

## Research Article

# Bar Adsorbent Microextraction with Carbon-Based Sorbent Layers for the Identification of Pharmaceutical Substances

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Received 21 September 2022; Revised 1 October 2022; Accepted 7 October 2022; Published 20 May 2023

Academic Editor: Debabrata Barik

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Thirteen carbon materials were tested as sorbent layers in bar adsorbent microextraction (BA $\mu$ E) to monitor hint amounts of 10 common pharmaceutical compounds (PhCs) in surface and groundwater matrices such as surface and groundwater, saltwater, spring water, and sewage. The persistence of trace amounts of three organophosphate insect repellent and cis and trans permethrin (PERM) in water quality matrices is suggested using bar adsorptive microextraction in conjunction with microliquid dissolution accompanied by significant volume injection-gas chromatography-mass spectroscopic analysis able to operate in the particular ion monitoring acquisition mode. Using BA $\mu$ E to compare several sorbent coatings (five porous carbon and six polymers), it was discovered that activated carbon (AC2) was the optimum compromise among specificity and effectiveness. 17-estradiol, estrone, sulfamethoxazole, diclofenac, triclosan, gemfibrozil, 17-ethinylestradiol, mefenamic acid, and clofibrac acid were chosen as system drugs to represent different treatment groups. Despite their lower porosity, statistics revealed that low-T-activated hydrochars, made from carbohydrates and a eutectic salt mixture at constant temperature (e.g., 180°C) and autogenerated pressures, could compete at the top level commercially carbonaceous materials in this purpose. These L-T-activated hydrochars had the best overall recovery (between 21.8 and 83.5 percent) for the simultaneous analysis of ten targeted PhCs with very different physical and chemical possessions, utilizing higher-efficiency liquid chromatography diode array identification.

## 1. Introduction

In recent decades, the main focus of the research has changed away from traditional pollutants and toward emerging pollutants, which pose a threat to the aquatic environment and health. Pharmaceutical and personal service goods (PPCPs) are a type of developing contaminant that has turned into a global environmental issue. Human and veterinary medications were used to treat or prevent diseases in humans, as well as antiseptics and perfumes for personal

care products like lotion, body cleansers, and sun protection, which are all found in pharmaceutical compounds. Most PPCPs can persist in sewage treatment plants if they are very slightly altered or even unaltered. Because of the continual discharge, they are semipersistent in the ecosystem and could be hazardous to nontarget creatures [1]. Environmentalists have a tough time analyzing PPCPs in various environmental specimens because of their low amounts in the environment and the complexity of the sample matrices. Empirical methodologies and approaches frequently stymie

research on the occurrence and distribution of PPCPs. For the removal of PPCPs, qualitative evaluation procedures, such as liquid-phase microextraction (LPME), solid-phase microextraction (SPME), and solid-phase extraction (SPE), have already been used. Automated analysis chemical sample collection procedures have been characterized by reduction and high throughput in recent years to improve selectivity and sensitivity, particularly for the determination of traces. Sorptive analytical techniques have already been widely developed and employed to identify the highest range of organic solute molecules in a variety of matrices. Solid-phase extraction, solid-phase microextraction (SPME), and, more lately, in the process of getting ready for phase separation, one of the most popular sorptive enrichment procedures utilized is called stir bar sorptive extraction, or SBSE for short. Sorptive extraction is the foundation of this technology. During this process, the solutes are extracted into a polymer, such as polydimethylsiloxane (PDMS), which is coated on a stir bar. It was created as a one-of-a-kind separation and purification analysis focusing on another principle such as SPME, and it is currently a widely utilized filter for leftovers of important organic pollutants in wastewater and a range of matrix [2].

In research applications, carbon-based nanoparticles have already been widely employed. Fullerenes, nanohorns, carbon nanofibers, nanotubes, and graphene, as well as their chemically processed equivalents, have all been explored as sorbents in sample processing. Noncovalent connections, such as stacking, hydrogen bonding, van der Waals' forces, hydrophobic interactions, and electrostatic forces, are possible thanks to the unique architectures of carbon-based nanoparticles. Carbon-based nanoparticles offer wide numerous applications in various sample preparation procedures, according to the aforementioned capabilities [3]. Although the rationale for selecting one allotrope over the other is always being debated, there is a vast range of carbon-based compounds that can be used in analytical techniques. Carbon nanotubes (CNTs) have shown considerable promise in a wide range of processes and applications since their first announcement in 1991. Physical and chemical qualities that are unmatched by almost all metal elements have been achieved by combining architectures, sizes, and topology. CNTs are indeed being recognized as an effective formulation in matrix-assisted laser dissolution ionization, as stationary phases in separation processes (capillary electrochromatography, high-efficiency liquid chromatography, gas chromatography, and capillary electrophoresis), and as new SPE materials in chemical analysis. In terms of this last use, the amount of research has expanded dramatically during the last two decades [4]. Ketamine (KET) was created in 1962 as a less hazardous alternative to phencyclidine (PCP), an anesthetic that had established a reputation for causing illusions and insanity. KET is an ideal drug for short-term medical processes in animals and in human medical treatment, particularly in children, advantages of fast onset and short sustained release with only subtle aerobic and resistance depressive episodes in contrast to other general anesthetics and the ability to inhale to maintain the anesthetic state [5]. The most significant drawback of KET is that it

has the potential to induce visual hallucinations that are analogous to those brought on by the use of lysergic acid diethylamide (LSD). Memory loss and ulcerative cystitis are two of the most serious side effects of using ketamine for recreational purposes. Memory loss, mood changes, respiratory distress, trouble with the bladder and urination, high heart rate, seizures, overdose, and other adverse effects may occur in the long term as a result of this medication. As a consequence, it was overused by medical workers at first, but it gradually gained popularity among youthful users during dance and rave gatherings.

Because of the widespread use of medications, their existence in the atmosphere has been documented in recent decades becoming a serious concern. Pharmaceuticals are discharged into the atmosphere in either their unmetabolized or metabolized form, mostly by homes, sewage treatment plants, institutions, industrial sites, and veterinary services. Based on the chemical features of each medicine, they all have polar features that make them easier to introduce into the water habitats, resulting in the poisoning of freshwater environments. Nonsteroidal anti-inflammatory drugs (NSAIDs), such as diclofenac (DIC), ketoprofen (KET), naproxen (NAP), and mefenamic acid (MEF), are one of the most widely used classifications of pharmaceutical drugs because they have a wide range of therapeutic characteristics, including antipyretic, analgesic, and anti-inflammatory characteristics [6]. Diuretics are still another category of pharmaceutical medications that are used to treat cardiovascular disease, high blood pressure, and edema, in addition to the purposes of doping, such as furosemide (FUR), despite the fact that the use of these drugs is prohibited in athletic competition. Because diuretics can produce rapid weight loss and can operate as masking agents both during and outside of competition, they are prohibited in all sports. Diuretics can also cause rapid weight loss. Mebeverine (MEB) is a musculotropic chemical element that operates on the smooth muscle cells of the digestive organs and is particularly effective against colonic spasms. Although the potential for these substances to cause harm to the ecosystem is unknown, endocrine disruption and the development of drug-resistant bacteria have indeed been described. Concerns about pharmaceutical abuse, forensic and sports doping instances, and drugs not being entirely removed by wastewater treatment plants (WWTPs) abound [7]. Moreover, urine is an underlying genetic structure to be analyzed for toxicants and therapeutic approach measurement reasons in biology and medicine, for a precise clinical explanation of metabolomic data in humans and other animals and technical fault of endocrine glands and crucial identification of pituitary tumors, that could be affiliated with many illnesses such as anorexia nervosa, breast cancer, and pseudohermaphroditism. The steroid hormones are produced in the human body by endocrine glands in free or conjugated form, and their primary method of metabolism of dietary in the human body is glucuronidation in the liver and excretion in urine; however, sulfated compounds have been reported in other instances [8]. Bioreactors, such as the enzyme-linked immunosorbent assay (ELISA), are quick and inexpensive for testing anabolic hormones, but they lack

