Evaluation of the synergistic effect in adsorption and ultrafiltration for the treatment of pharmaceutical sludge-washed leachate.

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Abstract:

Cellulosic sludge discharged from the pharmaceutical production industry possesses heterogeneous and complex physicochemical and biological properties. The disposal of nonrecyclable pharmaceutical sludge, particularly concerning leachate, continues to negatively impact storage and landfill sites. Treating leachate is often viewed as a poor investment. However, managing leachate at industrial storage areas and landfill sites is essential to ensure environmental safety. A straightforward batch adsorption system was investigated to implement a low-cost system in this context. This system utilized naturally activated carbons derived from coconut husks and papaya seeds as adsorbents, followed by ultrafiltration (UF) processed at room temperature. The primary treatment provided by the adsorption system significantly enhances the UF process by improving its speed. Most pollutant components are removed to the point of being untraceable. The average efficiency of the primary adsorption process was 58% for both Coconut Husk Activated Carbon (CHAC) and Papaya Seeds Activated Carbon (PSAC). However, the effectiveness of adsorption varied for different components, with removal rates ranging from 15% to 100% (untraceable). Direct UF treatment achieved a potential efficiency of 79% without adsorption but faced severe fouling issues, making it unsuitable for regular commercial use. The efficiency of the processes was evaluated through biochemical oxygen demand (BOD), chemical oxygen demand (COD), and 17 other removal parameters. The synergistic effect of combining adsorption followed by UF presents a technically and economically viable solution for future applications.

Keywords: Ultrafiltration, Activated carbon, Adsorption, Coconut husk, Leachate, Papaya seeds, Pharma sludge

1. Introduction

Several industrial and municipal waste sludges are disposing for landfilling every minute across the globe. Still, research and development strive for effective technology that is on par with treatment to meet circular economy implementation. Innumerable works are available on municipal sludge leachate treatment but less on industrial sludge-derived leachate. Conversely, aerobic mesophilic, thermophilic membrane bioreactors (MBR) in composite models are employed at a high rate for leachate treatment, mostly when spilling municipal sludge landfill sites. Practically, the leachate process is not in the interest of industry business as it is disposed of useless already. Even so, it might make a respective government responsible for environmental concerns. In this aspect, spending an immense cost on leachate treatment without direct compensation reduces either side's (Industry and Government) engrossment. Consequently, focusing on simple materials-constructed treatment techniques with economically viable systems could be more significant for the research and development community, even if it partially succeeded.

Researchers tried out a thermophilic bioreactor for the treatment of combined municipal landfill leachates taken from two different sites and reported the results in comparison to those of a mesophilic bioreactor. The thermophilic system performed well in removing Extracellular Polymeric Substances (EPS) and Volatile Suspended Solids (VSS), whereas the mesophilic system accomplished protein-carbohydrate (P/C) soluble and bound removal. Though thermophilic membrane systems are effective in the higher rate of removal, the drawback of the system is clogging the membrane very often, in addition to that extra operating cost for running at a higher temperature rate; on the other hand, mesophilic systems rest from frequently clogging and operate at room temperature which reduces the processing cost (Wichitsathian, 2004)

In another recent study, the municipal landfill leachate's adsorption kinetics was examined by different Super Adsorbent Polymers (SAP) as a comparison study. The chosen SAPs have specially made cross-linked structures for diapers and sanitary napkins. Each polymer was bound in a tea bag cover and immersed in a leachate solution. The polymers were also tested with tap water and deionized water to compare the effectiveness of adsorption at leachate and between the polymers (Feng et al., 2024). The same system may be adapted to examine the adsorption of industrial sludge leachate; however, it cannot be economically and quantitatively equivalent to handling tonnes of sludge landfilled, released leachate. In addition, a solution has yet to be found for the desorption of leachate from the cross-linked structures of polymers.

(Karunarathne & Amarasinghe, 2013) reported that activated carbon derived from sugarcane bagasse effectively eliminates phenolic compounds from aqueous waste. Phenolic compounds are widely present in many industrial discharges, and the isotherm study on sugarcane bagasse activated carbon in the removal of phenolic compounds falls on good ground

at the Langmuir model. A series of batch processes was carried out for the phenolic removal to derive the isotherm study. Hence, one can consider this kind of adsorbent and process for leachate treatment as low-cost fixation. In another work, low-cost adsorbent resource Carica Papaya seeds derived activated carbon was used for the adsorption of lead (Pb²⁺) through the up-flow fixed bed column. The effect of flow rate was investigated in this study at three different levels. Heavy metals and unknown bulk components present in effluent/leachate are predominantly common factors, and the process choice must be simple and effective in terms of technical and economic aspects. In this way, (Yelebe et al., 2014); and (Hwang et al., 1995) suggested adsorption (packed bed) could be a better choice as per their mathematical modeling simulation cum experimental investigation. Their approach agrees with other considerable researchers' experimental studies on bulk components and the removal of heavy metal contaminants. Hence, the adsorption of natural source-derived adsorbents was examined in the present report on real-time leachate.

(Gripa et al., 2023) employed a high-pressure membrane with an advanced oxidation process in the landfill leachate treatment to clear the macro and micro contaminants. This process attained 90% removal of contaminants, which is higher than the coupled RO and biological processes. In addition, the report deals with the ecotoxicological review of the leachate treatment. However, the feasibility of such a process system is set on failure due to higher energy demand. In another study, researchers clubbed the Reverse Osmosis (RO) process with solar distillate followed by a Moving Bed Biofilm Reactor (MBBR) in the landfill leachate treatment, elevating the removal of Ammonia, nitrogen, and phosphorus up to 88%. In this, nitrogen removal was achieved close to 98%. The retrieved organic micropollutants could be used in fertilizer industries as part of a circular economy. This integrated treatment may not be economically viable since the processes are fixed over the disposed leachate. Bhambore and Kumar employed a Sequencing Batch Biofilter Granular Reactor (SBBGR) in 2022 to treat toxic organic matter in municipal leachate. This study reported great effectiveness in COD, TOC, TSS, Total Nitrogen, etc. However, a review revealed that the SBBGR is affected by many factors and has drawbacks.

The Root Zone Treatment (RZT) system was carried out to remove specific matters of pharma and cosmetics from the municipal leachate by (Kumar et al., 2023). Though it is claimed to be an effective management system, the competence of plants and microorganisms to the various components and the extended process time is a hurdle to consider. Landfill leachate is a mixture of organic matter and inorganic salts treated by anaerobic reactors due to lower sludge production, cost-effectiveness, and energy conversion advantages. Meanwhile, the anaerobic process requires residence time holdup and a large land area to maintain the continuous outflow of leachate, which is a disadvantage (Ahmad et al., 2022). Solids Retention Time (SRT) and Hydraulic Retention Time (HRT) are significant parameters to study the efficacy of the treatment reactor done by (Roy et al., 2020), at Membrane Bioreactor (MBR) for the leachate treatment. As Extracellular Polymeric Substances (EPS) increased, more phosphorous removal was attained at low SRT. Simultaneously, HRT was carried out for 13-52 h, which has no considerable impact on the removal of recalcitrant COD, where the metal removal depends on the rapport of metals with the recalcitrant COD and the sludge concentration. However, MBR reported that the efficient treatment of biodegradable COD is high. This study is a reference for fixing parameters for the leachate treatment.

