lake is imperative to the benefit of the ecosystem and community surrounding it.

How serious is it?

The expansion of the human population causes increased human freshwater usage, as well as increasing wastewater production. This has resulted in an exponential rise of water demand over the past twenty years. As a result, farmers have been relying on untreated municipal wastewater from Chaohu Lake as a source for irrigating their crops, after having first depleted aquifers and local rivers. This wastewater contains high amounts of chemical and organic pollutants, such as microbial pathogens that have been increasing rates of cholera near the lake. One example, in 2010, the Information Office of Anhui Provincial Health Department reported a Cholera epidemic with 38 cases in one close by county (via Xinhua News, Sept 04, 2010). Cholera is a waterborne bacteria that causes frequent vomiting, diarrhea, and possible death. Water pollution is thus a pressing issue because it furthers the water crisis that is already looming.

Is there a solution?

To provide a satisfactory water treatment system that will lower the organic content in wastewater to acceptable levels for drinking and washing, several approaches have been adopted (5-6). Among all of them, the most efficient method by far is the biomembrane reactor (BMR) method, which uses a HFM to filter contaminated particles out of the wastewater. While BMR is quite effective at treating most urban wastewater, this filtration-based process cannot be used for treating most industrial wastewater as the organic compounds will penetrate through the HFM. Therefore, alternatives are needed to treat industrial wastewater.

In this study, we developed two new approaches towards solving this problem (Figure 1). One is the HFM based liquid-liquid micro-extraction (LLME) method. The logic is that HFM cannot only be used as the media for BMR, it also can be used as an extraction media when it is filled with organic solvent. In fact, people have used this LLME process to enrich and analyze trace levels of organic compounds in environmental samples (7). Here, we use the same principle of extraction but for a different purpose: wastewater treatment. It is expected that organic molecules in wastewater would be extracted into the organic phase inside the HFM while the organic concentration in water will be lowered. Another method is to use porous resins for adsorption of organic compounds and thus purify the wastewater. Here, we report the preliminary results for these new methods and demonstrate the effectiveness of these methods in wastewater treatment. Furthermore, it is shown that these new methods are not only reliable and robust, but also easy to scale up because, in principle, both are chromatographic methods, which can be scaled up to industrial levels, providing other conditions, such as a pump, is readily available.