specificity for the determination of trace and frequently produce a false-positive result. Because physiological tests lack sensitivities and efficiency, extraction methods became the analytical methods of choice, as they allow for the precise selection of relevant compounds of interest and are known to be particularly sensitive analytic methods. Bar adsorptive extraction (BAE), a new spontaneous emulsification technology that works in the static floating sample method, was launched in recent years. BAE has the benefit of being adjustable to more appropriate nanostructured adsorbents (e.g., polymers (Ps) and activated carbons (ACs)) depending on the nature of the operation. This innovative analytical approach has proven to be a wonderful alternative to the traditional sorption-based approaches for determining the concentration of medium polar-to-polar chemicals in aqueous fluids with good efficacy in various types of matrices [9]. New enhancements to the BAE methodology have recently been made, including shrinking the analysis equipment, reducing the liquids desorption quantity to the L level, and removing the solution switch phase. Furthermore, miniaturization of the BAE device utilizing a less sorptive stage produced excellent analytical results, while reducing the solvent enables a more environmentally responsible approach while maintaining high efficacy, making the analysis technique faster and more efficient.

Within that respect, and given the importance of carbonaceous materials as micropollutant adsorption process, it is worth considering the ability of different sources of carbon substances, such as carbohydrate-derived hydrochars and their enabled compadres, as coating stages for efficient removal of a variety of PhCs. Hydrochars are made by hydrothermally carbonizing carbohydrate precursors with water as the medium during mild process parameters. Hydrochars are essentially nonporous solids with a chemical nature rich in oxygen functional groups, as opposed to carbonaceous materials made using traditional activation methods. Before gas or liquid chromatographic, most methodological approaches described for minimal level measurement of PhCs in surface and groundwater matrix have included a sample preliminary design. Miniaturized passively sorption-based technologies, such as stir bar sorptive extraction (SBSE), bar adsorptive microextraction (BAE), and solid-phase microextraction (SPME), have recently emerged as perhaps the most relevant for determining polar to nonpolar chemicals in an aqueous medium. BAE is based on the implementation of this method of floating sampling technique, which allows for the selection of the optimal sorbent coating to ensure high effectiveness just on targeted PhCs [10]. The assessment of trace compounds in complicated construction collections has become increasingly significant in recent years because of the possible damaging consequences of trace components of the environment, food, drugs, and other environments on humans, animals, and ecosystems. These materials, nevertheless, are exceedingly complicated, and the solutes are present at minute levels, making analysis extremely challenging. As a result, the basic premise of this methodology procedure has become a significant aspect of the analysis to enrich trace components, increase method sensitivities, and remove interference com-

pounds [11]. PE is among the most widely utilized specimen processing techniques for preconcentrating analytes in a wide range of samples because of its characteristics of high enriched uranium component, low organic solvent consumption, high recovery, low cost, rapid phase separation, and the capacity to couple with various identification techniques in either an online or offline mode. It is common knowledge that the two most important considerations to make when utilizing SPE are the development of an effective technique and the selection of an adequate sorbent. In recent years, the key problems in terms of SPE techniques have been reducing the amount of experimental solvent used and the formation of toxic waste, saving employees' time and labour, bringing down expenses, and improving the efficiency of analyte separation. Verifying that the analytical system is operating appropriately is the first stage in the process of resolving issues relating to recovery or reproducibility in an experiment. Many residual constituents have indeed been extracted from various complicated samples employing innovations such as solid-phase microextraction (SPME), magnetic solid-phase extraction (MSPE), and dispersive solid-phase extraction (DSPE) using CNTs as sorbent materials [12].

Multiresidue research using gas chromatography is the most comprehensive chromatography approach for analyzing contaminants from water in samples collected (GC). Many of the chemicals of focus on environmental materials are likely to be absorbed and degraded on the column or injection, necessitating the use of volatile, high thermal stability molecules. As a result, investors can trade reactions that are required. Ultra-high-performance liquid chromatography (UHPLC) and liquid chromatography (LC) are currently being employed in conjunction with spectrometry (MS) to detect nontarget species solutes that are extremely polar and nonvolatile and have high molecular masses, rendering them incompatible with GC. As a result, a single research run can be used to evaluate or identify both targeted and nontargeted solutes. The use of a liquid chromatography-mass spectrometer, also known as an LC-MS, in conjunction with a sample preconcentration and clean-up stage is recommended due to the LC-high MS's specificity and sensitivity. In comparison to HPLC, the LC-MS method that was presented was more rapid, sensitive, and specific. In contrast to HPLC, LC-MS can be utilized in the analysis of mixtures that are only partially resolved. Exhaustive conventional pretreatment procedures such as liquid-liquid extraction (LLE) and solid-phase extraction (SPE) are being utilized to separate and preconcentrate diverse families of analytes from aquatic and terrestrial ecosystems [13]. Due to the necessity to reduce solution quantities and avoid utilizing harmful organic solvents throughout LLE and SPE, existing preconcentration techniques have been modified to develop innovative methodologies. As a result, nanotechnology becomes a critical component in achieving these goals, and new approaches have been created. Microextraction procedures are nonexhaustive preconcentration techniques that use a very small quantity of the extraction stage (in the order of a few liters) in comparison to the sample. Solid-phase microextraction (SPME) or solvent microextraction is used to recover particles from a

slight quantity of a solid or semisolid polymeric material (SME). Due to their significant structural variations, both procedures have a lot in common because they are both spontaneous emulsification methods. Due to their simplicity, efficiency, low cost, minimum extraction temperature, and outstanding ability to clean up specimens, both procedures are viable options for sample processing [14].

In the development of computational techniques, the preconcentration stage is critical. Typically, this stage takes up the majority of the time inside the investigation, with the accuracy and quality of the results being highly reliant on the procedure used to prepare the samples. Some traditional procedures, such as liquid-liquid extraction (LLE) and solid-liquid extraction (SLE), have certainly been frequently used for regular investigations with excellent results. However, there are several drawbacks, such as the usage of massive quantities of toxic organic liquids and the amount of time it takes for the extraction methods [15]. Furthermore, in LLE, achieving restricted sample preparation parameters and the likelihood of emulsion is a critical barrier to achieving the extraction accuracy and effectiveness of the assessment. Obtaining ecologically responsible analytical techniques becomes a key priority in a lot of labs, in addition to all these important challenges. As a result of this tendency, various spontaneous emulsification technologies have already been presented as viable “green” alternatives to the previously mentioned traditional approaches. These methods are useless organic substances and materials, and they enable the accurate and consistent identification of many analytes in a range of matrices utilizing an appropriate and efficient methodology.

