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Continuous Removal of Organic Micropollutants from Municipal Treated Effluents and Studying Kinetics of Removal of Methylene Blue as a Model Micropollutant Component in Batch and Continuous Flow Systems

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Abstract

This research investigates the effectiveness of granular activated carbon (GAC) in eradicating micropollutants (pharmaceuticals, dyes, pesticides….etc.) from treated effluents of municipal wastewater treatment plants. By using methylene blue as a model representative organic micropollutant, the study examines the mechanisms involved in its removal. Through batch experiments, the study demonstrates impressive removal efficiency; displaying an absorption capacity of 349.3 mg/g. Factors such as contact time, initial dye concentration and GAC particle size have an impact on the removal efficiency while pH levels (2-11) minimally affects the absorption process. The kinetics are analyzed utilizing Langmuir and Freundlich models. In continuous flow experiments, lab-scale GAC filters sustain remarkable removal efficiency for the target across various flow rates. The study also addresses scalability, revealing a reduction in removal percentages from 93.9% to 88.8% as flow rates increase from (1m3/h) to (5m3/h). These discoveries provide crucial insights into devising effective strategies to combat the potential dangers posed by micropollutants.

Keywords: Municipal effluents; Micropollutants; Continuous Removal; Granular Activated Carbon (GAC); Methylene Blue; Optimizations and Kinetics

1. Introduction

Micropollutants encompass a diverse group of organic compounds, such as pharmaceuticals, personal care products, pesticides, textile, …..etc. which ultimately find their way to municipal wastewater treatment plants and can easily contaminate the surrounding environment. While these compounds are typically present in low concentrations in wastewater, they can have detrimental effects on aquatic organisms, ecosystem functions, and human being. (Verlicchi et al., 2010; Ahammad et al., 2019). Fresh water scarcity effect dramatically many countries around the world, scientists have been forced to find solutions for reuse municipal wastewater treated effluent. Strong limitation for reusing municipal wastewater treated effluent was suggested to be the micropollutants (Dong et al., 2016; Gogoi et al., 2018; Yacouba et al., 2021). Numerous treatment technologies have been developed to eliminate micropollutants from municipal wastewater most of these technologies are

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complicated or highly expensive. Combination of membrane bioreactor (MBR), nanofiltration (NF) and advanced oxidation process (Ozonation) is utilized for getting rid of micropollutants from municipal effluents (Yacouba et al., 2021). Furthermore reverse osmosis (RO) had been investigated for high removal rate of the micropollutants (Garcia-Ivars et al. 2017, Licona et al. 2018). However, NF as well as Ro techniques have drawbacks related to the fouling problems in addition to the main famous limitation through using advanced oxidation routes which probably may cause more toxic byproducts than starting compound needing additional treatment to eliminate the added toxicity (Yacouba et al., 2021).

Pharmaceuticals and drugs or their derivatives normally excreted and reached the sewerage system. For long time ago methylene blue used as an effective compound in medications. It has been established that methylene blue is excreted through urine route which find the way to municipal wastewater treatment plants as an example of micropollutant (Disanto and Wagner 1972; Sörengård M. et al., 2019; Golovgo et al., 2020). Zapater-Pereyra et al., 2017, outlined a comprehensive review in the efficiency of using granular activated carbon (GAC) in treating water and wastewater. This type of carbon is distinguished by a high porosity with extensive surface area that can adsorb a wide range of pollutants and micropollutants (Zapater-Pereyra et al., 2017; Falås et al., 2015).

The adsorption mechanism involves both physical and chemical interactions between the micropollutants and the GAC surface. Physical adsorption occurs because of weak van der Waals forces, while chemical adsorption takes place through covalent or ionic bonds (Arévalo et al., 2019). The adsorption capacity of GAC is influenced by various factors, including the nature of the pollutants, properties of the GAC, and operating conditions (Li et al., 2020). There are two commonly employed adsorption systems for micropollutant removal: batch and continuous flow (Eusebi et al., 2019).