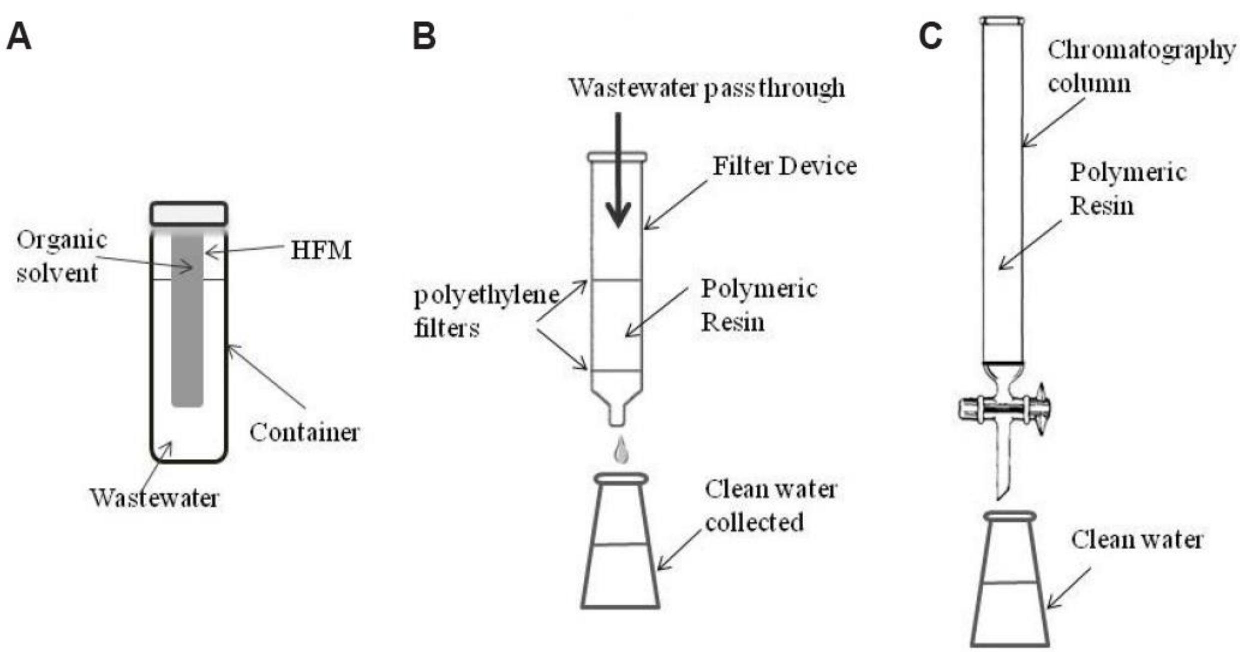

Figure 1. Illustration of the three types of devices used for wastewater treatment: (A) for LLME method; (B) for resin absorption technique; and (C) a column chromatography apparatus.

Results

Spectroscopic characteristics of wastewater samples

Wastewater samples usually have different spectroscopic characteristics. Upon visual inspection, the water collected from Chaohu Lake (Sample 1) had no color but was cloudy; while the industrial wastewater (Sample 2) was dark brown. During the treatment process for samples with color, color change could be used as a primary indication of the content change. However, for samples with no color, a UV Spectrophotometer was utilized to measure the spectroscopic characteristics. The result shown in Figure 2 indicated the absorbance in the UV range. A wavelength of 254 nm was used for the analysis of Sample 1 by HPLC.