Microbial colonies present in landfill leachate are also one of the primary factors that must suppressed. Adsorption is a simple, effective wastewater/leachate treatment process, but the adsorption capacity needs to improve by turning it into a superabsorbent nanocomposite. In this point, (Rezaei et al., 2024), developed a superabsorbent nanocomposite with an antibacterial effect by blending it with *Khuzestanica* essential oil, yielding more significant than 86% adsorption potential and with well-extended inhibition zones at the antibacterial activity. The biggest threat to environmental management is landfill leachate, which is derived from municipal wastes and discharged from various industries. Treating leachate washed out through sludges is the biggest challenge, as it has different compositions and physiochemical properties according to its sources. Consequently, different appropriate management systems are essential to the specific site to attain sustainable development goals (Dagwar & Dutta, 2024)

As leachate is a waste of waste, spending vast amounts on the RO membrane in the RO process of leachate is not a practical engineering value. Despite that, rejuvenating a used RO membrane is a sustainable and cost-effective approach. In addition, leachate passing through ultrafiltration before the RO process as primary treatment yields additional effective ensured (Mota et al., 2024). In an industrial 4. O era, Machine Learning (ML) can be adopted to predict leachate compositions from different sources and enhance the treatment process with more / accurate precision. A similar approach was performed (Gaur et al., 2024) by adopting ML tools such as Support Vector Regression (SVR), Artificial Neural Network (ANN), and Genetic Algorithm (GA). The merged process of coagulation and biological sponge iron reactor effectively removes COD and other pollutants from the leachate (Li et al., 2024). Optimization of waste leachate treatment methods was performed for 300 cities in China in terms of carbon emission, energy consumption, and economic cost. This study may help consider technological

and economic aspects of the environment (Han et al., 2024). To eradicate the high accumulation of organic matter, (Silveira et al., 2024) proposed a combined form of thermally activated persulfate and Fenton reagent utilized for precipitation method that is comfortable for on-site processes and recovers 95-99 % of nitrogen at zero liquid discharge. Another work, coagulation with flocculation process, claims 68-81% removal efficiency for color, polyphenols, and nitrates from the landfill leachate and optimized by RSM (Bouyakhsass et al., 2024). Adsorption, followed by filtration and Fenton's treatment, effectively removed heavy metals and organic matter at the lowest cost. Adsorption holds a stronger holdup in removing heavy metals from leachate than the other processes (Bhaskar et al., 2024).

Leachate leaked from Municipal Solid Waste (MSW) piles is highly contaminated with microorganisms, creating a pandemic environment. The treatment methods like AOPs, Biological cum membrane reactors are not considerably effective and also economically squander. To resolve this, (Tahsini et al., 2024) use the composting piles method, where the fresh leachate continuously spreads back over the composting piles by being blended with enzymes. This method yields good efficacy in product quality. (Smol & Generowicz, 2018a) suggested treating MSW leachate using a multi-step method called Multicriteria Decision Analysis (MCDA). In this method, the leachate goes through four stages, each with coagulation and filtration. Finally, it goes into the landfill again after the sewerage system. The electrocoagulation method indexed by RSM was recently applied for landfill leachate treatment by (Ameli et al., 2024). In a review of landfill leachate treatment, the Solar Photo Fenton treatment system efficiently enhances BOD, TOC, and biodegradability but does not work well for ammonia removal (Clemente et al., 2024b). A review article discussed the effectiveness of coagulation methods in landfill leachate treatment and concluded that this method effectively removes heavy metals, suspended particles, and organic matter. Wdowczyk (et al. (2024) indicate the contaminants' impact of landfill leachate at the groundwater level, which helps develop the operational process. Complete factors over landfill leachates' classification and physiochemical cum biological treatment reviewed by (El-Saadony et al., 2023); another work by (Clemente et al., 2024a) both help to adapt the characterization base of the present work. In recent days, microplastics have ubiquity in every environment's content. Hence, including leachate's risk impact and treatment efficiency is significant. These challenges can be achieved by incorporating the help of AI as a future technology (Zaman et al., 2024) (Igwegbe et al., 2024). Developing wetlands is another suggestion for leachate treatment (O'Connor & Courtney, 2020). Converting leachate waste and sludges into another form of valuable products

like biogas and pellet fuel format is another suggested approach (Abedi et al., 2023); (Pugazhenthi et al., 2024)

Most of the above reports dealt with MSW leachates and did not specify the source. Though the several treatment methods are diversified from filtration to RO processes, coagulation to future technology AI & ML, etc., the adsorption process played a vital role, followed by ultrafiltration, both effectively and economically. In the present report, specific industrial sludge having a cellulosic nature disposed of for landfill is taken for leachate derivation. The treatment method is simple adsorption of cellulosic leachate used by readily available coconut char and paprika seeds converted as activated carbons in the laboratory, followed by ultrafiltration in MBR.

2. Materials and Methods

2.1. Pharma leachate's properties study

Nearly all research focuses on the leachate of MSW landfills, which has led to curiosity about industrial landfill leachate exclusively from the pharmaceutical industry regarding research repercussions. The industrial estate of the Puducherry region in India is a hub of the pharmaceutical formulation and therapeutics industry, producing several tons of discharged sludges to landfills after the effluent treatment. The pharma sludge disposed to landfill is collected about the required amount through the appropriate authority and brought to the laboratory. The collected pharma industry sludge stored under a 4°C freezer was abundant in cellulose matter, which was seen explicitly, and other unknown contents or pollutants requiring characterization. The raw leachate is prepared by gently stirring the distilled water with pharma sludge for about one hour on a 20% by weight basis, followed by filtration using ordinary filter paper. Since the sludge is stored at a cold freeze, it cannot be contaminated by a microbial colony and is not required to be considered. Table 1 represents the executed characterization of the raw pharma leachate. For the testing, Indian Standards Methods are adapted to NABL aggregated laboratory instruments. In the determination, commonly expected high-toxic contamination components such as Arsenic (As), Cadmium (Cd), Lead (Pb), and Cyanide (CN) are found below the detectable range of 0.01 mg/l, hence, negligible in the treatment processes. Similarly, nitrite (NO₂) and sulfide (H₂S) are also ignorable from the obtained values. Nickel (Ni) and mercury (Hg) also have no trace in the leachate, where the test was conducted in another laboratory at the quality control unit of an industry.

S.No	Test Parameters	Test Methods	Obtained Values
1	pH @ 25°C	IS:3025 Part-11-1983(Reaff.2017)	5.49
2	Conductivity @ 25°C	IS:3025 Part-14-2013(Reaff.2019)	3040 µmhos/cm
3	Total suspended solids	IS:3025 Part-17-1984(Reaff.2017)	84 mg/L
4	Total solids	IS:3025 Part-15-1984(Reaff.2014)	2976 mg/L
5	BOD @ 27°C for 3 days	IS:3025 Part-44-1993(Reaff.2019)	432 mg/L
6	COD	IS:3025 Part-58-2006(Reaff.2017)	1356 mg/L
7	Total Arsenic as As	IS:3025 Part-65-2014(Reaff.2019)	BDL(DL:0.01 mg/L)
8	Cadmium as Cd	IS:3025 Part-65-2014(Reaff.2019)	BDL(DL:0.01 mg/L)
9	Total Chromium as Cr	IS:3025 Part-65-2014(Reaff.2019)	0.077mg/L
10	Lead as Pb	IS:3025 Part-65-2014(Reaff.2019)	BDL(DL:0.01 mg/L)
11	Zinc as Zn	IS:3025 Part-65-2014(Reaff.2019)	0.361 mg/L
	Ammonia		
12	(as total ammonia -N)	IS:3025 Part-34-1988(Reaff.2019)	30.8415 mg/L
13	Nitrate as NO ₃	IS:3025 Part-34-1988(Reaff.2019)	224 mg/L
14	Nitrite as NO ₂	IS:3025 Part-34-1988(Reaff.2019)	BDL(DL:0.005 mg/L)
15	Chloride as Cl	IS:3025 Part-32-1988(Reaff.2019)	652 mg/L
16	Sulphate as SO ₄	IS:3025 Part-24-1986(Reaff.2019)	411 mg/L
17	Sulphide as H ₂ S	IS:3025 Part-29-1986(Reaff.2019)	BDL(DL:0.01 mg/L)
18	Cyanide as CN	IS:3025 Part-27/sec 1-2021	BDL(DL:0.01 mg/L)
19	Total Organic carbon(TOC)	APHA 24TH Edn-2023-5310 B	712.2 mg/L

Table 1: Characterization of raw pharma leachate.

2.2. Process selection

Among the heavy metals determined, Zn is present in considerable amounts, and Cr is present in the least amount in the pharma leachate. This determination assists in opting for the appropriate treatment processes where BOD, COD, TOC, Cl, SO₄, NO₃, Total N, TS, TSS, and Conductivity for heavy metals side Zn and Cr, are present significant traces to remove through the suitable simple processes meanwhile economically viable. Since it is a leachate, the waste is mostly runoff from rainwater at the landfill area. It chose a straightforward, direct process readily available at the cheapest cost. To avoid any extra fees, it does not perform any additional enhancements to the conversion process. On the other hand, it is a verification study of the simple process to see how far it works for the specific pharma leachate. Based on the literature survey of (Piquero, 2005); (Visvanathan et al., 2007);adsorption and MBR processes are decided to verify the treatment of pharma leachate. Due to the initial verification process, the

stirring batch process for adsorption and MBR of ultrafiltration is adapted. Next, coconut husk and papaya seeds, which is ubiquitous cum cheapest materials of the Puducherry region, were chosen to derive activated carbon as adsorbents for the adsorption. The enhancing process of nano or magnetic adsorbents is avoided to keep the adsorbents and process at the lowest cost. The Polyvinylidene Fluoride (PVDF) membrane in the ultrafiltration system was selected for the MBR operation.