In batch systems, wastewater is mixed with GAC in a tank and allowed to settle for a specific period to facilitate the separation process, after which the treated water is discharged (Benner et al., 2019). Batch systems are simple and cost-effective but have relatively low treatment capacities and require significant land areas (Boehler et al., 2012). On the other hand, continuous flow systems involve passing wastewater through a GAC bed in a column (Radjenović et al., 2009). The GAC bed is continuously regenerated through backwashing or air scouring to remove the adsorbed micropollutants (Kümmerer 2013; V et al., 2009; Tang et al., 2019). Continuous flow systems offer higher efficiency and treatment capacities but are more complex and expensive (Tang et al., 2019; Omran et al., 2020; Li et al., 2019; El-Kashef et al., 2019). To achieve the maximum removal efficiency of micropollutants while minimizing operating costs, the optimization of GAC filters is crucial (Li et al., 2020; Flindt et al., 2007).

This optimization process entails selecting the appropriate amount of activated carbon, particle size, contact time, and regeneration method (Gu et al., 2003). The contact time between wastewater and GAC determines the degree of adsorption, while the regeneration method affects the durability and reusability of the GAC (Thomas 1944). The kinetics of micropollutant removal by GAC filters is a complex process influenced by factors such as the type and concentration of micropollutants, properties of the GAC, and operating conditions (Freundlich 1906). Various models, including Langmuir, Freundlich, Thomas, Bohart, and Yoon, can be used to describe this kinetics (Langmuir 1918). The intraparticle diffusion model considers the diffusion of micropollutants within GAC pores as an additional rate-limiting step (Bohart 1920). In treated industrial wastewater, multiple types of residual micropollutants are often present, leading to competition for adsorption sites on GAC particles (Yoon 1984). This competition can result in reduced removal efficiency and complicate the optimization of GAC filters (Baker and Lonsdale 1991).

Micropollutants have become a growing concern for environmental scientists, policymakers, and the public at large (Schepers et al., 2011). These pollutants are commonly found in wastewater and have negative impacts on aquatic life and human health (Yao et al., 2017). Consequently, there has been increasing interest in utilizing GAC filters to effectively remove micropollutants from wastewater (Shon et al., 2006). This paper will provide a thorough examination of professional materials and methods concerning the potential removal of micropollutants from municipal wastewater through

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the application of GAC filters in both batch and continuous flow systems (Zhang et al., 2014). The study will cover aspects of optimization, kinetics, and theoretical models to shed light on this critical area of research (Bhatnagar et al., 2018).

The novelty and significance of this work are concerned with continuous micropollutant removal. This research offers an innovative approach by focusing on the complete and continuous elimination of micropollutants from wastewater. The study demonstrates the feasibility and effectiveness of employing (GAC) filters in achieving not only high but sustained removal rates over time. This work has enhanced removal efficiency since the study provides insights into improving the removal efficiency of micropollutants from wastewater by exploring various factors such as contact time, initial pollutant concentration, GAC particle size, and pH levels, the research identifies key parameters that significantly impact removal rates. This helps in optimizing and tailoring the treatment process for superior pollutant removal. The kinetic analysis is included in this work by employing Langmuir and Freundlich models, the research conducts a thorough analysis of the kinetics involved in the adsorption process.

This analysis offers a comprehensive understanding of the adsorption behavior, providing crucial information on the capacity, efficiency, and factors influencing the removal process. The study extends its exploration to continuous flow experiments, which represents a departure from traditional batch experiments. This approach allows for a more practical and realistic simulation of real-world scenarios, demonstrating the effectiveness of GAC filters even under continuous flow conditions. Addressing the implications of scalability, the study reveals the impact of varying flow rates on removal efficiency. The findings showcase the decreasing removal percentages at higher flow rates, underscoring the necessity of considering scalability and practical applications when implementing GAC filters in large-scale wastewater treatment. Overall, this work's novelty lies in its comprehensive investigation into continuous micropollutant removal using GAC filters, its deep analysis of influential parameters, and its implications for real-world applications in municipal wastewater treatment for reuse. This offers promising strategies for the effective, ongoing removal of micropollutants from

wastewater, thereby contributing to the advancement of sustainable and efficient treatment practices.

