SIMULTANEOUS REMOVAL OF ACIDIC AND NEUTRAL POLLUTANTS FROM WATER USING MIXED-MODE RESINS

NUR SYAMIMI ANUAR, HAFIZA MOHAMED ZUKI, WAN MOHD AFIQ WAN MOHD KHALIK AND SAW HONG LOH*

Faculty of Science and Marine Environment, Universiti Malaysia Terengganu, 21030 Kuala Nerus, Terengganu, Malaysia.

Corresponding author: lohsh@umt.edu.my

Abstract: Polycyclic aromatic hydrocarbons and endocrine-disrupting phenols are both ubiquitous pollutants in the environment. Human activities through urbanisation and rapid industrialisation are at the forefront of global environmental pollution. Therefore, removing pollutants in miscellaneous characteristics is important to eliminate the stage-by-stage reduction of pollutants, especially from wastewater, for a cost-effective and time-effective treatment. A simple preliminary study was conducted for the concurrent removal of acidic 2, 4, 6-trichlorophenol (2, 4, 6-TCP) and neutral fluorene (FLU) from water by mixed-mode resins that consist of Anion Exchange Chromatography (AEC) and reversed-phase C18 sorbents. The one-variable-at-time approach was applied in the optimisation of the removal process, where sorbent dosage, exposing time, stirring speed, and sample pH were investigated to enhance the removal efficiency. Under the optimal conditions, 20 mg of each AEC and C18 successfully removed 74.8% of 2, 4, 6-TCP and 96.5% of FLU from the water sample spiked with 50 mg/L of 2, 4, 6-TCP and 0.5 mg/L of FLU that was pre-modified to pH 9 and agitated at 600 rpm for 10 min. The AEC and C18 achieved a removal capacity of 37.4 mg/g for 2, 4, 6-TCP and 0.48 mg/g for FLU, respectively, upon treating 20 mL of the water sample. The mixed-mode resins combine the capabilities of two different retention mechanisms and allow for the simultaneous removal of a broad range of compounds from environmental samples.

Keywords: Endocrine disruptors, fluorescence spectrophotometry, mixed-mode, polycyclic aromatic hydrocarbons, ultraviolet-visible spectrophotometry.

Introduction

Water is the main element for the vivacious cores of living beings. The continual increase of emerging contaminants in environmental water has been documented as a result of anthropogenic activities, the discharge of untreated industrial and sewage effluent, runoff from agricultural fields, agrochemicals, and so forth. Emerging water pollutants are substances or their by-products that are typically not present in monitored bodies of water but have the potential to penetrate them and harm both the ecology and human health. Some of the growing synthetic contaminants include medications, flame retardants, personal care products, and pesticides. These contaminants endanger both human and ecological health.

One of the hazardous organic chemicals typically found in ambient water is phenolic compounds. These substances, which include industrial effluents and conversion by-products from natural and manufactured chemicals like insecticides, which are discharged directly and indirectly into the environment. The fact that phenolic compounds are prioritised as pollutants because they are toxic to organisms even at low concentrations. This is one of the primary motivations for determining their presence in the environment. The United States Environmental Protection Agency (USEPA) has listed phenolic compounds as harmful substances and prioritises them as priority pollutants (Mainali, 2020). These phenolic compounds are dangerous to

health and can have both short-term and long-term impacts. Due to its harmful effects on people, the 2, 4, 6-trichlorophenol (2, 4, 6-TCP) was declared a major pollutant by the USEPA in 1976 (Zhu *et al*., 2021). Several methods for phenol detection have been established after years of research, including adsorption, solvent extraction, chemical oxidation, and microbial degradation (Anirudhan & Ramachandran, 2014).

The environment has been shown to include persistent organic pollutants such as Polycyclic Aromatic Hydrocarbons (PAHs). Because of the toxicity, mutagenic, carcinogenic and estrogenic impacts of several PAHs on humans, they have been classified as priority contaminants (Hussain *et al*., 2018). According to Felemban and co-researchers (2019), the main ways that PAHs reach water sources are through the combustion of fossil fuels, oil spills, road runoff, industrial effluent, leaching from wood that has been impregnated with creosote, and dry and wet depositions. As a result, detecting PAHs in drinking water, rivers, lakes, groundwater, wastewater, ocean, and sediments is of concern. In aquatic ecosystems, PAHs are hydrophobic substances that accumulate primarily as a result of anthropogenic and natural emissions. The PAHs composition in aquatic habitats is a reflection of their originating sources. Since some of the higher PAHs can reduce lung function, exacerbate asthma, and increase rates of obstructive lung disease and cardiovascular disorders, these PAHs can become harmful, especially if they are entering into the alimentary tract (Ambade *et al*., 2021). Finding a simultaneous method to remove and extract these pollutants is particularly crucial due to knowledge of the harmful effects of these phenolic compounds and PAHs, as well as the need to determine their presence in environmental samples to raise consumer awareness.