2.3. Experimental alignments

In the decided treatments, aligned adsorption is carried out first, followed by membrane filtration, and in each process, treated samples are taken for analysis. The alignment sequence of the experiments is shown in Fig.1. For the adsorption process, a rectangular tank with a onelitre capacity is set up with a stirrer. The rectangular shape is preferred because it provides a good mixing effect of adsorbents even without a baffle arrangement. For the same reason, impellers are also preferred to be square. The impact of sizes is not studied, so the values of sizes of adsorption setup are not mentioned.



Fig.1: Overview of the experimental alignment sequence of batch adsorption and UF process.

The UF had the arrangement to run around 60 ml/min by a 0.5 HP pumping motor, where the UF is fixed with a 0.02 μ m pores PVDF membrane. Both the inlet and outlet of the MBR are connected to the pressure gauges. In the membrane, an innovative idea was incorporated: a pressure transducer used in smartwatches was stuck at the membrane's in and

out the surface, where the membrane pressure is calculated just apparently, which can provide qualitatively useful results.

2.4. Experimental conditions

Prepared around 10 liters of leachate in bulk from the collected pharma sludge on a 20% weight basis. Two varieties of activated carbons produced from a single garden yield coconut husks and papaya seeds under 850-950 °C, treated with nitrogen and the standard phosphoric acid method, to make bulk quantities, several batches operated daily. The MBR-UF unit is fabricated by buying each required component separately with the help of a chemical and instrumentation engineer. Smartwatch transducer interpretation with membrane pressure detection is adapted from another study of IOT model integration and calibrated by applying it to known values. As mentioned in the beginning; to maintain the lowest cost operation, it is decided to perform it at room temperature alone. After being treated with the MBR-UF, the capacity of aqua life is tested using a simple fish tank method.

2.5. Characterization and instrumental analysis

A Muffle furnace with a nitrogen inlet of about 1200 °C capacity is employed for deriving activated carbon. A particle size analyzer is used to determine the distribution of particle sizes, and SEM is performed to verify the morphology of activated carbons. Adsorbed compositions are identified and compared by FTIR. Compounds before and after treatments detected by GC-MS. All other physiochemical characterization is performed through analytical methods at the NABL laboratory. Transport parameters such as pressure and flow rates are measured through gauges and flow meters, and the values are used to evaluate the operating conditions and find the optimum rate to fix at the prediction model.

3. Result and Discussion

3.1. Conditions Limited at the experiments

Since the treatment is related to disposed sludge-derived leachate waste required for bulk operation, the committed work conditions fixed to that should be minimal in economics, like utilizing naturally abundant materials as adsorbents without conversion of nano or magnetic materials or any high technological transfer. On the other hand, verifying the natural ability of chosen adsorbents to the specific pharma leachate would help improve the process further at the end of the determined drawback gaps. In this regard, the present work framed the natural adsorbent capacity in batch type followed by linked with simple membrane ultrafiltration to check at continuous process system. The adsorption and membrane filtration stick with the naturally fitted micron and, to some extent, the nano-level operation system.

3.2. Fixing of parameters and concentration

The leachate concentration was fixed on a 20% weight basis for the treatment process based on the average leaching range while raining (Randomly tested by spraying distilled water over the pharma sludge pile, the raining speed was not considered as it is an approximate determination). In addition, the UV-Spectroscopy absorbance was performed for various ranges of concentration from 5 to 30% in 5% increments, with good absorbance at 20% of the leachate concentration. The BOD5.20/COD ratio obtained at 0.318 indicates that the leachate is unsuitable for conventional biological treatment. The evaluated pH of 20% leachate acquired a 5.49 acidity nature, having good potential removal with coconut husk and paprika seedsderived adsorbents according to the point zero charge test. The works are preferred to present the treatment results regarding COD removal, which is a good indication of the treated level in a simple way (Sangeetha et al., 2023). No change was made in the pH, temperature, and concentration properties to verify the natural adsorption capacity of the selected adsorbents. An optimum contact time was observed at around 140 min at maximum removal for coconut husk and 210 min for paprika seed adsorbents, respectively, for the 20% concentrated leachate. Physicochemical properties were analysed alongside particle size distribution.SEM, FTIR, and GC-MS were conducted to explore potential applications. Adsorbents of activated carbons from coconut husk and papaya seeds varied with the concentration to observe the optimized adsorption rate obtained at 15% for coconut husk and 10% for papaya seeds derived adsorbents, respectively (all in weight percentage basis). After estimating the optimized leachate concentration, adsorbents' concentration, point zero charge effect, and adsorption time through experiments with UV absorbance, the best-obtained values are fixed as standard for further evaluation towards applications. The point of zero charge is expressed in Fig.2a,b for the activated carbons of coconut husks and papaya seeds, respectively. The optimized values are shown in Table 2.

Parameters	Coconut husks activated	Papaya seeds activated	
	carbon	carbon	
Pharma leachate concentration	$\approx 20\%$ (weight basis)	$\approx 20\%$ (weight basis)	
Adsorbents concentration	$\approx 10\%$ (weight basis)	\approx 15% (weight basis)	
Adsorption time	140 min	210 min	
Point Zero charge effect	@ 5.1 pH	@ 6.6 pH	

Table 2: The optimized	parameters of materials and	experiments
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Though the pH did not change for the experiment conditions, the pH was varied by using one normality of sulphuric acid and sodium hydroxide to achieve the desired point of zero charge of adsorbents. When the pH of coconut husk-derived AC is above 5, the surface is influenced by positive charges. For papaya seed-derived AC, it is above 6, and below those values are influenced by negative charges.



Fig 2: Point of zero charge of the AC from (a) Coconut husks, (b) Papaya seeds. *3.3. Particle size distribution of adsorbents*

Particle sizes play a vital role in the surface attraction of adsorbents towards adsorbates. Even so, lower-size particles work effectively by increasing surface area. Suppose the naturally obtained size of the particles meets considerably well. In that case, the cost of the process can be reduced effectively and economically. Hence, to validate the effect, particles of the naturally obtained size after the coconut husks and papaya seeds burned without oxygen at around 850-900 °C were employed in the present work, just after simple, gentle grinding. The comparative particle size distribution of AC from coconut husks and papaya seeds is displayed in Fig.3. AC of papaya seeds has a slightly larger particle size; however, the bandwidth of the size distribution to the intensity is almost closer to the core. The highest number of particles, nearly 50% and above, obtained a size of 1361 nm in papaya seeds AC and 1151 nm in coconut husk AC.



Fig.3: Comparison of the particle size distribution of adsorbents *3.4. Surface morphology and functional group characteristics of adsorbents*

This work attempted to directly activate carbon from coconut husks and papaya seeds for the adsorption of pharma leachate components. Scanning electron microscopy (SEM) analysis was performed for both the adsorbents of coconut husks and papaya seeds before and after the batch adsorption under the pharma leachate . The SEM analysis helps us understand the effect of adsorbents on the specific adsorbate (here, pharma leachate) based on the surface area morphology and can also qualitatively predict its attraction magnitude. Fig.4a appears for SEM captured on coconut husk AC before adsorption, and Fig. 4b appears after the adsorption. Only the microstructure of surface morphology was qualitatively determined before and after the adsorption; the images clearly show the transformation of structure and its pores between the early and later stages of adsorption for the SEM and FTIR reference,(Ashokan, Jaganathan, et al., 2024a) . Fig.4a and 4b over the coconut husk activated carbon clearly show the surface morphology with different focusing points changes in its corrugated formation to the porous structure, indicating good attraction of pollutant adsorbates. Similarly,



Fig.4a: SEM image of coconut husks' activated carbon before adsorption.



Fig.4b: SEM image of coconut husks' activated carbon after adsorption.