## 2. Related Works

The advancement, efficiency, verification, and implementation of a novel methodical technique for the perseverance of the six most common tricyclic antidepressant drugs (TCAs; trimipramine, mianserin, amitriptyline, imipramine, mirtazapine, and dosulepin) in urine matrix were determined, utilizing bar adsorptive microextraction technique (BA $\mu$ E). For the first time, researchers combined the latest generation spontaneous emulsification gadgets encased with suitable polymers, sorbent phases, and novel carbon materials compiled from biodegradable polymer squandering with large-volume injection-gas chromatography-mass spectroscopic analysis functioning in selected ion monitoring mode. Preliminary tests on sorbent coverings revealed that the polymeric phases function far better than the studied biosorbents, which were ineffective for use in spontaneous emulsification procedures. The limit of detection obtained for the six TCAs varied from 0.3 to 1.5 g L<sup>-1</sup> utilizing BA $\mu$ E covered with C<sub>18</sub> polymers under optimum experimental parameters, and weighted linear regression analysis yielded outstanding linearity ( $r^2 > 0.9961$ ) between 10.00 and 1000.00 g L<sup>-1</sup>. The proposed mathematical scientific method produced appropriate matrix effects (90.4–112.9 percent, RSD 13.8 percent), high recovery (92.4–111.6 percent, standard deviation 12.4 percent), and phenomenal overarching operational efficiencies (ranging from 84.8 percent to 124.4

percent, standard deviation 13.8 percent). The six TCAs were successfully screened in real urine samples using the designed and verified technique. In comparison to existing microextraction-based approaches, the suggested investigation system demonstrated to be an environmentally responsible and user-friendly way of monitoring trace amounts of TCAs in complicated urine composites. The major drawback of the research is only a limited amount of samples could be analyzed in the bar adsorptive microextraction application on determining the tricyclic antidepressants in a urine sample which is proposed by [1]. Pesticides are widely used in various fields to increase crop productivity by preventing pests from wreaking havoc. Triazine insecticides are a class of compounds that are applied frequently. They are distinguished by the presence of a modified C<sub>3</sub>H<sub>3</sub>N<sub>3</sub> heterocyclic ring. Triazine pesticides can be harmful to both persons and the aquatic resources they come into contact with as a result of their high level of toxicity and the toxic effect they generate. Triazines can be moderately irritating to the eyes and cause only slight irritation to the skin. The amount of these chemical components in samples collected, on the other hand, is very low. Furthermore, additional substances present in water specimens could obstruct the detection of triazine herbicides. For this reason, it is critical to establish preconcentration methodologies for the preconcentration of the target molecule as well as appropriate sample clean-up. Liquid-phase and solid-phase microextraction, dispersive solid-phase extraction, stir bar fabric phase sorptive extraction, magnetic solid-phase extraction, and sorbive extraction are only a few of the new extraction methods and miniaturized extraction methods that have recently been made. Researchers hope to address current developments in the separation of triazine pesticides from environmental water samples in this study. Novel preconcentration procedures and novel reducing agents developed for sorbent-based separation processes will be highlighted. The precision and sensitivity are very low when compared to other methods, and this is the major limitation of advanced extraction of triazine herbicides from a specimen of water [16].

The determination of this literature review is to expose readers to several ways of extracting vitamins using composites of detailed way levels. The most creative and fascinating preconcentration procedures dedicated to vitamin separation are critically described in research papers published in the recent five years. Only 40% of research in the last five years on vitamin assessment in the clinical and pharmaceutical sectors used some new or green specimen processing techniques. The lowering of solvent amounts and specimen turnaround times is, nevertheless, a widespread tendency. In the medical and pharmacological domains, the massive potential of spontaneous emulsification methods depending on nanostructures and esoteric solvents is yet to be completely realized. In light of the high cost of carbon-based nanoparticles, approaches for the separation of liquids using membranes that are based on neoteric liquids are likely to become more efficient for specimen preparation in the near future. When two liquids or gases that are miscible are separated by a thin gas or liquid film in a liquid membrane, the barrier that is generated by this film determines

the amount of mass transfer that occurs between the two phases. These extraction methods are very important for vitamin research because of their low cost, simplicity, environmental friendliness, speed, and high intangible resources. The major drawback of the research is that it is time-consuming when compared to other methods [10]. Safety-related researchers have very few alternatives for analyzing and processing the hazards due to the usage of a substance that has been recognized as a particular kind of explosive proliferation by the Yoshida association. To estimate explosive speed while necessitating further experimental results, oxygen equilibrium computations, the rule of 6, and an exploding carbonyl groups list are routinely used as sustainable solutions and statistically valid techniques. A full UN Movement of Carriage Of Goods testing regime, on the other hand, necessitates at least 2 kg of materials for the first experimental series, an exorbitant quantity that is also rarely available in starting pharmaceuticals. The O.R.E.O.S. approach, which integrates the three classic techniques for testing explosive characteristics with the onset of disintegration estimated by differential scanning, has indeed been created. The Yoshida association has indicated recognized energy substances as possibly capable of explosion proliferation, and this new assessment has indeed been demonstrated to be useful at categorizing substances in a scale-dependent approach. The tool can be tailored to any organization's current guidelines for dealing with functional materials. This evaluation must be useful to both pharmaceutical property developers and research institutions as a way to define substances that may require significant testing before being scaled up or to guide teamwork to better options. To simplify the process of obtaining such essential data, a brief discussion of the challenges connected with the transportation for the UN Series Assessment is also provided. Thus, the volatile hazard detection in the medicinal procedure based on the novel screening method and workflow failed to provide a proper accuracy rate and also consumes a large amount of time [1].

Solid-phase microextraction (SPME) is a preparative technology that is constantly evolving and has a broad array of applications. The type of fiber coating used in this process is critical for removal efficiencies. Commercial coatings now on the market have some limitations that have been overwhelmed by the creation of new coatings based on innovative materials, which have enhanced extraction selectivity, competence, and constancy. Medicinal and personal care products (PPCPs) are among the most common developing pollutants, yet some research suggests that these substances can have negative health effects. Because there are presently no formal monitoring guidelines for these chemicals, analytical techniques that allow their detection in organic pollutants must be developed. Because of the intricacy of samples collected and the small concentration values of these substances, preparative procedures effective in eliminating disruptions and preconcentrated present in the sample are required, and SPME is a potential option for doing so. The latest breakthroughs in SPME with traditional and innovative coatings, as well as its application for PPCP measurement in the samples collected, are reviewed in this chap-

ter. However, more investigation into the detection and characterization of these molecules is necessary for the implementation of solid-phase microextraction for the extraction of environmental pharmaceuticals [7].

### 3. Material and Methods

AnalaR NORMAPUR provided glucose, fructose, and sucrose and provided 99 percent lithium chloride (LiCl), and Acros Organics provided 98 percent zinc chloride (ZnCl), carbamazepine (99.0%), triclosan (97.0%), mefenamic acid (98.5 percent), and diclofenac sodium salt (99.0%). Sigma-Aldrich provided 17-estradiol (98.0 percent), estrone (99.0 percent), clofibrac acid (98.0 percent), sulfamethoxazole (98.0 percent), gemfibrozil (98.5 percent), and potassium carbonate ( $K_2CO_3$ , 99 percent). Riedel-de Haen provided 17-ethinylestradiol (98.0 percent) [17]. The chemical compositions of the PhCs investigated, as well as their solubility ratios, log KO/W, and pKa, are shown in Figure 1. The solvents employed were HPLC-grade alcohol (MeOH, 99.9%) and acetonitrile (Acetone, 99.9%) procured. Merck Millipore provided 99.5 percent sodium chloride (NaCl), while AnalaR (BDH chemicals) provided 98.0 percent sodium hydroxide (NaOH) pellets. Pancreatic provided 37 percent hydrochloric acid (HCl), 99.5 percent acetic acid, and 85 percent potassium hydroxide (KOH). Merck supplied the acrylic acid (AA, which has a purity of 99 percent). All of the different chemicals and volatile compounds were employed without further purifying, and the Milli-Q water yielded an ultrapure water process of filtration.