Deteriorating water quality is still a problem, particularly in wealthy countries. Both the World Health Organization (WHO) and the USEPA have established guidelines on the maximum allowable concentrations of 2, 4, 6-TCP and PAHs in drinking water are not exceeding 0.2 mg/L and 0.2 µg/L, respectively (WHO, 1996; Agency for Toxic Substances and Disease Registry, 2023). Nevertheless, Malaysia has not yet incorporated any of these guidelines into the local environmental rules and regulations. The 2, 4, 6-TCP and fluorene (FLU) were chosen as the model compounds in this study, allowing researchers to investigate the simultaneous removal of the two substances as a preliminary examination of the viability of using two different resins to selectively extract two substances with different properties at once.

Materials and Methods

Reagents and Chemicals

The reference standards, namely 2, 4, 6-TCP and FLU, Anion Exchange Chromatography (AEC) and C18 adsorbents (C18), were purchased from Sigma-Aldrich (St. Louis, MO, USA). HPLC grade methanol, analytical grade sodium hydroxide (NaOH) and 37% hydrochloric acid (HCl) were all obtained from Merck (Darmstadt, Germany).

Preparation of Standard Solutions

The standard stock solutions of 2, 4, 6-TCP (500 mg/L) and FLU (500 mg/L) were prepared in methanol. Serial working standard solutions and spiked samples of 2, 4, 6-TCP and FLU were prepared by diluting the standard stock solutions with 1×10^{-5} M of NaOH and deionised water, respectively. The standard stock solutions were stored at 4°C when not in use.

Ultraviolet-Visible Spectrophotometer and Fluorescence Spectrophotometer Analysis

The standard and sample solutions of 2, 4, 6-TCP were added into 10 mm of quartz glass cuvettes and detected at a maximum wavelength of 294 nm by an ultraviolet-visible (UV-Vis) spectrophotometer (Varian Cary 50 Conc, United States). On the other hand, the standard and sample solutions of FLU were added into 10 mm of quartz glass cuvettes and detected at the excitation wavelength and emission wavelength of 262 nm and 304 nm, respectively, with a fluorescence spectrophotometer (Varian Cary Eclipse, United States).

Removal of 2, 4, 6-TCP and FLU using Anion Exchangers and C18 sorbents

Approximately 20 mg of AEC and 20 mg of C18 were added into 20 mL of aqueous sample solution (pre-modified to pH 9). The sample solution was agitated at 600 rpm with a stir bar (5 mm diameter x 10 mm length) and a magnetic stirrer (Corning, United States) for 10 min. Next, the sample solution was filtered using a nylon syringe filter and analysed with the UV-Vis spectrophotometer at 294 nm for 2, 4, 6-TCP and fluorescence spectrophotometer at 262 nm (excitation) and 304 nm (emission) for FLU, respectively.

Optimisation of the Removal Process using AEC and C18

The removal process of 2, 4, 6-TCP and FLU was optimised using AEC and C18, respectively, before combining both AEC and C18 for the simultaneous removal of 2, 4, 6-TCP and FLU from the sample solution. The optimisation was performed using one variable at a time (OVAT) approach and the sample solutions were spiked with 50 mg/L of 2, 4, 6-TCP and 0.5 mg/L of FLU, respectively.

The effect of AEC dosage (5 to 20 mg), agitation speed (450-1050 rpm), exposing time (5-25 min), and sample pH (pH 3-9) were investigated for the removal of of 20 mL of 50 mg/L of 2, 4, 6-TCP. The same variables were investigated for removing FLU, except for sample pH. The optimal removal conditions were then adopted and applied for the simultaneous removal of 2, 4, 6-TCP and FLU from the sample solution.

Concurrent Removal Efficiency of Mixed-Mode Resins for the Removal of 2,4,6-TCP and FLU from Aqueous Sample Solution

The removal efficiencies of the AEC and C18 were calculated by the following equation:

Removal efficiency (%) = $(C_e - C_o)$ x 100 / C_o (1)

The removal capacity (q_e) was calculated according to the following equation:

$$q_e = (C_o - C_e) \, V / W \qquad (2)$$

where C_o and C_e are the initial and equilibrium concentrations of solutions (mg/L), respectively, V (L) is the volume of the solution, and W (g) is the mass of the dry resin used.