Fig.5a & 5b appeared below for papaya seeds activated carbon before and after adsorption, respectively, at different focus points and attracted pollutant components from the pharma leachate. The SEM results are justified qualitatively here and can be concluded through the FTIR output on CHAC and PSAC in Fig.6a and 6b, respectively, and IS analysis reported in section 3.5, comparative data of obtained results. In CHAC (Fig.6a), before adsorption, 4 Functional groups (FG) and 9 Fingerprint (FP) were available, where it turned to 5 FG and 22 FP after adsorption, likely In Fig.6b PSAC 4 FG and 9 FP before adsorption, 4 FG and 13 FP

after adsorption obtained. The result clearly states that CHAC performed more effectively than PSAC. FTIR results support SEM qualitatively.



Fig.5a: SEM image of papaya seeds' activated carbon before adsorption.



Fig.5b: SEM image of papaya seeds' activated carbon after adsorption.

The FTIR spectrum of coconut husk's AC before and after adsorption, like papaya seeds' AC, can be seen in Fig.6a and Fig.6b, respectively.



Fig.6a: FTIR report on coconut husk AC at raw and recovered properties interpreted.



Fig.6b: FTIR report on papaya seeds AC at raw and recovered properties interpreted. 3.5. Comparative analysis of results between CHAC and PSAC followed by UF

The efficiency of naturally activated carbon of coconut husk and papaya seeds alone is not expected to have better adsorption effectiveness; hence, the membrane ultrafiltration is fixed in the sequence followed by the adsorption process. The obtained results on pharma leachate over the adsorptions and membrane separation are reported as a comparative statement in Table 3. The pH of CHAC and PSAC both fall in the range of 7.8 -8.2 as the base regime; the pharma leachate attained pH 5.4, an acidic domain, indicating that the positive and negative attraction could improve adsorption. Fig.7 reports the pH variation after the adsorption process, where all moderately obtained close to 7 pH and may conclude both AC followed by UF have an equal impact (Singaravel, Ashokan, et al., 2024).



Fig.7: (a) Impact on pH after the adsorption and UF processes,(b) Effect of conductivity at different processes.

The conductivity of treated leachate did not have a better impact on both CHAC and PSAC adsorption, while UFs provided better reduction. Comparatively, PSAC-treated provided good adsorption, and CHAC-treated yielded better UF, as shown in Fig.7 (b). In TSS, CHAC In TSS, CHAC had a treatment efficiency of 38% and PSAC 50%. However, UF, followed by CHAC and PSAC, achieved a remarkable efficiency of 99%. as reported in Fig.8(a). To clarify the synergistic mechanisms, it must be noted that the enhanced performance observed in the adsorption-ultrafiltration (UF) process is attributed to the strong affinity between specific pollutant molecules and the functional groups on activated carbon (AC) surfaces. Coconut husk AC exhibited a higher increase in fingerprint and functional group signals in FTIR spectra post-adsorption, suggesting more significant molecular binding interactions compared to papaya seed AC. This stronger interaction likely facilitated a more effective initial removal of organics, subsequently reducing the fouling load on the UF membrane. In contrast, PSAC exhibited a relatively lower functional group transition, indicating weaker pollutant interactions and thus less effective pre-filtration, which may have contributed to the reduced total solids removal post-UF. Furthermore, membrane fouling was observed to be minimized in the CHAC+UF configuration due to the pre-adsorption of macromolecular and colloidal species, which are known foulants. The less efficient performance of PSAC, particularly for total solids, can also be attributed to its larger particle size distribution and lower porosity, which limited surface contact and adsorption depth,

thereby increasing the burden on the subsequent UF step. These findings highlight the importance of surface chemistry and pore characteristics of the adsorbents in achieving synergistic removal efficiency.



Fig.8 (a) Reduction of TSS at different adsorbents followed by UF, (b) Effect of removal in TS at different operations.

CHAC was reported at 75% for the removal of TS, followed by UF efficiently at 99%. PSAC-treated efficiency attained up to 72%, but it was followed by UF giving 84%, the reason for which is unknown (Fig.8 (b)

S.No	Test Parameters	Raw Leachate	CHAC Treated	UF Followed by CHAC	PSAC Treated	UF Followed by PSAC
1	pH @ 25°C	5.49	6.84	7.34	7.52	7.19
2	Conductivity @ 25°C(µmhos/cm)	3170	2040	236	2260	258
3	Total suspended solids(mg/L)	136	84 (38%)	BDL(DL:1.0)	68 (50%)	BDL(DL:1.0)
4	Total solids (mg/L)	2976	748 (75%)	BDL(DL:2.0)	842 (72%)	134 (84%)
5	BOD @ 27°C for 3 days(mg/L)	624	192 (69%)	BDL(DL:4.0)	184 (70%)	BDL(DL:2.0)
6	COD(mg/L)	1356	306 (77%)	BDL(DL:0.01)	467 (66%)	BDL(DL:4.0)
7	Total Arsenic as As(mg/L)	BDL(DL:0.01)	BDL(DL:0.01)	BDL(DL:0.01)	BDL(DL:0.005)	BDL(DL:0.01)
8	Cadmium as Cd(mg/L)	BDL(DL:0.01)	BDL(DL:0.01)	BDL(DL:0.01)	BDL(DL:0.01)	BDL(DL:0.01)
9	Total Chromium as Cr(mg/L)	0.090	0.077	BDL(DL:0.01)	BDL(DL:0.01)	BDL(DL:0.01)
10	Lead as Pb(mg/L)	BDL(DL:0.01)	BDL(DL:0.01)	BDL(DL:0.01)	BDL(DL:0.01)	BDL(DL:0.01)
11	Zinc as Zn(mg/L) Ammonia	0.361	0.26 (28%)	BDL(DL:0.01)	0.306 (15%)	BDL(DL:0.01)
12	(as total ammonia - N)(mg/L)	30.84	BDL(DL:0.01)	BDL(DL:0.01)	16.1 (48%)	4.19 (74%)
13	Nitrate as NO ₃ (mg/L)	224	94 (58%)	12 (87%)	8.69 (96%)	6.44 (26%)
14	Nitrite as NO ₂ (mg/L)	1.132	BDL(DL:0.01)	BDL(DL:0.01)	BDL(DL:0.01)	BDL(DL:0.01)
15	Chloride as Cl(mg/L)	738.2	652 (12%)	36.9 (95%)	437.1 (41%)	38.9 (91%)
16	Sulphate as SO ₄ (mg/L)	427.2	111 (74%)	9.9 (91%)	159.7 (63%)	17.1 (89.2%)
17	Sulphide as H ₂ S (mg/L)	3.84	BDL(DL:0.01)	BDL(DL:0.01)	BDL(DL:0.01)	BDL(DL:0.01L)
18	Cyanide as CN(mg/L)	BDL(DL:0.01)	Not Tested	Not Tested	Not Tested	Not Tested
19	Total Organic carbon(TOC)(mg/L)	919	112.2 (88%)	BDL(DL:0.01)	179.6 (80%)	8.39 (95%)
		R				

Table 3: Comparative results of CHAC, PSAC adsorption and followed by UF

In terms of BOD removal efficiency, CHAC treatment attained 69%, and PSAC finished with 70%. The BOD was completely swept at UF, followed by both ACs (Fig.9).



Fig.9: Removal of BOD efficiency at different processes.

Fig. 10 shows the COD removal capability: CHAC achieved 77%, PSAC reached 66%, and the continuation of UF on both ACs successfully eliminated the COD. Arsenic (As), cadmium (Cd), and lead (Pb) were found to be untraceable, with chromium (Cr) being the least traceable element in the raw leachate and not undergoing substantial reduction in the CHAC process. In contrast, both PCAC and ultrafiltration (UF) processes effectively reduced Cr to an untraceable level. Nitrite and sulphide exhibited the same lack of traceability, being removed throughout all the adopted processes without detection. Zinc (Zn) saw only a 28% reduction in CHAC and a 15% reduction in PSAC. Furthermore, the continued UF yield for both activated carbons was undetectable (see Fig. 11). Ammonia was primarily removed through the CHAC process, followed by UF. However, in the case of PSAC followed by UF, the reduction was limited to approximately 48%. The PSAC treatment achieved an 84% removal of nitrogen, though it did not eliminate it (see Fig. 12). When it comes to nitrate, PSAC performed exceptionally well, achieving a reduction of about 96%, while UF reached only 26%. In the CHAC process, there was a 58% reduction, with UF achieving a subsequent 87% reduction (see Fig. 13).