2. Materials and Methods

2.1. Materials

Fig. 1 presents more illustrations of experimental setups since A) represents a continuous lab-scale GAC plant and the description of a compact lab-scale setup featuring a continuous flow system with (GAC) for treating model wastewater. The plant is equipped with monitoring instruments to investigate related kinetics. The system constitutes some elements such as GAC columns for continuous flow, pumps for wastewater circulation, monitoring instruments for kinetic analysis, and inlet and outlet connections for wastewater. B) presents the continuous large-scale GAC plant and the description represents an enlarged version of the lab-scale setup, now designed for real wastewater treatment applications. This large-scale plant allows the implementation of the treatment technology in practical scenarios. The system displays many elements such as larger GAC columns for increased capacity, advanced instrumentation for real-time monitoring, integration with a real wastewater source, and control panels for system management. C) presents a multi sieves apparatus which constitutes an apparatus designed for the determination of particle size distribution. Multiple sieves with varying mesh sizes are arranged systematically to separate and classify particles present in the sample. This part contains some items such as sieves of different mesh sizes, shaking or vibrating mechanisms for efficient sieving, collection pans for separated particles, and sample input and output ports. These descriptions aim to provide a conceptual understanding of each component in the figure. For a more visual representation, you may consider using graphic design software or consulting with a graphic designer to create an illustrative diagram based on these textual descriptions. The investigation encompassed a diverse array of substances and tools, including reagents and devices detailed in the following sections. Granulated activated carbon (GAC) was acquired from Carbo Tech AC GmbH, located at Elisenstrasse 119, D-

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45139 Essen, Germany. Municipal wastewater treatment plant located at ISWA, Uni-Stuttgart, D-70569 Stuttgart, Germany consists of main treatment units; primary sedimentation, aeration parallel with rotating biological contactors (RBC), secondary sedimentation and finally microfiltration. Treated effluent collected after microfiltration was the main source of the target micropollutant. Methylene blue was supplied by Merck, Germany. pH adjustments were made using (1 N) HCl and NaOH solutions. pH levels were measured with a WTW pH meter, and batch experiments were conducted in 1-L glass beakers using a 6-set Jar-Test device.

2.2. Methods

2.2.1. Batch Experiments by 6-set Jar Test

The 6-set Jar Test is a laboratory procedure commonly employed in water treatment and environmental engineering to evaluate the efficiency of coagulants and flocculants in the removal of impurities, such as suspended particles, from water. The test involves using six laboratory beakers or jars to simulate and optimize the coagulation and flocculation processes on a small scale. The primary purpose of the 6-set Jar Test is to determine the optimal dosage of coagulants or flocculants needed for effective water treatment. It helps assess the settling characteristics of suspended particles under different conditions. Six identical jars or beakers are filled with a representative water sample from the source that needs treatment. Different dosages of coagulants or flocculants are added to each jar. This creates a range of concentrations to observe the impact on coagulation and flocculation. The content in each jar is mixed using a stirrer or paddles. The mixing speed and duration simulate the process of coagulation and flocculation in a larger treatment system. After mixing, the contents are allowed to settle. This phase imitates the sedimentation process in a water treatment plant. The clarity and quality of the water in each jar are observed after settling. This includes looking for the formation of flocs and the clarity of the supernatant. The dosage that produces the clearest supernatant water with well-formed and

settled flocs is considered the optimal dosage for treatment. The test can be repeated with adjustments to dosages to fine-tune the process. Turbidity measurements or other relevant parameters may be taken to quantify the effectiveness of the treatment at different dosages. The results, including the optimal dosage and observed changes, are documented for further analysis and as a reference for the full-scale treatment plant. In this manuscript, Jar Test is used as mixing apparatus.

2.2.2. Continuous Flow Experiments

Continuous flow experiments were performed using a laboratory-scale GAC plant (Fig. 1-A) and a Large-Scale GAC plant (Fig. 1-B). The laboratory-scale plant comprised a 15.5 cm column packed with 50 g of activated carbon, totaling 200 ml. In contrast, the large-scale GAC plant had a 2 m³ volume with a height of approximately 3.8 m, including a 40 cm washing unit. The plant was filled with 1000 kg of mixed GAC, equivalent to a height of about 3 m. Wastewater entered through an up-flow path circulated through the GAC filter, and the treated effluent was released at the filter's summit. Compressed air, directed towards the plant's base, conveyed contaminated activated carbon and some water to the washing unit, where it was cleansed and rejuvenated. The rejuvenated GAC descended to the filter's surface, and the cyclic process continued. Wastewater from the washing unit was accumulated and pumped into the activated sludge tank, serving as a seed agent to enhance the precipitation process. The treated water was then discharged into a nearby surface water body, ensuring proper management of the effluent. Particle size distribution in (GAC) was assessed using a multi-sieve apparatus (Fig. 1-C), segregating it into three distinct size categories. The study employed two primary methodologies: batch and continuous. Batch experiments utilized the 6-set Jar Test to optimize activated carbon dose, particle size, pH, contact time, and initial dye concentration. Continuous experiments employed a Lab-Scale plant (Fig. 1-A) to ascertain the most effective flow rate and develop kinetic models. The Lab-Scale plant was then upscaled to a Large-Scale GAC plant (Fig. 1-B) positioned downstream of the secondary