Results and Discussion

Screening of 2, 4, 6-TCP and FLU Spectra

The 50 mg/L of 2, 4, 6-TCP was prepared in 1 x 10^{-5} M of NaOH at pH 9 to deprotonate the 2, 4, 6-TCP. The 2, 4, 6-TCP is an acidic compound with an acid dissociation constant (pKa) of 6.23 (Shanaah *et al*., 2023). When the standard solution was modified to pH 9, the 2, 4, 6-TCP existed in anionic form. The spectrum of 2, 4, 6-TCP was screened in the UV and visible region from 200 to 800 nm using a UV-Vis spectrophotometer. The maximum wavelength of 2, 4, 6-TCP was then determined at 294 nm based on the highest absorbance obtained from the spectrum, as shown in Figure 1a. The spectrum of deprotonated 2, 4, 6-TCP was employed instead of the protonated compound because the study was related to the anion exchange process.

The 0.5 mg/L of FLU was prepared in deionised water before the screening of the spectrum using a fluorescence spectrophotometer. The FLU was excited in the UV region from 200 to 380 nm and the emitted light was given off upon relaxation of the compound. The excitation and emission wavelengths of FLU were then determined at 262 and 304 nm based on the highest absorbance obtained from the spectra, respectively, as shown in Figure 1b. The emission spectrum of a fluorophore is typically a mirror image of the absorption spectrum as a result of the transition from the ground to the first excited state because the emission of a photon frequently leaves the fluorophore in a higher vibrational ground state (Swaminathan, 2023).
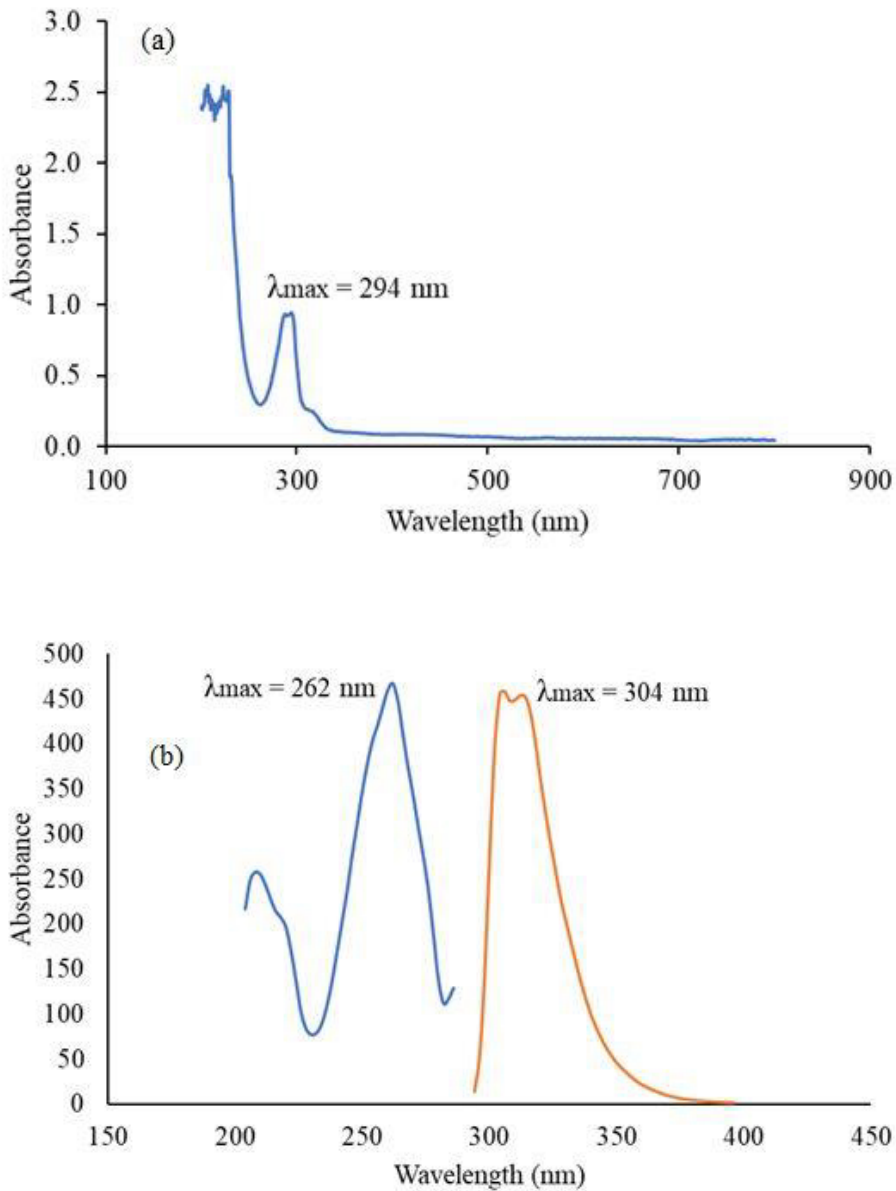
Figure 1: (a) Spectrum of 2, 4, 6-TCP and (b) FLU