Fig.12: Nitrate removal at adsorption and UF

Chloride removal was ineffective at CHAC, achieving only about 12%. In contrast, PSAC showed a performance of 41%. When examining ultrafiltration (UF), the best results were seen after treatment with CHAC, reaching 95%, while UF following PSAC attained 91%.

The chloride removal adsorption system performed poorly at CHAC but was comparatively better at PSAC, with a 41% removal rate, followed by UF at 91%, as illustrated in Fig. 14. Regarding sulfate removal, CHAC outperformed PSAC with a removal rate of 71% compared to PSAC's 63%. Both UF processes achieved similar results, with CHAC performing at 91% and PSAC at 89%, as shown in Fig. 15. Lastly, regarding removing total organic carbon (TOC), CHAC achieved a remarkable 95%, while PSAC reached 80%. However, UF after CHAC yielded untraceable levels, whereas UF after PSAC performed well at 95%, as depicted in Fig. 16 (Jayaraman et al., 2024). To avoid misinterpretations in reporting these results, the underlying reasons for these differences need to be explored in a separate study focused on the mechanisms involved, highlighting a research gap in this area be interpreted as an individual study of mechanisms, which opens a research gap (Bhambore & Suresh Kumar, 2022).



Fig.14: Indicating level of sulphate removal.



Fig.15: Report on TOC removal at different processes 3.6. Analysis of GC-MS on the feasibility of recovering circular economy products

Determining compounds through GC-MS (Gas Chromatography-Mass Spectrometry) will significantly enhance the circular economy process by facilitating the recovery of products from waste. This approach also supports carbon trading through green technology for wasteto-product recovery. The compounds identified through the reference library from earlier studies on raw pharmaceutical sludge leachate, CHAC, and PSAC-treated solutions meet various industrial requirements. These compounds can be explored as a distinct research domain, contributing to the development of Industry 4.0-based downstream industries that support rural development. In the current GC-MS study, the reference library is utilized, as done in the pharmaceutical sludge pellet fuel research (Ashokan, Dhairiyasamy, et al., 2024). The raw and treated leachate samples are mixed with hexane, a non-polar solvent widely used in industry for product recovery (Ashokan et al., 2023). The compounds extractable by hexane are suitable for separation using downstream processes such as distillation and chromatography techniques. Initially, blank hexane was tested under GC-MS to differentiate between the compounds in the solvent and those in the leachate (El Mouhri et al., 2020). The results of the calibrated test are shown in Fig. 17, and the details of the compounds are presented in Table 4. The peaks obtained, and the corresponding compounds are listed to help identify and classify the compounds integrated with the leachate. Fig. 18 illustrates the GC-MS run for raw leachate, with the list of compounds provided in Table 5. The GC-MS results for the CHAC-treated solution are displayed in Fig. 19, followed by the compound list in Table 6. Similarly, it presents the results for the PSAC-treated solution, with Table 7 listing the respective compounds and their peak data (Singaravel, Veerapandian, et al., 2024).

Chromatogram Hexane -08.06.2024 D:\Hexane -08.06.2024.QGD



Fig.16: Blank hexane run at GC-MS.

	Table.4: Compounds in	nterpreted from	the library	for blank	hexane at	GC-MS.
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Peak							
	R.Time	Area	Area%	Height	Height%	A/H	Name
Ι	7.917	958997	0.52	91532	0.54	10 48	1.2-Benzenedicarboxylic acid, dimethyl ester (
2	7.983	903160	0.49	105017	0.61	8 60	3-Pyridinecarboxaldehvde, oxime (CAS) Nico
3	8.194	1354911	073	121558	0.71	1 1.15	1.2-Benzenedicarboxyiic acid, dimethy l ester (
4	9.811	116873730	63 35	4949159	28.94	2361	1,2-Benzenedicarboxylic acid, diethyl ester (C
5	11.917	120775	0.07	54286	0.32	2.22	Heneicosane
6	12.052	311526	0.17	90723	0.53	3.43	Cvclohexasiloxane, dodecamethyl-
7	12 902	18488760	1002	2870452	1678	644	1.2-Benzenedicarboxylie acid. bis(2-methylnr<
8	13.416	179981	0.10	64081	0.37	2 81	1.2-Benzenedicarboxyiic acid. bis(2-methvli>r<
9	13.530	2042099	1.11	403978	2.36	5.05	7,9-D i -tert-butv 1 -1 -oxasp iro(4,5)deca-6,9-dier
10	13 665	555142	030	186849	1 09	2 97	Octasiloxane, 1.1.3.3.5,5.7.7.9.9.11.11.13,13,
11	13.923	8617389	467	1444994	8.45	5.96	Dibutvl phthalate
12	14.345	802566	044	223543	131	3 59	HexadecanaJ
13	14.667	499343	0.27	59489	0.35	839	3,5-Cyclo hexadiene- 1,2-dione, 3,5-bis(1.1-din
14	14.971	66836)7	3.62	1701126	9.95	3 93	n-Nonadecanol-1
15	15 140	1571961	0 85	359663	2 10	437	TETRACOSAMETHYLCYCLODODECASI
16	15.397	400488	0.22	71912	0.42	5.57	1.2-Benzenedicarboxylie acid. mono(2-ethvlhi
17	15.525	568383	0.31	201207	1 18	2 82	Hexadecanoic acid, 2-methylpropyl ester
18	16.721	858276	0.47	294819	1 72	2 91	Cyclononasiloxane, octadecamethyl-
19	17.691	3115105	1.69	673875	3 94	4 62	cis-Vaccenic acid
20	18.018	137063	0.07	47184	0.28	2 90	Octadecanoic acid. 2-methylpropyl ester
21	18.338	416355	0.23	57315	0 34	726	SILIKONFETT SE30 (GREVELS)
22	18.732	1123026	0.61	277906	I 62	4.04	EICOSAMETHYLCYCLODECASILOXANI
23	18.968	325559	0.18	79086	0.46	4.12	Hexanedioic acid, bis(2-ethvlhexyl) ester
24	21.480	1179485	0.64	233415	1 36	5 05	EICOSAMETHYLCYCLODECASILOXANI
25	22.202	16390216	8.88	2439536	1426	6.72	1.2-Benzenedicarboxylic acid. bis(2-ethvlhexv
		184477913	100.00	17102705	100 00		



Fig.17: Raw leachate derived from pharma sludge run at GC-MS.

Table 5: Compounds interpreted from the library for raw leachate at GC-MS.

	Peak Report TIC								
Peak#	R.Time	Area	Area%	Height	Height ⁰ /»	A/H Name			
1	5.617	1319873	0.86	700361	2.52	1.88 Dodecane. 4,6-dimethyl-			
2	8.347	2240094	1.46	885670	3 18	2.53 Heptadecane			
3	8903	811662	053	353190	1 27	2 30 Octadecane (CAS) n-Octadecane			
4	9828	41518219	27 02	2919933	1050	14 22 1,2-Benzenedicarboxvlic acid, diethyl ester (C			
5	10.050	1310820	0 85	559074	2.01	2 34 Heneicosane			
6	10.939	2708127	1 76	1265736	4 55	2.14 2-methyloctacosane			
7	11 431	978887	064	508491	1 83	1 93 Eicosane			
8	12.922	8490299	5.52	1857896	668	4.57 1,2-Benzenedicarboxvlic acid, butyl 8-methvlr			
9	13.017	2313569	1.51	610909	220	3 79 Hexadecane, 2,6,11,15-tetramethyl-			
10	13 208	1542253	1 00	408669	1 47	3 77 Nonadecane (CAS) n-Nonadecane			
11	13.298	6561845	427	2164106	7 78	3.03 Hexadecane, 2.6, H. 15-tetramethyl-			
12	13.433	1433859	0.93	300817	1 08	4.77 Tetracosane			
13	13.608	931255	0.61	201936	0.73	4.61 Tetradecane, 4-methyl-			
14	13.664	746894	0.49	344212	1.24	2.17 Docosane (CAS) n-Docosane			
15	13.735	2199691	1.43	929566	3 34	2.37 6,6-Diethvlhexadecane			
16	13.939	2880483	1.87	709479	2.55	4.06 Dibutvi phthalate			
17	14.679	1485039	0.97	651145	2 34	2.28 Pentacosane			
18	14.985	3829724	249	981502	3.53	3 90 n-Nonadecanol-1			
19	15.083	3094797	2.01	602926	2.17	5 13 Hexadecane. 2,6.10,14-tetramethvl- (CAS) Ph			
20	15 150	4840915	3 15	629306	2 26	7 69 Tetracosane			
21	15.322	5860218	3.81	1216243	4.37	4.82 2-methyloctacosane			
22	15.452	9184059	5.98	2099645	7.55	4 37 5,5-Diethvlheptadecane			
23	15 533	1900317	1.24	493867	1 78	3 85 Hexadecane, 2.6, 11.15-tetramethyl-			
24	15.672	12641868	8.23	1147635	4.13	11.02 HEXACONTAN			
25	15.892	2088538	1.36	702045	2 52	2 97 Eicosane			
26	17.468	3891020	2.53	442501	1.59	8.79 Tetrapentacontane			
27	18.100	2339986	1.52	773400	2.78	3 03 Dotriacontane			