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sedimentation tank and microfiltration unit in the ISWA municipal wastewater treatment plant. A spectrophotometer monitored and quantified pollutant concentrations. The treated wastewater, originating from a biologicalaerobic treatment plant, underwent comprehensive analysis for micropollutants. Spectrophotometry measured micropollutants by assessing the spectral absorption coefficient SAC254, providing insights into remaining dissolved organics (Karsten et al., 2013).

Fig. 1: A) Continuous Lab-scale GAC-Plant: used for the treatment of model wastewater and for finding related kinetics B) Continuous Large-scale GAC plant: used for application of the treatment technology in real wastewater C) Multi sieves apparatus: utilized for particle size distribution.

3. Results and Discussions

3.1. Properties of GAC and Wastewater

Table 1 presents the particle size distribution of the (GAC) before any treatment, indicating the percentage distribution of GAC particles within various size ranges. The separation process yielded 15.239 kg of GAC, and the particle sizes were categorized. The distribution highlights that a significant portion of the GAC falls within the range of 2400 μm - 1400 μm, constituting 45.15% of the total. This size range likely includes larger particles that may contribute to the overall filtration and adsorption capabilities of the GAC. The finer fractions, represented by particles greater than 1250 μm, 900 μm, and 630 μm, make up 1%, 36%, and 12% of the total, respectively. These finer particles could enhance the surface area available for adsorption and contribute to the effectiveness of GAC in capturing contaminants. The smallest size categories, including particles greater than 560 μm, 500 μm, and 250 μm, account for 4.8%, 0.37%, and 0.68%, respectively. While these fractions constitute a smaller percentage of the total mass, they may play a crucial role in providing additional active sites for adsorption and improving the overall efficiency of the GAC. The particle size distribution is a crucial parameter as it influences the adsorption capacity and filtration performance of the GAC. The diverse range of particle sizes observed in Table 1 suggests that the GAC has a varied structure, potentially offering a well-balanced combination of adsorption capabilities. The effectiveness of GAC in water treatment processes often relies on the interplay of different particle sizes, providing an optimal surface area for the adsorption of contaminants.

Table 1: Particle size distribution using 15.239 kg of GAC before treatments

2400 μm -1400 μm	>1250 μm	>900 μm	>630 μm	>560 μm	>500 μm	>250 μm
45.15 %	1.0 %	36.0 %	12.0 %	4.8%	0.37%	0.68%

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Table 2 provides a comparison of wastewater characteristics before and after treatment, highlighting the changes in various parameters following the treatment process. The parameters examined include Chemical Oxygen Demand (COD), Total Nitrogen, and Total Phosphorus, with values presented in milligrams per liter (mg/L). The average values for municipal wastewater influent and treated effluent are reported. The significant reduction in COD from 326 mg/L in the influent to 18.9 mg/L in the effluent demonstrates the efficacy of the treatment process in removing organic pollutants. COD is a key indicator of the amount of organic matter in wastewater, and the substantial decrease indicates successful organic pollutant removal. The reduction in total nitrogen from 41.8 mg/L to 22.4 mg/L suggests the effective removal of nitrogen compounds during the treatment.

Nitrogen compounds, including ammonia and nitrate, are common pollutants in wastewater, and their decrease signifies improved water quality. The treatment process has notably decreased the total phosphorus content from 4.6 mg/L in the influent to 0.22 mg/L in the effluent. Phosphorus removal is crucial as it is a limiting nutrient in water bodies, and excessive phosphorus can contribute to eutrophication. The substantial reduction reflects the efficiency of the treatment in controlling phosphorus levels. In summary, Table 2 indicates that the treatment process has effectively improved the quality of the wastewater by reducing the concentrations of COD, total nitrogen, and total phosphorus. The lower values in the treated effluent suggest the successful removal of organic and nutrient pollutants, demonstrating the potential of the applied treatment technology in enhancing water quality.