Calibration of 2, 4, 6-TCP and FLU Standard Solutions

A series of working standard solutions (seven points) of 2, 4, 6-TCP in the range of 0.8 to 100 mg/L were prepared by diluting the 500 mg/L 2, 4, 6-TCP standard stock solution with 1×10^{-5} M of NaOH. The absorbances of 2, 4, 6-TCP working standard solutions were measured with a UV-Vis spectrophotometer at a maximum wavelength of 294 nm. Results indicated the UV absorbances responded linearly to the concentrations of 2, 4, 6-TCP spiked in NaOH solutions. An excellent correlation was obtained with a coefficient of determination R^2 of 0.9988. The results revealed a strong relationship between the concentrations of 2, 4, 6-TCP and UV responses. Hence, the UV-Vis spectrophotometer was suitable to apply as the quantitation method for the 2, 4, 6-TCP.

A series of working standard solutions of FLU in the range of 0.2 to 10 mg/L were prepared by diluting the 500 mg/L of FLU standard stock solution with deionised water. The absorbances of FLU working standard solutions were measured with a fluorescence spectrophotometer at excitation and emission wavelengths of 262 and 304 nm, respectively. The results revealed that the absorbances responded linearly to the FLU concentrations spiked with deionised water. An excellent correlation was obtained with a coefficient of determination, R^2 of 0.9941. The results revealed a strong relationship between the concentrations of FLU and fluorescence responses. Hence, the fluorescence spectrophotometer was suitable to apply as the quantitation method for the FLU.

Optimisation of the Removal Process using AEC and C18

In this study, AEC was targeted for the removal of 2, 4, 6-TCP by the anion exchange process. The deprotonated 2, 4, 6-TCPs were in anionic form, and they exchanged with the hydroxide ions on the AEC, which then succeeding the removal. On the other hand, reversed-phase C18 sorbents were employed to remove the hydrophobic and neutral FLU by adsorption mechanism. The optimisation study was conducted by using the deionised water samples that were pre-modified to pH 9 and spiked with 50 mg/L of 2, 4, 6-TCP and 0.5 mg/L of FLU.

Effect of Agitation

In this study, the samples were agitated with a stir bar and a stirrer with a controllable speed. Agitation is the key factor controlling the removal mode. A suitable stirring speed is needed to enhance the mixing of the sample solution with the resins, thus, allowing for the reaction to take place. This study investigated the stirring speeds ranging from 450 to 1050 rpm. Figure 2(a) shows that the highest removal effectiveness of 2, 4, 6-TCP (75.6%) was achieved at 600 rpm, whilst the highest removal of FLU (96.9%) was maximum at 450 rpm. Generally, a low mixing speed with a considerably short mixing time can increase the removal of pollutants in the sample, while an excessively fast mixing speed and considerably short mixing time can yield a poor removal of pollutants in the sample (Getahun *et al.*, 2023). In slow mixing, the sample was stirred to encourage the adsorption and anion exchange to take place. Stirring too fast may disrupt the process and thus cause insufficiency in contact. The 600 rpm was chosen for further experiments because the removal of FLU was reduced by 1% only from 600 rpm to 450 rpm, whereas the removal of 2, 4, 6-TCP was magnified by 8.6% from 450 to 600 rpm. Despite the different resins used, agitation was required to detach and disperse the resins (De Gisi *et al.*, 2016). Notably, once the stirring speed was enough to disperse the resins, the further increase did not offer an improvement in the removal. On the contrary, a low removal of the analytes might be observed.