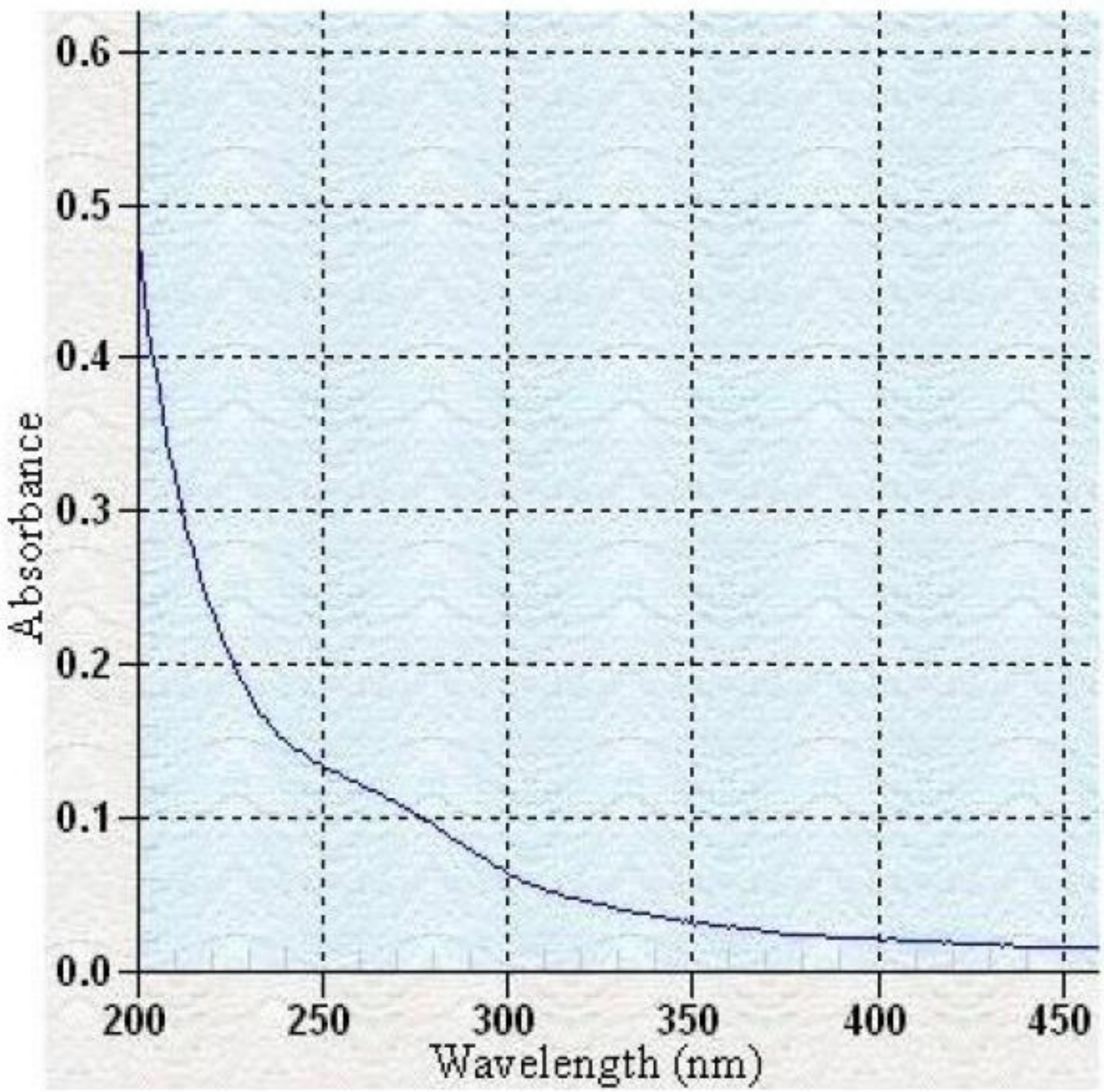

Figure 2. Spectroscopic characteristics of the water sample from Chaohu Lake (Sample 1).

Results of LLME method

The fundamental principle of LLME is the difference in partition ratio for organic pollutants between the organic phase and the aqueous phase in and outside of the HFM. In general, a partition coefficient, P, is the ratio of concentrations of compound A in the two phases of a mixture of two immiscible liquids at equilibrium (8-9). The partition coefficient is a measure of the difference in solubility of compound A in these two phases and can be expressed as:

$$\log P = \log \frac{[\mathrm{A}]_o}{[\mathrm{A}]_a}$$

Where $[A]_o$ and $[A]_a$ are the concentration of A in the organic phase and the aqueous phase, respectively.

Since the value of P is relatively large, it is usually expressed in logarithmic form, i.e. log P. The log P value is also known as a measure of lipophilicity. Thus, a higher log P value indicates greater hydrophobicity and intends to be more soluble in the organic phase. For example, a log P of 3 indicates that its concentration in the organic phase is 1,000 times as high as in the aqueous phase.

By definition, P is the ratio of concentrations of unionized compound between the two immiscible solvents. To measure the partition coefficient of ionizable solutes, the pH of the aqueous phase is adjusted such that the predominant form of the compound is un-ionized. Alternatively, a different parameter called the distribution coefficient, D, is used for the ratio of the sum of the concentrations of all forms of the compound (ionized plus un-ionized) in each of the two phases as shown in the equation below:

$$\log D = \log \frac{[\mathrm{A}]_o}{[\mathrm{A}]_a + [\mathrm{A}^-]_a}$$

Where $[A\text{-}]_a$ is the concentration of deprotonized A (assuming A is monoprotonic acid). The logarithm of D is called log D, which is pH dependent. For un-ionizable compounds, log P = log D at any pH. Log D can be determined using this principle.