*3.1. Characterization and Synthesis of Carbon Factor.* Varied synthesis techniques were employed to create nonporous hydrochars, along with reactivated hydrochars and stimulated carbons with medium, acidic/basic surface composition and higher surface areas, and various topologies, to achieve substances with a distinct texture and surface morphology. Hydrothermal carbonization (HTC) of carbohydrates was used to make the carbon hydrochars: 16 mL of  $1.6 \text{ mol L}^{-1}$  glucose or sucrose concentrations were placed in a sterilizer and warmed at  $190^\circ\text{C}$  for 5 hours. As per the carbohydrate precursor (glucose or sucrose, accordingly) and HTC temperatures, these specimens are classified as HG/190 or HS/190 [18]. A similar process was used to make enhanced sucrose-derived hydrochars, but acrylamide (i.e., 27.14 and 7 wt.%) was added to the sucrose aqueous medium. The improved hydrochars were given the designation HSAx/190, with x denoting the proportion of acrylic acid present. Chemical activation of the high-T-activated hydrochars was done as previously stated. HS/H800 and HS/C800 high-T-activated hydrochars were made by activating 2 g of sucrose-derived hydrochars with 5 g of  $K_2CO_3$  and potassium hydroxide for 1 hour at  $900^\circ\text{C}$ , respectively.

The investigation on glucose has an impact on the production of low-T-activated hydrochars. In a nutshell, 11.26 grams of eutectic zinc chloride/lithium chloride salt mixture was ground and homogenized in an agate filling; then, 4.6 grams of a cellulose precursor (F—fructose, S—sucrose, and G—glucose,) was introduced, and the combination was

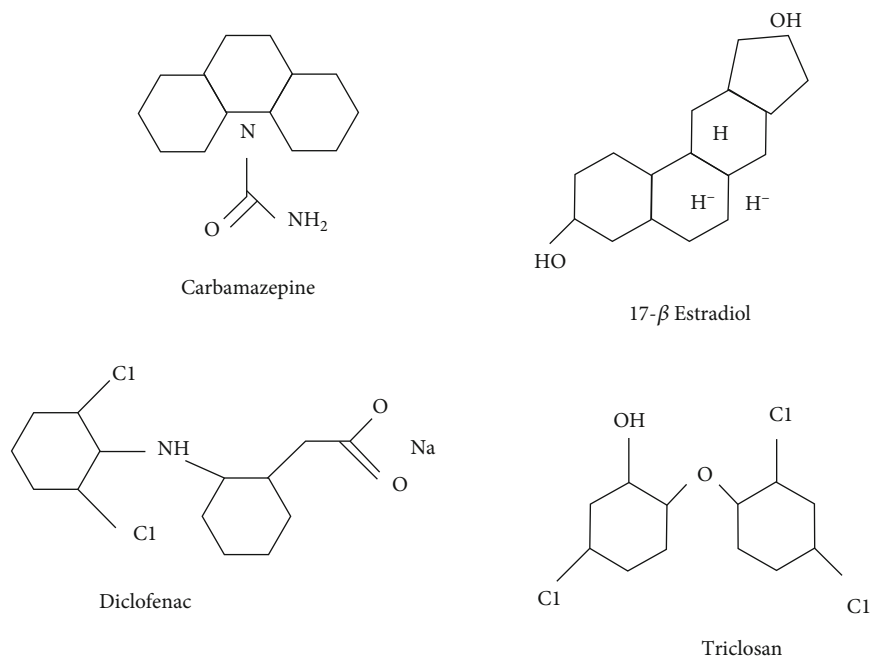


FIGURE 1: Different chemical structures utilized.

ground until a homogeneous sample was obtained in a Teflon-lined stainless steel sterilizer, the carbohydrate:eutectic salt mixture was injected (35 mL). The sterilizer was locked, agitated forcefully, and positioned in an oven at 180°C for 17 hours after adding 2.3 mL of ultrapure liquid [19]. After evaporation to ambient conditions, the low-T-enabled hydrochars were thoroughly soaked in purified liquid until no sodium hypochlorite anions could be detected (i.e., silver chloride is added, and there is no rainfall). The materials were washed, dehydrated at ambient pressure, crushed, and sieved to retain particulates with diameters of less than 0.148 mm (mesh 100). The low-T-activated hydrochars were designated as Hy/LiZn180, with  $\gamma$  denoting the carbohydrate precursors (HF/lithium and zinc180, HG/lithiumzinc180, and HS/lithiumzinc180, respectively) and “lithiumzinc180” denoting the eutectic mixture and synthesis temperatures. Using saccharides rather than biomass alone as a source of precursors for carbon compounds has many benefits, including the absence of emissions, the repeatability of the compounds, and the command over the morphology of the product. Monosaccharides are the simplest form of carbohydrates since they cannot be broken down by hydrolysis into lesser forms of carbohydrates. All of these are important factors in the production of high-purity carbon adsorbent materials, which are necessary for efficient chemical microextraction [19]. Steam activation of enlarged corkboard grains at a semi-industrial level was carried out as per the methodology used to produce the activated carbon material Cork/S800. In contrast, the profitable ground-activated carbon (PAC) products CN1 from Cabot-Norit (Com/CN1, provided) and R from Riedel-de Haen were evaluated. Chemical activation with  $H_3PO_4$  was used to make the commercial activated carbon Com/CN1. Particle diameters in all carbon compounds

examined are below 0.149 mm on (mesh 100) average [20]. Additional information on the production and description of several of these carbon-based compounds has before been published, and it is included in Table 1 for comparability.

**3.2. Carbon Particle Characterization.** Nitrogen gas adsorbents at -196°C in an autonomous volume device from micromeritics were used to analyze the geometric characteristics of carbon-based composites (model ASAP 2010). The materials (60–100 mg) were caused by trauma at 120°C overnight (16 hrs) under suction (compression 10–2 Pa) before Nitrogen adsorption [21]. The  $A_{BET}$ , apparent surface area, was calculated from nitrogen gas adsorbate in the  $p/p^0$  region of the adsorbent plot, which guarantees an optimistic intercept on the BET plot’s ordinates ( $C$  greater than zero) and a linear rise of  $n^{ads}(2-p/p^0)$  with  $p/p^0$ . The entire pore volume,  $V^{Total}$ , was calculated using the Gurvich rule. The isotherm was utilized to determine the micropores utilizing the  $s$  technique. The total small pore size,  $V^{\alpha Total}$ , relates to apertures with a breadth of 2.0 nm; the ultramicropore quantity,  $V^{\alpha ultra}$ , to holes with a diameter of 0.8 nm; and the super-micropore volume,  $V^{\alpha super}$ , to holes with a width of 0.8 nm to 2.1 nm.

The surface modification of the substances was evaluated utilizing reversed mass analytical balance and a symphony SP70P pH meter to determine the pH at zero charges and point of zero charges. The compounds’ diffused reflection infra-Fourier transform (DRIFT) spectra were acquired using a Nicolet Magna-IR 560 spectrophotometer equipped with a very sensitive mercury cadmium telluride detectors (MCT-A) operating under cryogenic conditions. The DRIFT technique is a sort of spectroscopy that involves measuring the diffuse reflection of a single pulse of infrared radiation

TABLE 1: Exterior assets of carbon sorbent.