Chromatogram CAC -08.06.2024 C:\Users\TBI\Desktop\CAC -08.06.2024.QGD



Fig.18: CHAC-treated leachate run at GC-MS.

Table 6: Compounds interpreted from the library for CHAC at GC-MS.

		Peak Report TIC				
Peak#	R. Time	Area	Area%	Height	Height%	A/H Name
1	5.614	1258350	0.97	644975	2.54	1 95 Dodecane. 4,6-d ¡methyl-
2	8.343	2824210	2.17	1106817	4.35	2.55 Heptadecane
3	8.708	1059900	0.82	205062	081	5 17 Phenol, 3,5-bis(1,1-dimethvJethyl)-
4	8.899	1142432	0.88	475338	1 87	2.40 Heptadecane
5	9.822	50632396	3898	3869743	1522	13 08 2,4-Imidazolidinedione l-[[(5-nitro-2-furanyl
6	10.042	5307671	409	1193300	4 69	4 45 Iron, tricarbonyi[N4phenvI-2-pyridinylmethyli
7	10.242	2683018	2.07	234552	0 92	11 44 Heneicosane
8	10.933	3425128	2 64	1621513	6.38	2.11 5,5-Diethylheptadecane
9	11.426	1230923	0.95	633610	2 49	1.94 Dodecane. 2.6.11-trimethyl-
10	12.918	8775989	6.76	2003871	788	4.38 1,2-Benzenedicarboxylic acid, butyl 8-methylr
II	13.000	2441765	1 88	756405	297	3.23 Tricosane (CAS) n-Tricosane
12	;3.158	1172629	0.90	284552	1 12	4 12 Hexadecane, I-iodo-
13	13.202	1013000	0.78	406532	1.60	2.49 Eicosane
14	13.294	6135240	4.72	2155120	848	2.85 Octacosane
15	13.425	942021	0.73	235393	0 93	4.00 2-Bromotetradecane
16	13.667	1283233	0.99	261317	1.03	4 91 6,6-Diethvlhoctadecane
17	13.730	2166236	1.67	850639	3.35	2.55 Heptadecane
18	13.935	2429818	1 87	603205	2.37	4.03 Dibutvl phthalate
19	14.982	3907987	3 01	916756	361	4 26 n-Pentadecanol
20	15.075	1748592	1.35	454691	1.79	3.85 Hexadecane, 2.6,10.14-tetramethvl-(CAS) Ph
21	15 148	960765	074	308913	1 21	3.11 Tetracosane
22	15.308	2407850	1 85	505181	1 99	4 77 Tritriacontane
23	15.447	5634343	4.34	1464612	5.76	3.85 Pentadecane. 2,6.10,14-tetramethvl-(CAS) Pr
24	15.534	930043	0.72	338451	1.33	2.75 5-Butyl-5-ethylpentadecane
25	15.783	1415777	1.09	287870	1.13	4 92 Sulfurous acid, octadecvl 2-propvl ester
26	15.886	1595092	1 23	649252	2.55	2 46 2-methyloctacosane
27	17.697	1983880	1.53	437851	1 72	453 I4-BETAH-PREGNA



Table 7: Compounds interpreted from the library for PSAC at GC-MS.

Peak Report TIC								
			Area					
Peak	R.Time	Area	%	Height	Height%	A/H	Name	
1	5.628	7527609	1.58	3815903	2 69	I 97	Dodecane, 4.6-dimethyl-	
2	8 263	8510575	1 78	2267996	1 60	3 75	Heptadecane	
3	8 350	23821894	4 99	8655007	6 1 1	2 75	Eicosane	
4	8.904	10985837	2 30	4398796	3 10	2.50	Nonane, 5-butvl-	
5	10.650	10291580	2 15	3483885	2 46	2 95	IRON. TRICARBON YLfN-tPHENYL-2-PYI	
6	10.758	12500186	2 62	2875417	2.03	435	Decane, 1-iodo-	
7	10.820	7051112	1 48	3332926	2 35	2 12	Tetratetraco mane	
8	10 938	33021537	691	12230707	863	2 70	Tetracosane	
9	11.033	8645329	1 81	2678361	1 89	323	Heptadecane. 8-methyl-	
10	11.090	5863469	1.23	2491298	1 76	2.35	Pentadecane, 8-hexyl-	
II	11.192	15593178	3 26	1695556	120	9.20	Hexadecane, 1-iodo-	
12	11.430	14361296	3.01	6570242	464	2.19	HEXADECANE, 2,6,10,14-TETRAMETHYI	
13	12.476	8204006	1.72	3781731	2.67	2.17	Triacontane	
14	12.930	25069372	5.25	5923501	4 18	423	OCTACOSANE	
15	13.008	13879856	2.90	4428394	3.13	3 13	Eicosane	
16	13.167	7714938	1.61	3516461	2 48	2.19	Tetracosane	
17	13.206	12599788	2.64	4631293	3.27	2.72	Tetratriacontane	
18	13 298	50596746	10 59	13236852	9 34	3 82	5,5-Diethvl pentadecane	
19	13.425	12192658	2.55	2901491	2.05	420	HEXACOSANE	
20	13.608	12931036	2.71	2918908	2 06	4.43	Decane, 1-iodo-	
21	13.657	10676118	2.23	4036342	2.85	2.64	6,6-Diethvl octadecane	
22	13.733	33833285	7.08	8621856	609	3 92	Squalane	
23	14.676	7357574	1 54	3731999	2 63	1 97	Hentriacontane	
24	14.795	7361950	1 54	2503420	1 77	2 94	TRICOSANE	
25	15.053	33659168	7.04	4298606	3 03	783	Heptadecane. 3-methyl-	
26	15.150	10785961	2.26	2269683	160	4 75	Dotriacontane	
27	15.3)7	16547502	3.46	4115195	2.90	402	Tetracosane	

Raw leachate, with CHAC and PSAC treated solutions, exhibited a common compound characterized by a peak at around 5.6, identified as Dodecane 4.6 Dimethyl. At the peak range of 8.3, Heptadecane was present in all three types of leachates, both raw and treated. Between the ranges of 13.2 and 13.6, raw leachate showed the compound 6,6-Diethylhexadecane, while

CHAC-treated leachate contained 6,6-Diethyloctadecane, and PSAC-treated leachate featured 5,5-Diethylpentadecane (Smol & Generowicz, 2018b). The differences among these compounds were notable within a short range of peaks. Around the 15.3 peak range, each type of leachate yielded different compounds: raw leachate produced 2-methyloctacosane, CHAC-treated solution yielded Tritriacontane, and PSAC-treated leachate resulted in Tetracosane. Similarly, at the peak of 15.8, raw leachate produced Eicosane, CHAC-treated solution yielded 2-methyloctacosane again, and PSAC provided Heneicosane, specifically 10-methyl (Ashokan, Jaganathan, et al., 2024b). Additionally, the raw leachate and each processing method resulted in unique compounds, as listed in Table 8.