Based on the above partition theory, it is easy to see that even a small volume of organic solvent can be sufficient to extract a large number of compound A if its log P value is high. Therefore, it is possible to use HFM as a means of performing the liquid-liquid extraction process to extract organic components in wastewater into the organic phase inside the HFM. The porous HFM serves as a barrel between the two phases but allows compounds to pass through and reach equilibrium between the organic and aqueous phases in and out of the HFM. This method was applied to 50 mL of Sample 1. Six HFM tubes filled with octanol were placed in the beaker for a two-hour treatment. The treated sample was then analyzed by HPLC. The level of organic content in the treated versus untreated wastewater was significantly reduced, as shown in Figure 3A and B. However, the residual absorbance in the treated sample suggested that there were some detectable organic contents after Sample 1 was treated. The detectable contents may be due to remaining organic pollutants in the water at equilibrium. This is understandable as organic compounds that can dissolve in water usually do not have high log D values. Compounds with high log P value do not dissolve in water well. It is possible that the extraction solvent, octanol, which is supposed to be immiscible with water, actually leaked out from the HFM into the aqueous phase and contributed to residual absorption. By changing octanol to dodecane with higher log D values, there was no leakage found and the treated wastewater was completely cleaned as shown in Figure 3C, which was comparable with the distilled water (Figure 3D). The results demonstrated that the method was effective for removing organic containments from wastewater when the proper organic extraction solvent is used.