Categories	Carbon particles	Structural assets	External assets (pH point of zero charge)
Hydrochar	Acrylic acid-modified hydrochars <sup>c</sup>		
	(i) HSAA7/190	NP	≈3
	(ii) HSAA27/190		
	(iii) HSAA14/190		
	HC <sup>b</sup>		
(i) HS/190	NP	3	
Stimulated carbon	Commercial		
	(i) Com/CN1	Apparent surface area ≈1000 m <sup>2</sup>	5.2
	(ii) Com/R		
SAC <sup>a</sup>	Area = 750 m <sup>2</sup> /g	≥2	
Activated hydrochar	High-T-activated hydrochars <sup>d</sup>		
	(i) HS/C800	Apparent surface area = 1352 m <sup>2</sup> /g	≈5
	(ii) HS/H800		
	Low-T-activated hydro chars		
	(i) HG/LiZn180	Apparent surface area (HG/LiZn180) = 528 m <sup>2</sup> /g	2.8-3.2
	(ii) HF/LiZn180	Apparent surface area (HF/LiZn180) = 408 m <sup>2</sup> /g	
(iii) HS/LiZn180	Apparent surface area (HS/LiZn180) = 488 m <sup>2</sup> /g		

by a sample and then applying a Fourier transform to the spectrum that is acquired from this measurement. Each spectrum was acquired by accumulating 256 scans with a resolution of spectrum range of 2 cm<sup>-1</sup> in the mid-IR (4000-700 cm<sup>-1</sup>) spectral band utilizing dusted materials with no KBr additions [22]. The thermal assessment was conducted on 14 mg of material at a constant rate pass-through of mL min<sup>-1</sup> of nitrogen gas up to 900°C. After 3 hours of exposure to 600°C in the air (50 mL min<sup>-1</sup>), the quantity of the low-T-reactivated hydrochars was evaluated utilizing a similar apparatus (constant mass).

Monthly, the standard solution combination and individual security solution of each PhC (1,000.0 mg L<sup>-1</sup>) were individually produced in methanol and maintained at 5°C. In most experiments, the working standard mixture (1.0 mg L<sup>-1</sup>) utilized for confounding was generated daily in the very same organic liquid. For optical verification, methanol-diluted standard combination solutions were utilized. Samples were gathered around the urban region [23]. Seawater measurements were extracted along the shore, and lake samples of water from an underground lake and tap water specimens were gathered from the public water distribution system. The water samples were taken for the initial solvent evaporation, filtering is done, and the wastewater samples were also collected from different plants. All the specimens are gathered in amber glass vials that are screened with screening paper and stored at -20°C.

#### 4. Bar Absorption Methodology

The BAE gadgets (diameter of 3 mm and length of 7.6 mm) were made internally, as previously stated. The gadgets were incubated at ambient temperature after being constructed in

a closed container flask. Before usage, the BAμE electronics were washed with methanol and ultrapure water [24]. Because microextraction bars are comparatively cheap, quick to make, and use very minor quantities of sorbent material coatings, they were thrown after each usage to eliminate any potential contamination. In the BAμE-LD process, a 26 mL volume of a water specimen was placed in a matching glass flask, accompanied by a BAμE device covered with carbon-based material sorbent covering and a traditional Teflon constant agitation bar. The tests were carried out in a multiple access constant agitation plate at ambient temperature for 16 hours at 1,000 rpm (pH 2.0). The gadgets were taken from the specimens with clean tweezers after the extraction method, dehydrated for a few minutes with a lint-free paper, and inserted into a glass vial insertion containing 100 L of ACN before ultrasonic treatment at ambient temperature for one hour [25].

Following LD, the gadgets were withdrawn, 100 L of distilled water was introduced, the vials were mixed thoroughly for 6 s and sealed, and the HPLC-DAD study was applied. The sample preparation technique (SAM) was used to analyze real water specimens, with four stimulation scales reaching from 7.0 g L<sup>-1</sup> to 105.0 g L<sup>-1</sup> for all PhCs under investigation and blank tests (no spiking—“zero-point” assays) [26]. Unless otherwise stated, all BAμE-LD tests were repeated three times. The HPLC-DAD samples were analyzed using the same apparatus and technique as previously mentioned in the literature review, with the accompanying alterations [27]. Apparatus stability was determined by infusing different stock keys with concentrations ranging from 10.0 to 30.0 g L<sup>-1</sup> (according to the chemical) to 5,000.0 g L<sup>-1</sup>, where correlation ratios ( $r^2$ ) of more than 0.98 were obtained for the active compounds. Peak areas

TABLE 2: Porous carbon textural properties.

Specimen	$V^{\text{total}}$	$A_{\text{BET}}$	$V^{\text{meso}^{\text{a}}}$	$V^{\text{total}^{\text{b}}}$	$\frac{\alpha_5 \text{ method}}{V^{\alpha \text{ super}^{\text{d}}}}$	$V^{\alpha \text{ ultra}^{\text{c}}}$	pH
HS/LiZn180	0.48	488	0.34	0.13	0.13	0	3.2
HG/LiZn180	0.59	530	0.48	0.12	0.12	0	3.1
HF/LiZn180	0.29	406	0.15	0.13	0.13	0	2.8
HS/H800	1.11	1376	0.05	1.09	1.09	0	4.1
HS/C800	0.63	2432	0.02	0.63	0.28	0.34	4.4
Com/R	0.65	965	0.38	0.29	0.19	0.11	6.4
Cork/S800	0.44	618	0.29	0.18	0.08	0	5.2
Com/CN1	0.45	1180	0.69	0.29	0.31	0.11	$\geq 12$

<sup>a</sup> denotes the mesopore volume, <sup>b</sup> denotes the overall micropore volume, <sup>c</sup> denotes the ultra-microscope volume, and <sup>d</sup> denotes the super-micropore volume.

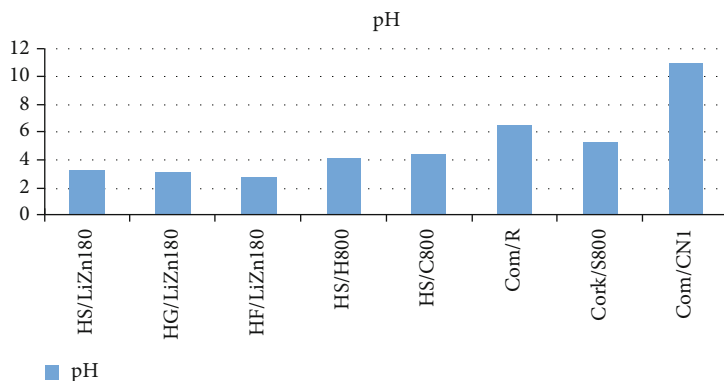


FIGURE 2: pH value of various specimens.

from each test were matched to the top regions of the procedure utilized for the spike to calculate restoration. The susceptibility of the experimental method is demonstrated using detection limits (LODs) and quantitation (LOQs) determined with signal-to-noise ratios (S/N) of 3/1 and 10/1, correspondingly, for all the PhCs under research, which varied at a different range. The accuracy of the equipment was tested by injecting a standard combination ( $n = 7$ ,  $01.2 \text{ mg L}^{-1}$ ), which resulted in comparative standard deviations of less than 2.8 percent [28].

## 5. Result and Discussion

Thirteen carbon-based materials were investigated as sorbent coverings again for the extraction of PhCs utilizing 17-estradiol, triclosan, 17-ethinylestradiol, carbamazepine, and diclofenac, as inclusion complexes to maximize the microextraction effectiveness by the BA $\mu$ E-LD method. As shown in Table 2, these carbon elements are available to describe a broad range of image characteristics (from nonporous to high porosity specimens with  $A_{\text{BET}}$  up to  $2400 \text{ m}^2/\text{g}$ ), surface characteristics (neutral, acidified, or basic, with  $\text{pH}_{\text{PZC}}$  varying from 2 to 11), and morphological characteristics (e.g., pointed, circular, and spongelike). Carbon-based coverings have very different sizes and shapes on the micro-nanoscale, as shown by micrographs [17]. The assessment experiments were performed in triplicate with ultrapure samples collected and treated at a concentration of

$15.0 \text{ g L}^{-1}$ . The recovered rates were utilized to monitor the effectiveness of the thirteen carbon-related sorbent substances, which were characterized as the quantity of PhC measured after and back removal with bar adsorptive microextraction equipment. pH value of various specimens is shown in Figure 2.