Table 2: Wastewater characterizations before and after treatment

Parameters	Municipal wastewater influent*	Treated Effluent*
COD, mg/L	326.0	18.9
Total nitrogen, mg/L	41.8	22.4
Total Phosphorus, mg/L	4.6	0.22

*Average of five samples

3.2. Batch Experiments Optimization of pH, GAC Dose, Contact Time, and Initial Concentration of Methylene Blue

To optimize the procedures for the removal of micropollutants from real treated effluent of municipal wastewater, a series of batch trials were conducted using a representative organic contaminant. Methylene blue dye was specifically chosen as a suitable model contaminant for adsorption by (GAC). The refinement of the process was achieved through 6-set-jar test experiments. The efficiency in eliminating methylene blue (MB) at a concentration of 6 mg/L was assessed with a (GAC) removal, as described in the context of the study, is effective across various levels of acidity in wastewater streams. If the study provides evidence or experimental results demonstrating the effectiveness of the adsorption process across a range of pH levels, and if this information was not well-established or documented in previous literature, then it could be

dose of 2 g/L and agitation at 200 rpm for 120 minutes. The progress of dye removal was monitored at 30-minute intervals.

The efficiency graph (Fig. 2-A) revealed that the removal efficacy remained relatively consistent across different pH values (2-11), with a slightly higher preference observed at pH 2. This observation suggests the viability of the adsorption process for eliminating pollutants across a spectrum of acidity levels present in wastewater streams. The statement suggests that the adsorption process for pollutant considered a promising finding. The removal of dye is closely linked to the (GAC) dosage. Various GAC doses (1 g/L, 2 g/L, 3 g/L, and 5 g/L) were employed to achieve an approximate pH level of 7. The use of different GAC amounts resulted in complete dye removal, although at different timeframes.

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Higher GAC doses led to shorter times for total elimination. For instance, a higher dose (5 g/L) achieved complete dye removal within 60 minutes, whereas a lower GAC dose (1 g/L) required 180 minutes for full elimination. Fig. 2-B illustrates the impact of GAC dosage on the percentage of methylene blue dye removal. The outcomes demonstrate that higher doses reduce removal time, while lower doses provide cost-efficiency, striking a balance between time effectiveness and cost savings. The results indicate that higher doses result in reduced removal time, while lower doses are cost-effective, offering a trade-off between time efficiency and cost savings" implies a crucial aspect of the experimental outcomes in the context of pollutant removal using (GAC).

The observation that higher doses of GAC lead to reduced removal time suggests that increasing the amount of GAC enhances its adsorption capacity. With more active sites available, the pollutant molecules are adsorbed more rapidly, resulting in a quicker removal process. This finding is valuable in practical applications where time efficiency is a critical factor. Faster pollutant removal can be advantageous in scenarios where rapid water treatment is required, such as in emergency response situations or high-demand industrial processes. The statement suggests that lower doses of GAC are cost-effective. This can be interpreted as a trade-off where, despite a potentially longer removal time, the economic benefits of using less GAC may outweigh the extended treatment duration. In real-world applications, cost-effectiveness is a key consideration. If achieving a certain level of pollutant removal is acceptable over a more extended period, using lower GAC doses becomes economically viable. The study's findings provide insights into the delicate balance between time efficiency and cost savings. Depending on specific requirements and constraints, water treatment operators can make informed decisions on the appropriate GAC dosage for their particular scenario.

The concept of a trade-off implies that there is no one-size-fits-all solution. Decision-makers must carefully weigh the advantages of faster pollutant removal against the economic considerations of GAC usage. Lower GAC doses may have positive implications for resource sustainability, as they indicate a potential reduction in the overall consumption of GAC material. Considering the life cycle of GAC production and disposal, a reduction in

GAC usage could contribute to minimizing the environmental impact associated with its extraction, manufacturing, and eventual disposal. Generally, the results highlight the practical considerations that arise when optimizing GAC usage for pollutant removal. The balance between higher doses for faster removal and lower doses for cost-effectiveness is a nuanced decision that depends on specific operational needs and economic factors.