Effect of Exposure Time

Exposure time is another key parameter affecting pollutant uptake by resins. This is because it provides information on the sorption kinetics of the pollutant for a given initial dosage of the

resin (Panda *et al*., 2017). The effect of exposure time in the range of between 5 and 20 minutes was examined. Figure 2(b) shows the maximal exposing times of 2, 4, 6-TCP and FLU were attained at five and 15 minutes, respectively. Decreasing and plateau trends were observed for the removal of 2, 4, 6-TCP and FLU beyond the above exposing times, respectively, as summarised in Figure 2(b). This concluded that an ion exchange is a fast reaction process as compared with adsorption (Ye *et al*., 2019). The rate of adsorption depends on the available exposed surface, and C18 sorbents are the microparticles that might limit the adsorption (Li *et al*., 2021). A compromise on exposing time of 10 minutes was suggested for subsequent experiments because the removal of FLU at 10 minutes was 89.7%, whereas the removal of 2, 4, 6-TCP was achieved at 71.2%.

Effect of Sample pH

Sample pH is critical for acidic and basic analytes. They need to be modified into appropriate forms to promote high retention of the analytes depending on the nature of the resins. The acid dissociation constant (pK_a) of each compound must be taken into account to ensure that, at that particular pH, the analytes are charged and can interact with the resins, which are also charged at the working pH. In this study, 20 mg of each AEC and C18 were employed for the removal of 2, 4, 6-TCP and FLU. The effect of sample pH was examined in the range of between pH 3 and pH 9 to investigate the optimal pH for the removal of 2, 4, 6-TCP from spiked deionised water. Conversely, sample pH was not studied for the removal of FLU because FLU is a neutral compound that is not affected by the change of sample pH and allows for adsorption on C18 (Bernal *et al*., 2017). Figure 2(c) shows the removal of 2, 4, 6-TCP was feasible at all sample pHs studied. However, the removal of 2, 4, 6-TCP was optimal when the sample pH was at pH 9. This is because the pK_a value of 2, 4, 6-TCP is 6.23, and they exist in anionic forms at pH 9. It is beneficial for the anion exchange process with AEC. A decline in removal was noticed when the removal was conducted in sample pH ranging from pH 3 to pH 7. This was because the 2, 4, 6-TCP occurred in molecular or neutral form when the pH was two units smaller than the pK_a, and parts of them were not completely charged, too, when the pH was not 2 units larger than the pK_a. The obtained results confirmed that at basic conditions, the 2, 4, 6-TCP carried a dominant O^- group, which was negatively charged, and the surface of AEC was positively charged, giving rise to a high electrostatic attraction between AEC and the 2, 4, 6-TCP (Cui *et al*., 2021).