In Table 2, the extraction effectiveness of the ceramic materials for x PhCs is extremely reliant on either the sort of product or the targeted pharmacological molecule.

In Figure 3, utilizing commercial and lab-made heterogeneous catalysts, the effect of adsorptive selection on the recovered rates of the five PhCs was investigated. In this, C1 to C5 represent the five types of carbon materials such as carbamazepine,  $17\alpha$ -ethinylestradiol,  $17\beta$ -estradiol, diclofenac, and triclosan.

The nonporous hydrochars in the figure managed to recuperate diclofenac, and though the specimens HG/190 and HS/190 were intelligent to retrieve around 50% of the residual PhCs, the acrylic effects on the chemical hydrochars (HSAAx/190) failed to recover 17-estradiol and 17-ethinylestradiol. The acid low-T-stimulated hydrochars shown in Figure 4 with micro-/mesopore network and medium surface energy, on the other hand, enabled the recovery of the five targeted PhCs. Additionally, with the exception of carbamazepine, the strip that was manufactured using specimen HS/LiZn180 as a coating enabled a recovery that was comparable to that of the finest activated carbon for all PhCs (range from 43 to 80 percent). The advertising



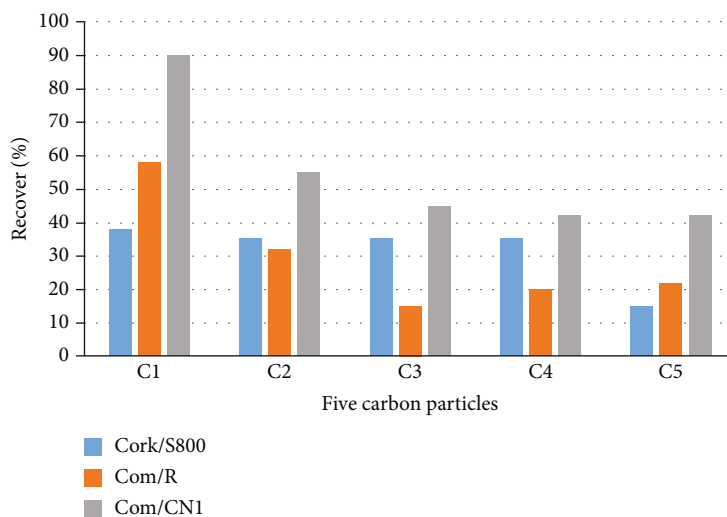


FIGURE 3: Hydrochars based on lab-made carbon materials.

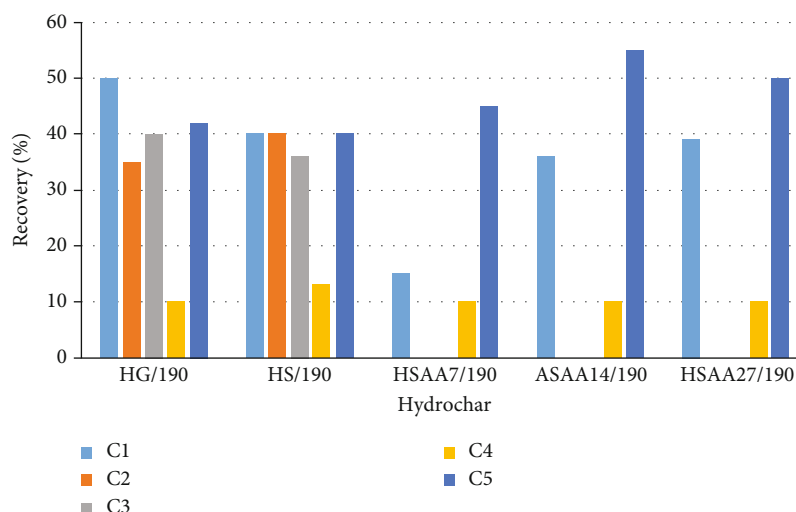


FIGURE 4: High-T-activated hydrochars based on lab-made carbon materials.

specimen Com/CN1 with an adsorbent region greater than 1000 m<sup>2</sup>/g, a micro+mesopore framework, and a slightly acidic identity significantly outperforms the steam-enabled cork carbon with a reduced surface region and basic identity, along with the elevated stimulated hydrochars mentioned in Figure 5.

Figures 6–9 show how the qualities of the thirteen composites discussed above affect their effectiveness as sorbent coverings. The four graphs show the relationship among specified carbon characteristics (pH<sub>PZC</sub> against A<sub>BET</sub>, V<sup>micro</sup>, V<sup>total</sup>, and percent V<sup>meso</sup>) and the percentage of PhCs removed (17-ethinylestradiol, carbamazepine, 17-estradiol, diclofenac, and triclosan). At small pH<sub>PZC</sub> attributes related to the proportions of micropores around 20% and 60%, and hence the occurrence of a micro- and mesopore system, the frequency of instances related to deletions in the first quadrant is consistently larger.

The percentage frequency elimination (in quartiles) attuned for the elimination variety of each PhC is shown by circles, with S1 equating to the top 25% deletion and S4

corresponding to the lowest 25% elimination, and circle diameters are directly proportionate to the proportion of occurrence.

It was reasonable to infer that (i) entirely microporous-stimulated carbon atoms with just an acidified exterior perform badly in the recovery of many PhCs, most likely due to irrevocable (good separation with poor back extraction) adsorbent. (ii) Basic stimulated carbons with a micro-mesopore system effectively reduce healing efficiency improvements than acidic contemporaries. (iii) Basic photocatalysts with a micro-mesopore system produce low retrieval efficiency improvements than acidic contemporaries. To summarize, these findings suggest that when selecting an appropriate carbon coated for BAμE-LD/HPLC-DAD to guarantee good recovery, reducing agents with a well porous assembly in the micro- to mesopore region, as well as acidic functional group, must be considered (i.e., phenol and a carboxylic acid, see DRIFT spectra information in sympathetic data). These carbon-based

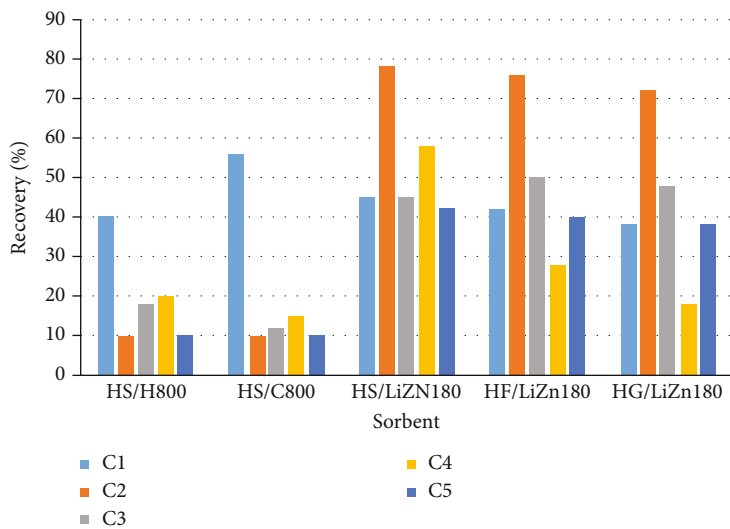


FIGURE 5: Sorbent Coating obtained by BAμE.