The use of (GAC) with varied particle sizes, namely GAC≥900 μm, GAC<900 μm, and mixed GAC, exhibited distinct effectiveness in pollutant removal (refer to Fig. 2-C). The results demonstrate that as the particle size decreased, the removal efficiency increased, while the absorption capacity amplified with longer contact times. The limited difference observed between mixed (GAC) and particle size greater than 900 μm in terms of adsorption efficiency for Methylene Blue (MB) can be attributed to several factors.

The adsorption capacity and efficiency of GAC are influenced by its surface characteristics, such as pore structure and specific surface area. If the mixed GAC and the larger particle size GAC have similar surface properties, their adsorption performance may not exhibit significant differences. The efficiency of adsorption is often influenced by the contact time between the adsorbent (GAC) and the adsorbate (MB). If both mixed GAC and larger particle size GAC have comparable contact times during the adsorption process, their performance may converge. Pore diffusion within the GAC particles can impact the rate of adsorption. If both mixed GAC and larger particle size GAC have similar pore diffusion characteristics, it may lead to comparable adsorption behavior. The nature of the adsorbate, in this case, Methylene Blue, may play a role. If MB has a higher affinity for specific sites on GAC that are consistent across different particle sizes, the variation in adsorption efficiency may be limited. The composition and distribution of GAC in the mixed sample could influence its overall adsorption capacity. If the mixture is homogenous and well-blended, it may exhibit performance similar to larger particle size GAC. Factors such as pH, temperature, and initial concentration of MB can affect adsorption behavior. If the experimental conditions were chosen in a way that minimizes the impact of particle size variation, it could contribute to the observed similarity in adsorption performance. If the particle size range of the larger GAC is not significantly

different from the mixed GAC, the variations in adsorption behavior may be subtle. It's possible that the conditions tested favor both mixed GAC and larger particle size GAC equally, minimizing the observable differences in adsorption efficiency. Generally, the minimal difference between mixed GAC and particle size greater than 900 μm may result from the interplay of various factors related to the adsorption process, the specific characteristics of GAC, and the experimental conditions employed in the study. Further detailed investigations and analysis of these factors could provide insights into the observed similarities in performance.
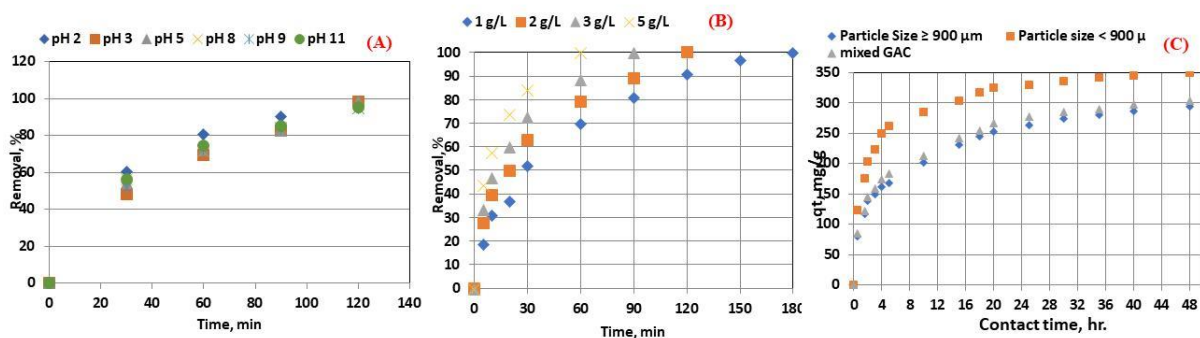

Fig. 2: A) Effect of pH on the removal efficiency of MB by GAC at different contact times B) Effect of GAC dose in removal efficiency of MB at different contact times C) Effect of contact time on dye removal exploring the breakthrough and reaching equilibrium.

A concentration of 2 g/L of (GAC) at pH 7 was utilized for 120 minutes with stirring using the Jar Test method. The effectiveness of dye absorption exhibits an increase with higher initial dye concentrations, allowing more dye molecules to occupy the available active sites on the GAC (refer to Fig. 3-A & Fig. 3-C). The removal efficiency of the dye from wastewater is influenced by various factors, with the concentration of the dye playing a significant role.