Effect of Resin Dosage

Resin dosage is one of the most significant operating parameters in pollutant removal. Hence, to study the effect of resin dosage, the amounts of AEC and C18 in the range of 5 to 20 mg were examined to investigate the capacity of AEC and C18 in removing the 2, 4, 6-TCP and FLU from 20 mL of spiked sample solutions. The same size of the magnetic stirrer and hot plate were used to avoid any uncertainty caused by apparatus deviation. A blank sample was also prepared to function as a negative control. It was found that the blank sample without the addition of AEC and C18 attained negligible descent after 10 min of exposing time. Figure 2(d) shows the removal of 2, 4, 6-TCP and FLU was enhanced by the increasing of AEC and C18 dosage. When more resins were introduced in the sample solution, the availability of active sites was greater for the reaction to take place (Angerasa *et al*., 2021). The results indicated that the removal of 2, 4, 6-TCP was more than 70% when 20 mg of AEC was added to the 20 mL of spiked sample. Then, the removal of FLU was almost complete (96.5%) when 20 mg of C18 was added to the 20 mL of spiked sample. Therefore, this suggested that 20 mg of each AEC and C18 were chosen in the subsequent experiments to ensure the absorbance of FLU in the UV region did not interrupt the quantitation of 2, 4, 6-TCP while applying the UV-Vis spectrophotometer for the determination of 2, 4, 6-TCP.
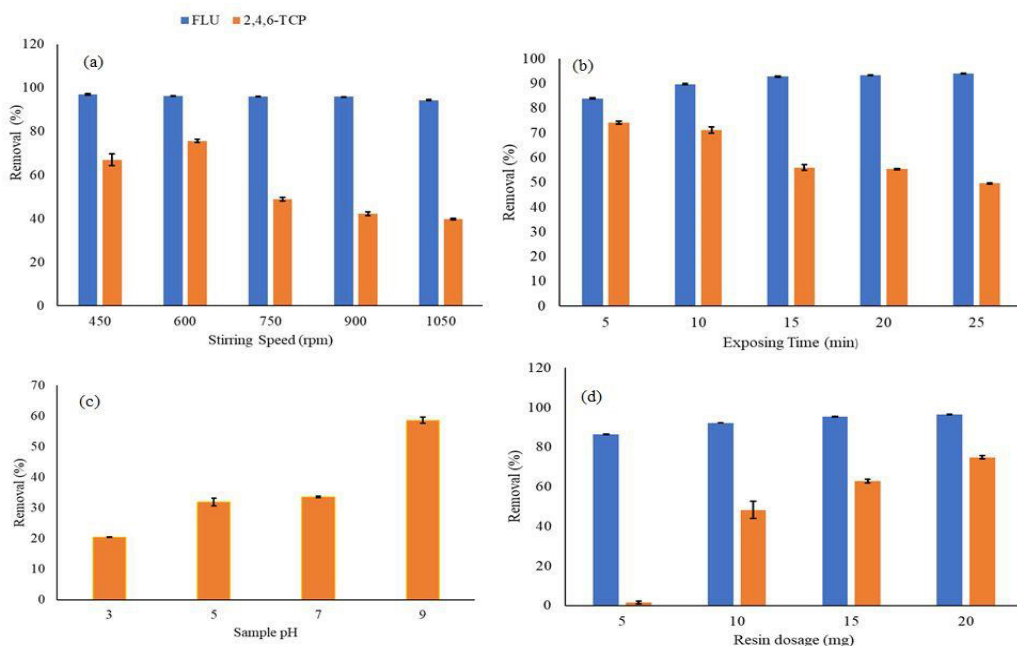
Figure 2: Effect of agitation (a), exposing time (b), sample pH (c) and resin dosage (d) on the removal of 2, 4, 6-TCP and FLU from the spiked deionised water

Concurrent Removal of 2, 4, 6-TCP and FLU from Aqueous Sample Solution by Mixed-Mode Resins

The efficiency of AEC and C18 for the removal of 2, 4, 6-TCP and FLU from the 20 mL of spiked sample solution by mixed-mode resins composed of 20 mg of each of the AEC and C18 was then determined using the optimal removal conditions. The removal was performed by stirring the sample solution (pre-modified to pH 9) spiked with 50 mg/L of 2, 4, 6-TCP and 0.5 mg/L of FLU, respectively, at 600 rpm for 10 min. Table 1 summarises the removal efficiency and capacity of both AEC and C18 using the specified conditions.

Table 1: Removal efficiency and capacity of mixed-mode resins for the removal of 2, 4, 6-TCP and FLU from the spiked sample solution.

Resin	Removal Efficiency	Removal Capacity
AEC	74.8% of 2, 4, 6-TCP	37.4 mg of 2, 4, 6-TCP/g of AEC
C18	96.5% of FLU	0.48 mg of FLU/g of C18

Selectivity of the resin is one of the main criteria for achieving good accuracy and sensitivity. The mixed-mode resins consisted of commercially available AEC and C18, which were dependent on two different mechanisms to remove the targeted analytes. The AEC was solely for the removal of deprotonated 2, 4, 6-TCP in anionic forms, whilst the non-polar C18 was uniquely for the adsorption of neutral and hydrophobic FLU. To attain good accuracy when chromatographic separation was not conducted using high-performance liquid chromatography,

one of the analytes must not absorb or absorb insignificantly in the UV region. This was achieved by completely removing the FLU and quantitating the FLU with a fluorescence spectrophotometer. The study concluded that the mixed-mode resins successfully removed their target analytes without interrupting the distinctive mechanism of each resin.

Conclusion

The simultaneous removal of acidic 2, 4, 6-TCP and hydrophobic FLU from water by mixed-mode resins was successfully performed by applying anion exchangers and reversed-phase C18 sorbents, respectively. The quantitation of both 2, 4, 6-TCP and FLU was successfully performed by UV-Vis and fluorescence spectrophotometry, respectively, without having to apply chromatographic separations. This was because the removal of FLU was almost complete, and its absorption in the UV range was insignificant to interrupt the quantitation of 2, 4, 6-TCP. On the other hand, the 2, 4, 6-TCP was not a fluorophore. The study could proceeded with further investigation into the desorption of both analytes from the resins to succeed in a microextraction technique with mixed-mode resins.

Acknowledgements

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