S.No	Raw Leachate	CHAC Treated	PSAC Treated
1.	Octadecane (CAS) n- Octadecane	Phenol, 3,5-bis(1,1- dimethylethyl)-	Triacontane
2.	1,2- Benzenedicarboxylic acid, diethyl ester	Heptadecane	Decane, 1-iodo
3.	Pentacosane	2,4-Imidazolidinedione, 1-[[(5-nitro-2-furanyl	Hentriacontane
4.	Tetrapentacontane	Iron, tricarbonyl[N- (phenyl-2- pyridinylmethyl)	Dotriacontane
5.	Dotriacontane	5,5-Diethylheptadecane	Pentadecane, 8- hexyl
6.	1H-Purin-6-amine, [(2- fluorophenyl)methyl]	2-Bromotetradecane	Heneicosane, 10- methyl
7.	Squalene	n-Pentadecanol	Pentatriacontane
8.	Bis(2-ethylhexyl) phthalate	14BETAH- PREGNA	-
9.	-	Tetracosane	-
10.	-	1H-Purin-6-amine, [(2- fluorophenyl)methyl]-	-
11.	-	Nonane, 5-butyl	-

Table 8: Unique compounds present in raw, CHAC, and PSAC

The compounds presented in leachates have multiple potentials for various applied product formation at various applications. Exploration of interpreted compounds towards industrial applications will initiate a significant regime in Industry 4.0 and provide a good scope for industrial research and development (Tsompanoglou et al., 2024). The compounds found in leachates have numerous potential applications for the production of various products investigating these compounds for industrial uses could lead to significant advancements in Industry 4.0, SDG and offer promising opportunities for research and development in the industrial sector.

3.7. Synergetic impact of adsorption cum ultrafiltration

Collected sludge from the pharmaceutical industry was used to derive leachate for adsorption, followed by ultrafiltration using a polyvinylidene fluoride (PVDF) membrane with a pore size of 0.02 μ m. This sludge was previously recovered from a Membrane Bioreactor (MBR) during effluent treatment in the industry, which has a membrane size of approximately 0.45 μ m. As a result, the particles of sludge that did not pass through the 0.45 μ m MBR pores were effectively filtered using the 0.02 μ m membrane in the ultrafiltration unit, specifically for the derived leachate. The assembled ultrafiltration unit operated under vacuum pressure, utilizing two separate membranes: one for coconut husk activated carbon (CHAC) and another for papaya seeds activated carbon (PSAC). The unit was constructed with assistance from Ultra Scientific Supplies in Pudukkottai, Tamil Nadu. It was designed solely for sample collection of the permeate that passed through the membrane after the adsorption process, operating at a capacity of one litre with a flow rate of 10 litres per hour. The transmembrane pressure varied between 32 and 42 kPa (Wdowczyk et al., 2024).

There has been limited study on the dynamics of membrane process parameters, such as Reynolds number, permeation rate, and fouling rate, which typically exhibit linear behavior or little change over a short duration. Conversely, the membrane-processed leachate, following adsorption through CHAC and PSAC, underwent physicochemical property analysis in an accredited laboratory. However, conducting a dynamic study of the ultrafiltration membrane process is crucial, and it needs to be run with larger quantities over extended periods throughout the year to verify its technical and economic viability. In summary, from this preliminary study, it is observed that the ultrafiltration load is minimized by utilizing the output from the earlier adsorption process. This synergetic effect contributes to the overall feasibility of the system. The water released by the UF was tested using a few country fish, which survived well. The results of the study on the respective parameters are awaiting further investigation.

4. Conclusion

The results obtained from the various physiochemical analyses conducted in this study demonstrate that the synergetic effect of adsorption with ultrafiltration (UF) yields a viable system. Although both adsorbents show an average removal efficiency of 58%, each one demonstrates better rejection few of a few individual components. Considering the availability and processing capacity, coconut husk presents a promising opportunity for commercial development due to its abundance. Additionally, the results from gas chromatography-mass spectrometry (GC-MS) and the performance of papaya seed-activated carbons (ACs) indicate that certain individual components can be removed more efficiently. This opens up greater potential for startup opportunities focused on transforming waste into value, promoting a circular economy, and developing sustainable technologies.

References

- Abedi, S., Nozarpour, A., & Tavakoli, O. (2023). Evaluation of biogas production rate and leachate treatment in Landfill through a water-energy nexus framework for integrated waste management. *Energy Nexus*, *11*, 100218.
- Ahmad, I., Jasni, A. B., Abdullah, N., Krishnan, S., Koji, I., Chelliapan, S., Yuzir, A., & Nasrullah, M. (2022). Landfill management and efficacy of anaerobic reactors in the treatment of landfill leachate. In *Techno-economics and Lifecycle Assessment of Bioreactors* (pp. 69–92).
- Ameli, F., Hashemi, H., Samaei, M. R., Asgari, E., & Fazli, M. M. (2024). Enhanced reducing leachate pollution index through electrocoagulation using response surface methodology. *Heliyon*, 10, e38134.
- Ashokan, A., Dhairiyasamy, R., & Rajendaran, S. (2024). Investigating the influence of nanosilica incorporation on mechanical characteristics of steel fiber-reinforced concrete to mitigate solid waste and environmental contamination. *Energy Sources, Part A: Recovery, Utilization and Environmental Effects*, 46(1), 131–147. https://doi.org/10.1080/15567036.2023.2282146
- Ashokan, A., Jaganathan, S., Rajendran, S., & Dhairiyasamy, R. (2024a). Analysis of environmental performance indicators for concrete block manufacturing: embodied energy, CO2 emissions, and water consumption. *Environmental Science and Pollution Research*, 31(6), 8842–8862. https://doi.org/10.1007/S11356-023-31786-W
- Ashokan, A., Jaganathan, S., Rajendran, S., & Dhairiyasamy, R. (2024b). Sustainable strategies for reducing environmental impact in concrete block manufacturing: a comprehensive life cycle assessment. *International Journal of Green Energy*, 21(1), 187– 204. https://doi.org/10.1080/15435075.2023.2281331
- Ashokan, A., Rajendran, S., & Dhairiyasamy, R. (2023). A comprehensive study on enhancing of the mechanical properties of steel fiber-reinforced concrete through nano-silica integration. *Scientific Reports*, *13*(1). https://doi.org/10.1038/S41598-023-47475-0
- Bhambore, N., & Suresh Kumar, M. (2022). Municipal solid waste generation, management scenarios, and leachate treatment using sequencing batch biofilter granular reactor.

Process Safety and Environmental Protection, 167, 454–468. https://doi.org/10.1016/J.PSEP.2022.09.027

- Bhaskar, S., Rashmi Sree, K. N., Apporva, K. V, & Sreenivasa, M. Y. (2024). Adsorption Advanced oxidation process (AAOP) for the heavy metals and organic matter removal from leachate using combined filtration -Fenton's and Photo-Fenton's treatment. *Journal* of Environmental Management, 371, 123009.
- Bouyakhsass, R., Souabi, S., Rifi, S. K., Bouaauda, S., Taleb, A., Madinzi, A., Kurniawan, T. A., & Anouzla, A. (2024). Applicability of central composite design and response surface methodology for optimizing treatment of landfill leachate using coagulation-flocculation. *Chemical Engineering Research and Design*, 197, 669–684.
- Clemente, E., Domingues, E., Quinta-Ferreira, R. M., Leitao, A., & Martins, R. C. (2024a). European and African landfilling practices: an overview on MSW management, leachate characterization, and treatment technologies. *Journal of Water Process Engineering*, 66, 105931.
- Clemente, E., Domingues, E., Quinta-Ferreira, R. M., Leitao, R., & Martins, R. C. (2024b). Solar photo-Fenton and persulphate-based processes for landfill leachate treatment: A critical review. *Science of the Total Environment*, *912*, 169471.
- Dagwar, P. P., & Dutta, D. (2024). Landfill leachate a potential challenge towards sustainable environmental management. *Science of the Total Environment*, 926, 171668.
- El Mouhri, G., Merzouki, M., Belhassan, H., Miyah, Y., Amakdouf, H., Elmountassir, R., & Lahrichi, A. (2020). Continuous Adsorption Modeling and Fixed Bed Column Studies: Adsorption of Tannery Wastewater Pollutants Using Beach Sand. *Journal of Chemistry*, 2020(1), 7613484. https://doi.org/10.1155/2020/7613484
- El-Saadony, M. T., Saad, A. M., El-Wafai, A., Abou-Aly, H. E., Salem, H. M., Soliman, S. M., El-Mageed, T. A. A., Elrys, A. S., Selim, S., Abd El-Hack, M. E., Kapacherry, S., El-Tarabily, K. A., & AbuQamar, S. F. (2023). Hazardous wastes and management strategies of landfill leachates: A comprehensive review. *Environmental Technology & Innovation*, *31*, 103150.
- Feng, W., Zhang, K., Zohuriaan-Mehr, M. J., Kabiri, K., & Jin, C. (2024). Unlocking the application potential of superabsorbent polymers in landfill leachate treatment. *Polymer Testing*, 138, 108537.
- Gaur, V. K., Gautam, K., Vishvakarma, R., Sharma, P., Pandey, U., Srivastava, J. K., Varjani, S., Chang, J. S., Ngo, H. H., & Wong, J. W. C. (2024). Integrating advanced techniques and machine learning for landfill leachate treatment: Addressing limitations and environmental concerns. *Environmental Pollution*, 354, 124134.
- Gripa, E., Daflan, S. D. A., Almeida, R., Fonseca, F. V, & Campos, J. C. (2023). Landfill leachate treatment by high-pressure membranes and advanced oxidation techniques with a focus on ecotoxicity and by-products management: A review. *Process Safety and Environmental Protection*, 173, 747–764.