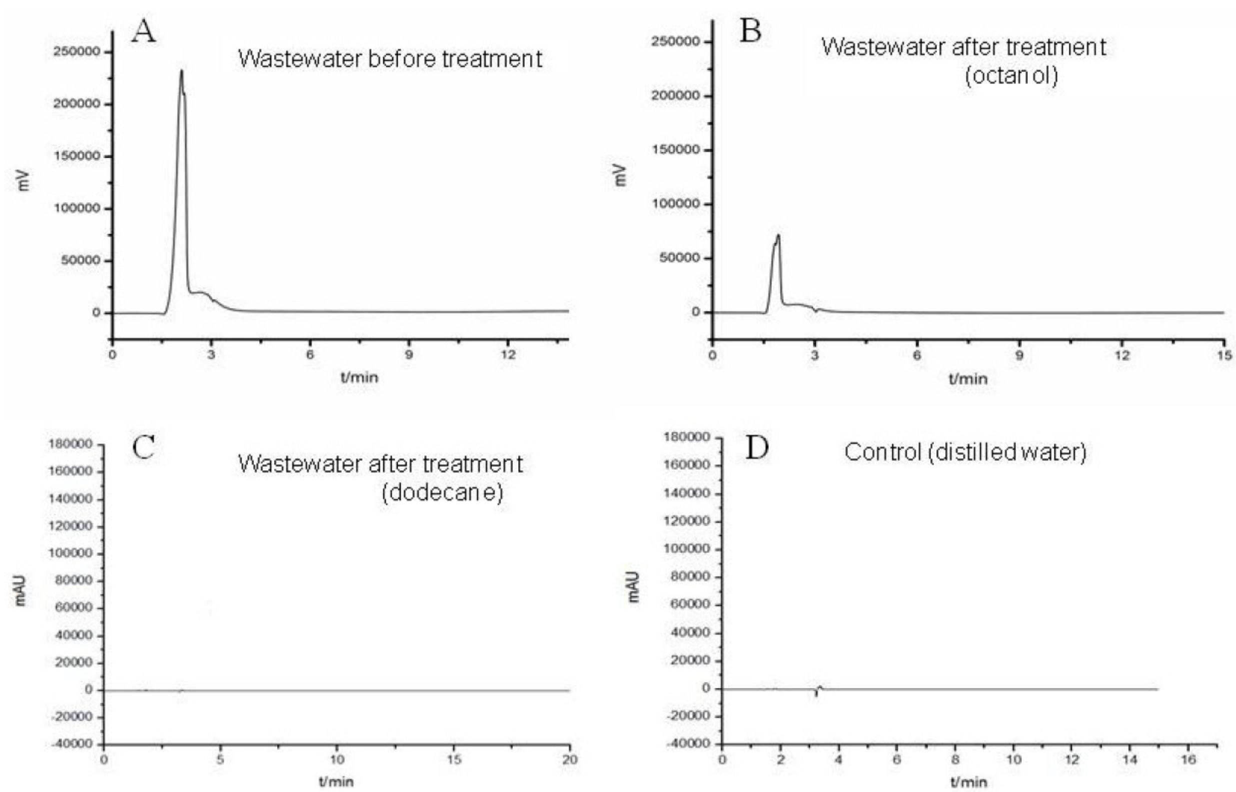

Figure 3. HPLC chromatograms recorded for Sample 1 in the treatment using LLME method: (A) chromatogram of Sample 1 before the treatment; (B) chromatogram of Sample 1 after the treatment with octanol; (C) chromatogram of Sample 1 after the treatment using dodecane; and (D) chromatogram of control sample (distilled water).

Results of Resin based Method

In addition to the LLME method, another method was to use polymeric resin to extract organic pollutants out of wastewater. The resins had the advantage of being applicable to a wide pH range and a broad spectrum of affinity for various organic containments. Our study focused on testing different types of resins, the proper levels of resin vs. the amount of samples, as well as the extraction time. The experimental conditions were optimized to give the best extraction efficiency. Furthermore, we also examined multiple stages of treatment to enhance the results.

Sample 2 was a good example of complex wastewater and its current treatment practice is distillation and burning. Using the resin (Resin A) as a solid media to extract pollutants, the sample appearance changed from a dark brown (Figure 4A) to a yellowish color (Figure 4B). Since this resin is a neutral particle, it has its limitations in dealing with charged species. Figure 4B indicated that there must be some charged species in Sample 2, which could not be removed from water by this resin alone. Thus, a new resin with a negative charge (Resin B) was used for the second stage of treatment and the color disappeared completely (Figure 4C), compared to the tap water control.

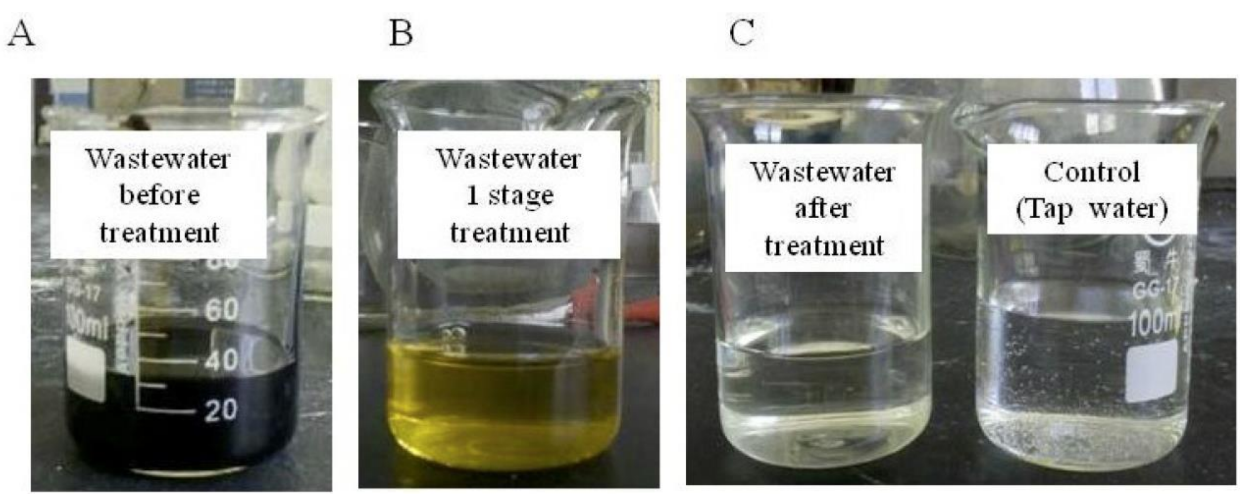

Figure 4. Visual appearance of the wastewater Sample 2: (A) the original sample before the treatment; (B) after 1st stage treatment with Resin A; and (C) after 2nd stage treatment with Resin B and tap water (as control).