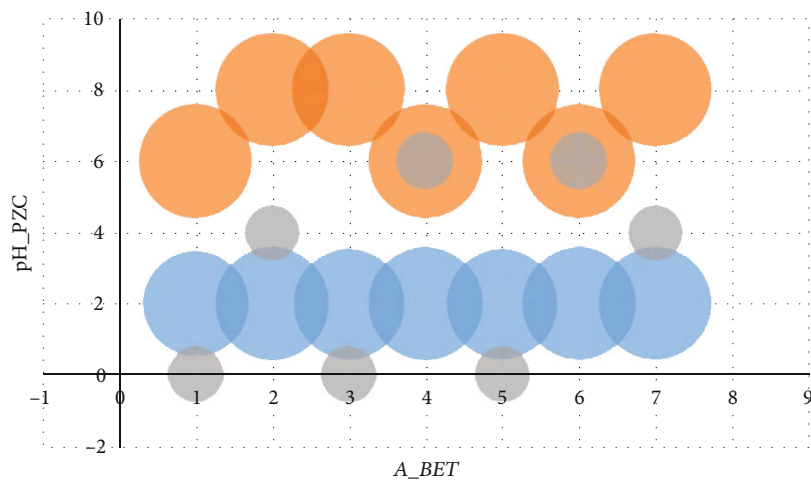


FIGURE 6: Point-of-zero charge vs. BET.

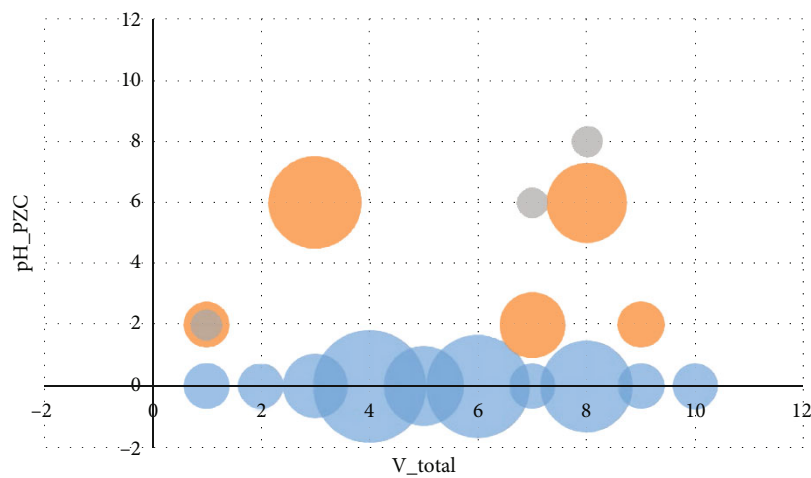


FIGURE 7: Total pore volume.

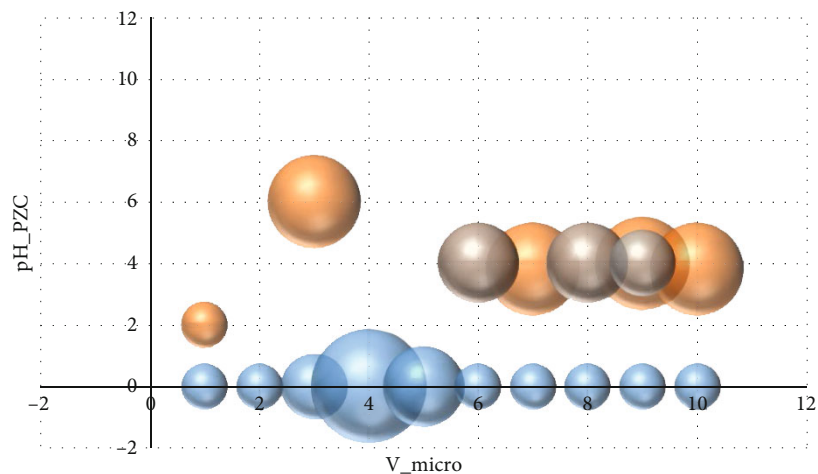


FIGURE 8: Micropore volume percentage.

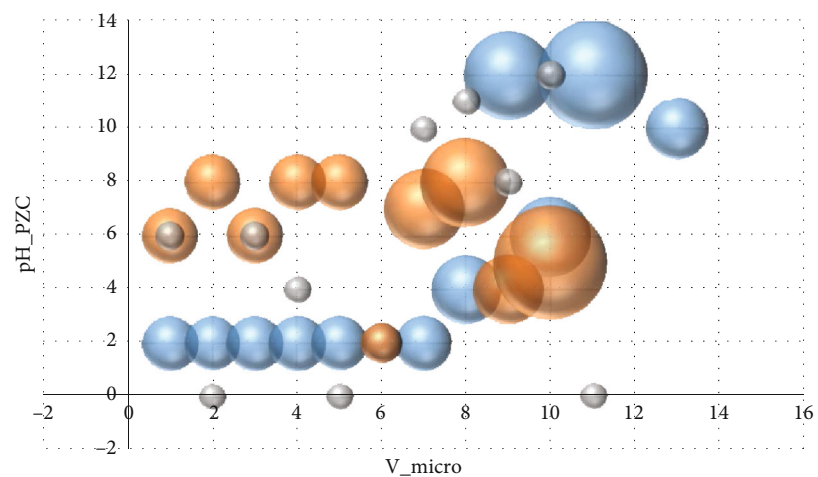


FIGURE 9: Mesopore volume percentage.

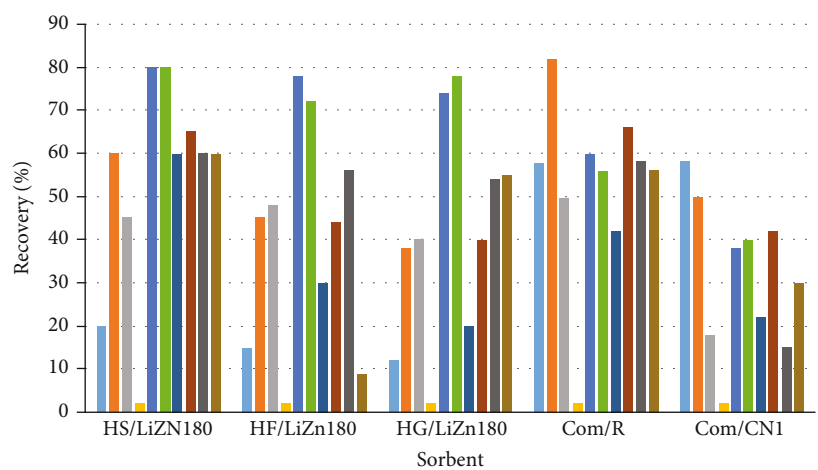


FIGURE 10: Sorbent selective effect.

materials were subsequently investigated as sorbative coverings for the extraction of ten PhCs and compared against commercial PACs given these partial estimates for the low-T-activated hydrochars with a total of five objectives men-

tioned in Figure 10. As can be shown, neither of the composites was able to restore clofibric acid underneath the evaluated laboratory conditions, despite the recovery of close to 50% for the other strong acid chemicals [17].