- Han, Q. L., Zhaa, H. I., Wei, G. X., Liu, H. Q., Zhu, Y. W., Li, T., Lin, Y. F., & Su, X. R. (2024). Optimizing waste leachate treatment for environmental and economic sustainability: Insights from a bottom-up study of over 300 cities. *Sustainable Production and Consumption*, 49, 304–317.
- Hwang, K. S., Jun, J. H., & Lee, W. K. (1995). Fixed Bed Adsorption for Bulk Component System, Nonisothermal and Non-adiabatic Model. *Chemical Engineering Science*, 50(5), 813–825.
- Igwegbe, C. A., Lopez-Maldonado, E. A., Landazuri, A. C., Ovuoraye, P. E., Ogbu, A. I., Vela-Garcia, N., & Biolowiec, A. (2024). Sustainable municipal landfill leachate management: Current practices, challenges, and future directions. *Desalination and Water Treatment*, 320, 100709.
- Jayaraman, D., Alagesan, P., Thangavel, S., & Dhairiyasamy, R. (2024). Investigating the effect of cashew nutshell liquid and aluminum powder on the mechanical and thermal properties of epoxy resins. *Revista Materia*, 29(4). https://doi.org/10.1590/1517-7076-RMAT-2024-0719
- Karunarathne, H. D. S. S., & Amarasinghe, B. M. W. P. K. (2013). Fixed bed adsorption column studies for the removal of aqueous phenol from activated carbon prepared from sugarcane bagasse. *Energy Procedia*, *34*, 83–90.
- Kumar, M., Silori, R., Mazumder, P., & Touseef, S. M. (2023). Screening of pharmaceutical and personal care products (PPCPs) along waste water treatment system equipped with root zone treatment: A potential model for domestic waste leachate management. *Journal* of Environmental Management, 335, 117494.
- Li, Y., Xue, J., Zhaa, W., He, Z., Yang, L., Wang, X., Yang, S., Li, W., & Li, J. (2024). Coagulation coupled with batch biological sponge iron reactor for efficient treatment of leachate from waste transfer stations. *Journal of Water Process Engineering*, 67, 106115.
- Mota, A. F. L., Miranda, M. M., Moreira, V. R., Moravia, W. G., Paula, E. C. de, & Amaral, M. C. S. (2024). Rejuvenated end-of-life reverse osmosis membranes for landfill leachate treatment and reuse water reclamation. *Journal of Water Process Engineering*, 66, 105963.
- O'Connor, G., & Courtney, R. (2020). Constructed wetlands for the treatment of bauxite residue leachate: Long term field evidence and implications for management. *Ecological Engineering*, 158, 107076.
- Piquero, R. E. (2005). Design fabrication and initial evaluation of an upflow fixed bed adsorption column for lead (Pb2+) using carica papaya seeds.
- Pugazhenthi, A., Srividhya, P. K., Suresh, S., Arun, C., Sivaranjani, V., & Kumar, A. A. (2024). Production of pellet fuel conversion from the sludge derived in excipient manufacturing at the pharma industry. In *From Waste to Wealth* (pp. 965–988). Springer – Singapore.

- Rezaei, A., Monfared-Hajishirkiaee, R., Hosseinzadeh-Moghaddam, S., Behzadi, M., & Shahangian, S. S. (2024). Enhancing leachate management with antibacterial nanocomposites incorporating plant-based carbon dots and Satureja Khuzestanica essential oils. *Colloids and Surfaces B: Biointerfaces*, 245, 114296.
- Roy, D., Drogui, P., Tyagi, R. D., Landry, D., & Rahni, M. (2020). MBR Treatment of leachates originating from waste management facilities: A reference study of the design parameters for efficient treatment. *Journal of Environmental Management*, 259, 110057.
- Sangeetha, A., Gandhimathi, R., & Nidheesh, P. V. (2023). Treatment of stabilized landfill leachate using pyrite-activated persulfate oxidation process. *Process Safety and Environmental Protection*, 171, 413–422.
- Silveira, J. E., Garbellini, L. R., Ribeiro, A. R., Yepez, A., Furlanetto, T., Oliveira, G. M., Paz, W., Pliego, G., Zazo, J. A., & Casas, J. A. (2024). An approach to highly polluted wastewater management for zero liquid discharge: The case of landfill leachate. *Process Safety and Environmental Protection*, 184, 672–679.
- Singaravel, D. A., Ashokan, A., Rajendran, S., & Dhairiyasamy, R. (2024). Influence of nanoceramic addition on the performance of cement-based materials. *Revista Materia*, 29(3). https://doi.org/10.1590/1517-7076-RMAT-2024-0267
- Singaravel, D. A., Veerapandian, P., Rajendran, S., & Dhairiyasamy, R. (2024). Enhancing high-performance concrete sustainability: integration of waste tire rubber for innovation. *Scientific Reports*, 14(1). https://doi.org/10.1038/S41598-024-55485-9
- Smol, M., & Generowicz, A. (2018a). Treatment of the municipal landfill leachate including selection of the best management solution. *Desalination and Water Treatment*, 117, 229– 238.
- Smol, M., & Generowicz, A. (2018b). Treatment of the municipal landfill leachate including selection of the best management solution. *Desalination and Water Treatment*, 117, 229– 238. https://doi.org/10.5004/DWT.2018.22468
- Tahsini, M. J., Nikaeen, M., & Nafez, A. H. (2024). Biological treatment of compost leachate: Assessing the efficacy of composting process and bioaugmentation of composting piles. *Environmental Technology & Innovation*, 36, 103859.
- Tsompanoglou, K., Iliopoulou, A., Mastoras, P., & Stasinakis, A. S. (2024). A new approach on the management of landfill leachate reverse osmosis concentrate: Solar distillation coupled with struvite recovery and biological treatment. *Chemosphere*, *366*, 143574. https://doi.org/10.1016/J.CHEMOSPHERE.2024.143574
- Visvanathan, C., Choudhary, M. K., Montalbo, M. T., & Jegatheesan, V. (2007). Landfill leachate treatment using thermophilic membrane bioreactor. *Desalination*, 204, 8–16.
- Wdowczyk, A., Szymańska-Pulikowska, A., & Gupta, A. (2024). Application of selected indicators to assess contamination of municipal landfill leachate and its impact on

groundwater. *Water Resources and Industry*, 32, 100265. https://doi.org/10.1016/J.WRI.2024.100265

- Wichitsathian, B. (2004). Application of membrane bioreactor system for landfill leachate treatment.
- Yelebe, Z. R., Yelebe, B. Z., & Samuel, R. J. (2014). Design of fixed bed column for the removal of metal contaminants from industrial waste water. *Journal of Engineering and Applied Sciences*, 5(2), 68–77.
- Zaman, F., Rahman, Md. A., Haque, Md. M., Akbor, Md. A., & Tareq, S. M. (2024). Pervasiveness and classification of microplastics in Landfill Leachate: Impacts, risks, and treatment efficiency. *Chemosphere*.

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