In another case, the sample had to go through repeated treatment of the same resin (Resin A) before a satisfactory result was achieved. Figure 5 shows the chromatograms overlaid after repeated wastewater cleanup of Sample 3, indicating the contaminants were gradually reduced in multiple steps of the cleanup process.

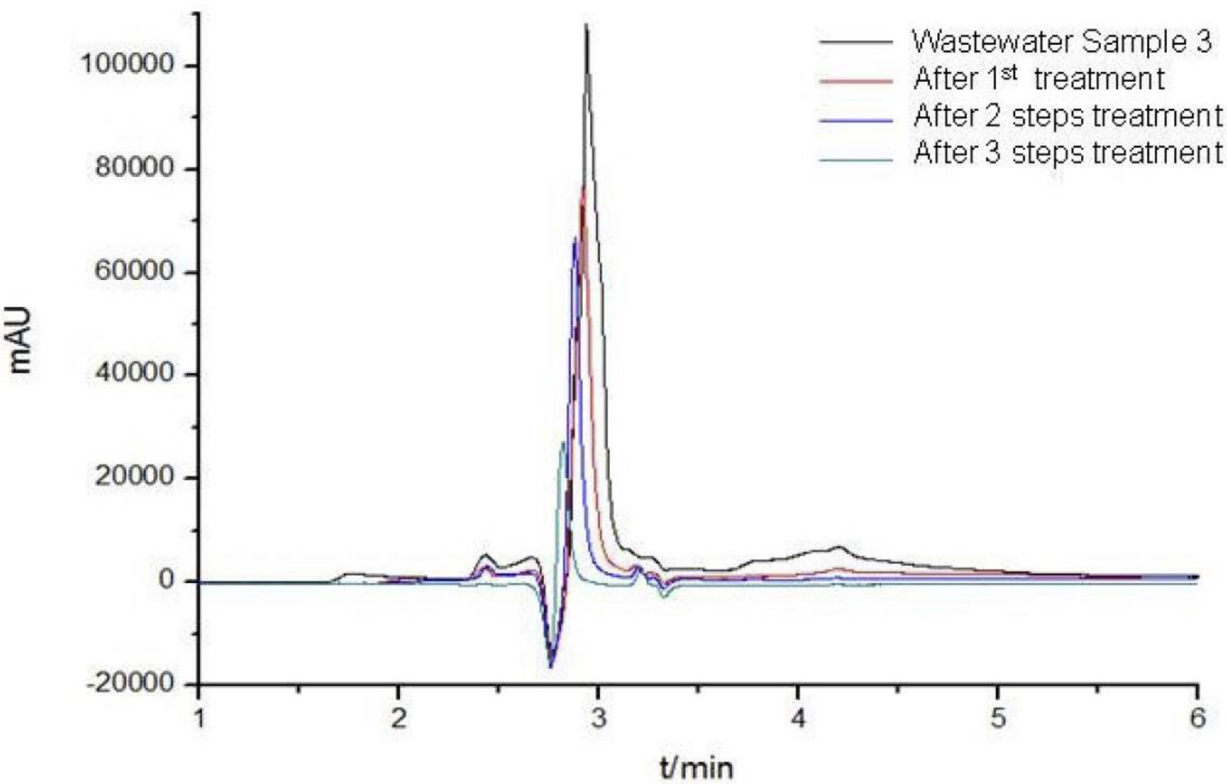

Figure 5. HPLC chromatograms of Sample 3 with repeated treatment using Resin A, demonstrated the decrease of wastewater containment signature peak after multiple steps of treatment.