Firstly, there is a finite number of active sites available for adsorption on the (GAC), resulting in competition among more dye molecules at higher concentrations. Consequently, some dye molecules may not find available sites for adsorption, thereby reducing removal efficiency (Abdelfattah et al., 2022a). Secondly, a saturation effect occurs at higher dye concentrations, where active sites on the GAC become saturated more quickly. Once the active sites are saturated, the GAC becomes less effective in adsorbing additional dye molecules.

The concentration of the dye in the wastewater substantially impacts the efficiency of the treatment process. Generally, as the dye concentration increases, the efficiency of dye removal decreases (refer to Fig. 3-B & Fig. 3-D). This decline in removal efficiency with increasing dye concentration can be attributed to several factors.

This saturation effect leads to reduced removal efficiency with increasing dye concentration. The third factor relates to diffusion limitations, as higher dye concentrations can increase mass transfer resistance. This higher concentration may hinder the diffusion of dye molecules to the surface of GAC particles, limiting contact and reducing removal efficiency (Abdelfattah et al., 2022b).
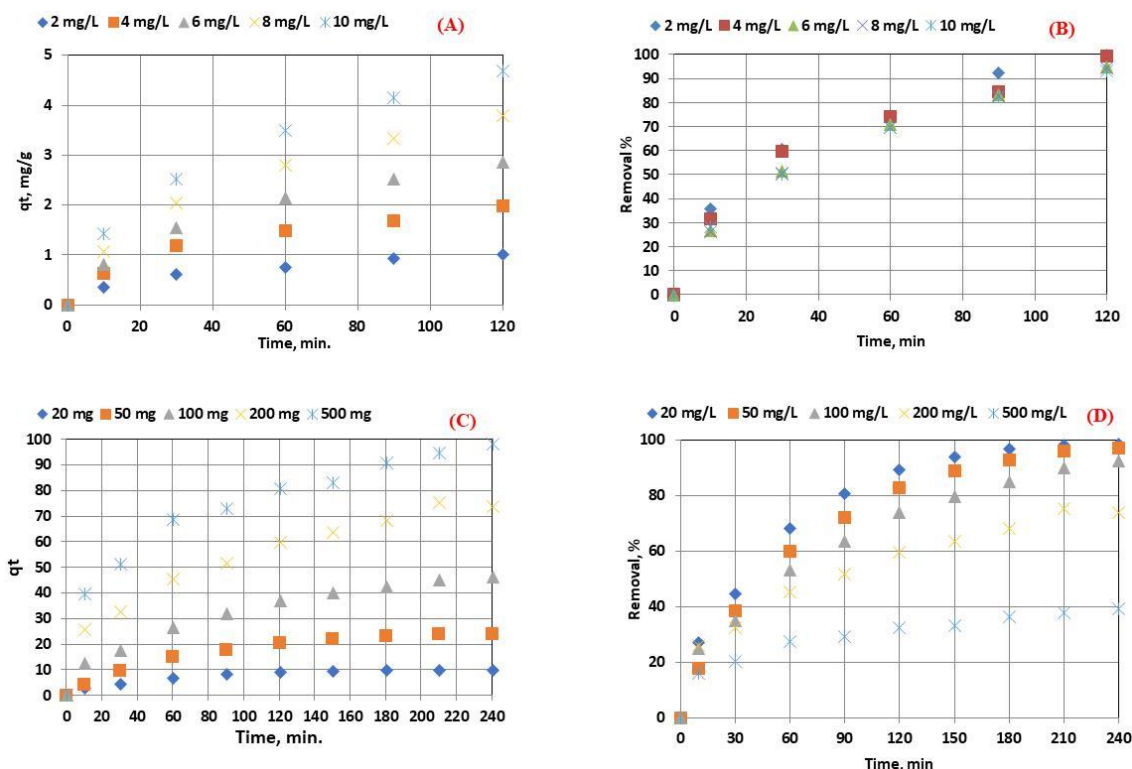
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Fig. 3: A) Initial low-range concentration of MB (2-10 mg/L): effect on dye uptake by GAC B) Initial low-range concentration of MB (2-10 mg/L): effect on percentage removal of dye by GAC C) Higher initial concentration of MB (20-500 mg/L): effect on dye uptake by GAC D) Higher initial of MB (20-500 mg/L): effect on percentage removal of dye by GAC