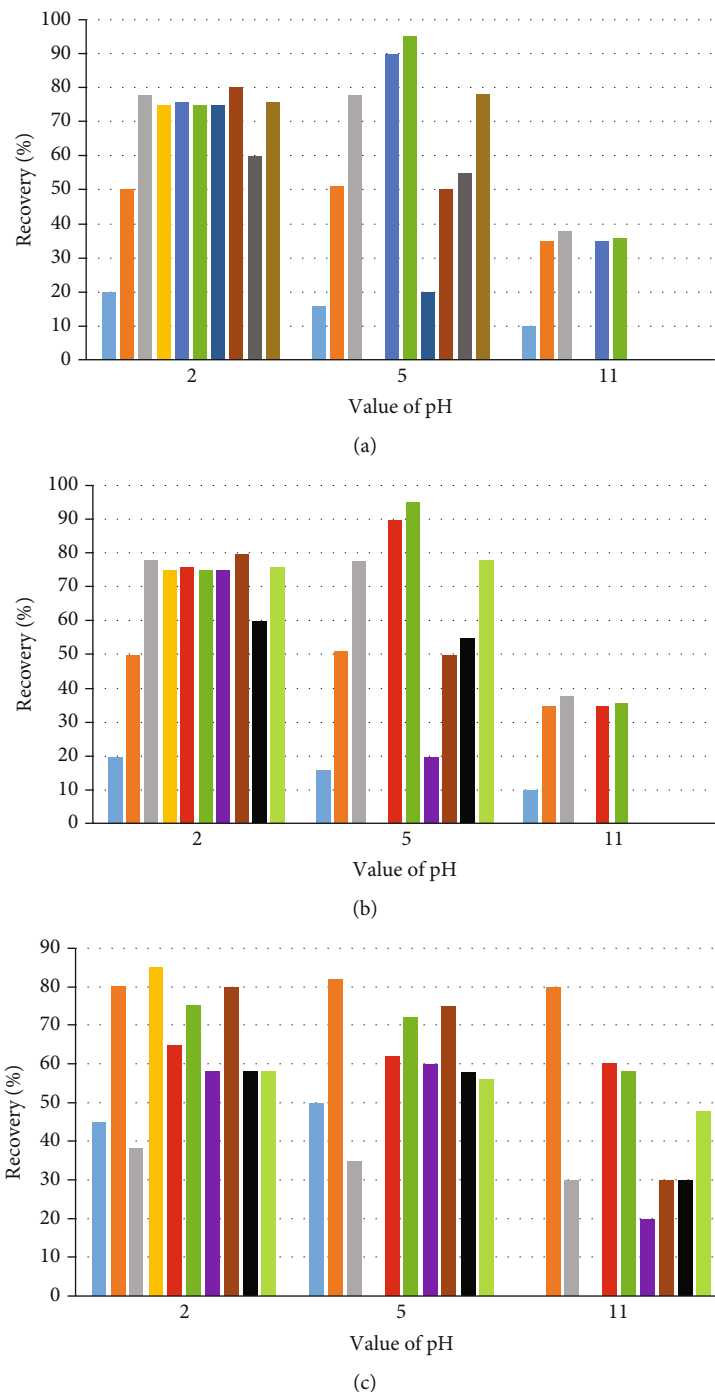


FIGURE 11: (a) HF/LiZN180. (b) Com/CN1. (c) Sorbtive layer.

Clofibrac acid and sulfamethoxazole get one solubility than the other targeting PhCs, and they have the lowest log  $D$  readings (log  $D$  0.7-0.8) at pH 5.5, making them the most hydrophobic molecules in the set. Moreover, because clofibrac acid is produced in the elemental state at pH 5.5, it has stronger hydrophilicity, limiting the possibility of contact with the high sorption substance and subsequent removal. The bulk of PhCs performed poorly in Com/R, except for sulfamethoxazole and carbamazepine. The LD variables, ionic strength, balance time, stirring speed, matrix orienta-

tion, and samples pH were examined after picking the best efficiency activated carbon via BA $\mu$ E for the measurement of the desired PhCs from aqueous solutions. All of the improvement findings, excluding the former, which would be described later, may be found in SI. In the testing methods, optimum time is important, and while one hour of back-removal time is sufficient to ensure optimal recovery, the supreme retrieval rates are only achieved after 16 hrs of removal time [19]. The aqueous matrix's chemical compositions were also evaluated, including initial

concentration, initial concentration, and polarization. The recovered rates for the BA $\mu$ E systems at varying solution pH among 2.1 and 11.1 for the three chosen carbon coverings are shown in Figures 11(a)–11(c). The recoveries of all the targeted means that exist were influenced heavily by the solution pH, apart from carbamazepine recoveries with specimen Com/CN1.

This was partly anticipated, given that the ion or neutrality states of PhCs in water, or the net charge density of carbon-based compounds, are all affected by this variable. Clofibrac acid, the component with the lowest pKa value, was recovered with rates ranging from 80 to 95% for all of the sorbtive phases that were assessed in an environment with a pH that was acidic. The extent of acid dissociation can be predicted based on the numerical value of the constant Ka. In addition, the value of the pKa is inversely proportional to the strength of the acid. The pH change between 2.0 and 11.0 did not allow considerable recovery augmentation for sulfamethoxazole, which, like clofibrac acid, is hydrophobic and extremely fluid permeable. This could be owing to its complicated fractionation. The findings, nevertheless, unambiguously revealed that the concentration of the anion exchange sulfamethoxazole speciation (pH > 5.5) has a deleterious influence on its recuperation, similar to what has been observed with clofibrac acid. Mefenamic acid, gemfibrozil, and diclofenac, all of which have negative log *D* values at pH 11.0, are also unrecoverable at the extraction's basic pH.

In the figure each colour bar represents 10 carbon material where blue represents C1, orange represents C2, grey represents C3, yellow represents C4, red represents C5, green represents C6, violet represents C7, brown represents C8, black represents C9, and light green represents C10. To recapitulate, the BA $\mu$ E(HS/LiZn180)/HPLC-DAD system outclasses well-developed pretreatment enhancement methodologies and powerful quantitative methodologies because it achieves good rehabilitation for a significant number of PhCs with distinguishable hydrophobic/hydrophilic characteristics, when HPLC-DAD quantitative measurements are used. The combination of the optimized BA $\mu$ E (HS/LiZn180) approach with more influential measurement techniques is predicted to the chosen PhCs; the impressive outcomes of this proof-of-concept portend promising outcomes for extra courses of contamination, such as the difficult polar groups.

## 6. Conclusion

Thirteen carbon substances have been evaluated as sorbent coating materials for bar adsorbent microextraction accompanied by microliquid extraction and high-efficiency liquid chromatography-diode array discovery procedure for the concurrent analysis of suggestions of different PhCs from profitable and lab-made carbon materials, H-T-activated hydrochars, hydrochars, and L-T-activated hydrochars. Due to a hierarchy porous structure in the full micro-mesopore spectrum associated with a rich chemical nature constituted of acid O groups that favored both accumulation (separation) and desorption (back extraction) of the active

compounds, the carbon, made at the lab, low-T-activated hydrochars demonstrated to contend with promotional activated carbon sorbent materials for the richness of PhCs, contributing to the exceptional productivity at the trace concentrations. The analytical and numerical approach was shown to be both ecologically friendly and simple to adopt. It also had great sensitivity and robustness, as well as a short surface area/volume requirement. Moreover, the new microextraction-based approach appears to be acceptable for compliance with EU Decision 2015/495 and USEPA requirements for PhC tracking, particularly when integrated with tandem mass spectrometry instruments, which could offer additional information.

## Data Availability

The data used to support the findings of this study are included within the article. Further data or information is available from the corresponding author upon request.

## Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

## Acknowledgments

The authors appreciate the supports from Mizan Tepi University, Ethiopia for the research and preparation of the manuscript. This work was funded by the Researchers Supporting Project Number (RSP2023R429) King Saud University, Riyadh, Saudi Arabia.

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