Discussion

We have evaluated an HFM based LLME method to extract organics out of wastewater. This method is effective for removing organic pollutants. However, it is necessary to choose the right organic solvent to improve the extraction efficiency. Octanol, though the most common organic solvent used for measuring log D values in many analytical methods, is not totally immiscible in water. It tends to permeate the membrane and move into water and becomes a new organic pollutant to the water. Therefore, for the purpose of wastewater treatment of reducing COD, octanol is not the ideal choice. Dodecane is the best solvent for this purpose. Another effective means of extracting organic molecules is to use solid microspheres. The resins are suited for a wide range of pH and possess a broad spectrum of affinity to extract various organic compounds. Thus, they can be used for removing both lipophilic and hydrophilic contaminates in wastewater. In some cases, due to the complexity of the wastewater, the samples need repeated treatment with the same resin before a satisfactory result can be achieved. In other cases, using multiple resins is necessary to completely remove visible organic contaminants.

Methods

Chemicals and materials

Methanol, octanol, and dodecane were obtained from Tianjin Kewei Chemical Co. Ltd. Neutral and ionic polymeric resins (Resin A and Resin B), silica gel bounded with hydrosilane, porous polyethylene filters, and syringe barrels were obtained from Tianjin Aumi Scientific Co. Ltd. Three different wastewater samples were used for testing the methods: the sample from Chaohu Lake (Sample 1) and two industrial wastewater samples (Sample 2 and 3).

Wastewater treatment Devices

HFM based LLME device (Figure 1A): HFM tubing was cut into certain lengths (~5 cm) with one end of each piece sealed by heating. Organic solvents, such as octanol or dodecane were filled into the HFM through the open end using microliter syringes. The HFM was placed inside a 5 mL vial filled with wastewater. Samples at different time points (e.g, 30 min, 1 hour, 2 hours…up to 8 hours) were taken to evaluate the effectiveness of the extraction. The liquid, both inside and outside of the HFM, was taken out and analyzed by HPLC to determine the effectiveness of the extraction. For a large volume of samples, multiple pieces of the HFM tubing were placed in a beaker. The top ends of the HFMs were held together with the opening facing upwards. For example, 10 pieces of HFM tubing were used to treat 100 mL of wastewater.

Solid-phase extraction device (Figure 1B): A polyethylene filter was placed inside a flat bottom empty 30 mL plastic syringe barrel. A few grams (~5 grams) of either polymeric resin or hydrosilane bound silica gel were poured in and another polyethylene filter was capped onto the top of the resin. About 8 mL of methanol was passed through the filter to clean out any undesirable disparities and the eluate was discarded. Then, a 5 mL wastewater sample was pushed through the resin and the eluate was collected in a glass beaker for analysis.

Column chromatographic device (Figure 1C): This device is also resin-based similar to the second device shown in Figure 1B, but larger in scale. 100 g of pre-wetted resin was placed in a glass column (5×30 cm) with a porous bottom. Then, 500 mL of wastewater was poured in from the top and eluate was collected in a vacuum flask for analysis. A vacuum was applied at the bottom on the vacuum flask to facilitate the flow process.

Spectroscopic Analysis of Samples

A single-beam 752pc Spectrophotometer (Tianjin Precision Instrument Co. Ltd.) was used to measure the spectroscopic characteristics of the wastewater to establish a basis for selecting a proper wavelength for HPLC determination.

HPLC Analysis of Samples

An aliquot of each of the wastewater samples being treated with one of the aforementioned methods was then analyzed using an HPLC instrument that consists of an LDC Constrametric 3500 gradient pump and a UV detector (detection at 254 nm). A BauloTM Stablebond ODS HPLC column (Tianjin Aumi Scientific Co. Ltd) was used with 50% methanol as the isocratic mobile phase.

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