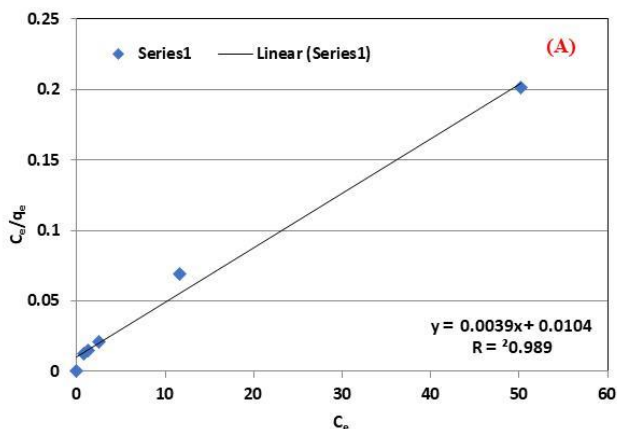### 3.3. Adsorption Isotherm in Batch Conditions
3.3.1. Mixed AC

The data presented in Fig. 4-A elucidates the Langmuir isotherm and its associated parameters concerning the adsorption of (MB) on mixed (GAC). Each parameter imparts specific characteristics to the adsorption process. The slope, indicative of the Langmuir constant associated with adsorption energy, is 0.0039, suggesting a relatively low energy of adsorption. Meanwhile, the intercept, representing the equilibrium concentration of adsorbate molecules on the adsorbent surface, is 0.0104, indicating a small amount of adsorbate present at equilibrium. The maximum monolayer adsorption capacity of the adsorbent (q_m) is 256.4103, implying a relatively high adsorption capacity for MB. KL, another Langmuir constant linked to the rate of adsorption, has a value of 0.375, indicating a moderate rate of adsorption. The RL value, also known as the separation factor, ranges from 0.026 to 0.229, signifying highly favorable adsorption of MB onto the mixed GAC. The coefficient of determination (R^2) is 0.989, indicating a strong correlation between

the Langmuir model and the experimental data. This underscores the adequacy of the Langmuir isotherm in describing the adsorption behavior of MB on the mixed GAC. To summarize, the Langmuir parameters suggest that the mixed GAC exhibits a high adsorption capacity for MB, and the Langmuir isotherm model aligns well with the experimental data, providing valuable insights for predicting and understanding the adsorption process for removing MB from wastewater using mixed GAC.

Regarding Fig. 4-B, it depicts the Freundlich adsorption isotherm and its associated parameters. The slope, representing the Freundlich constant related to adsorption intensity, is 0.3126, indicating moderate adsorption intensity. The intercept, linked to adsorption capacity, is 4.3454, signifying a relatively high adsorption capacity for MB on the mixed GAC. The 'n' value, determining adsorption intensity, is 3.198976, suggesting favorable adsorption behavior. Furthermore, the natural logarithm of KF and KF itself highlights a relatively high adsorption capacity for MB on the mixed GAC, providing useful insights into the adsorption process. The coefficient of determination (R^2) for the

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Freundlich model and the experimental data is 0.9589, indicating a reasonably strong correlation. This suggests that the Freundlich isotherm is reasonably suitable for predicting and describing the adsorption behavior of MB on mixed GAC. In

essence, the Freundlich parameters indicate moderate to high adsorption intensity and capacity for MB, offering valuable insights into optimizing MB removal from wastewater using mixed GAC.

Slope	Intercept	q_m	K_l	R_l	R^2
0.0039	0.0104	256.4103	0.375	0.026-0.229	0.989
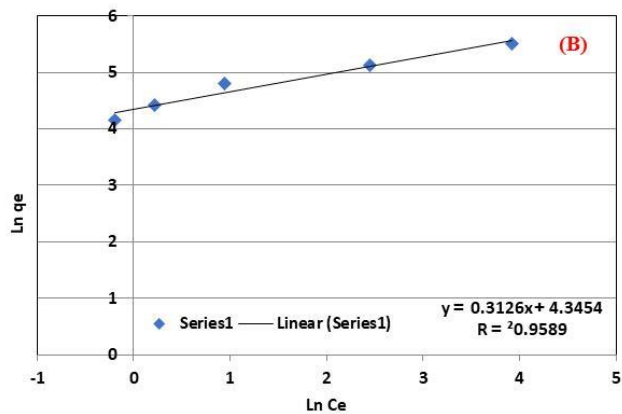
Slope	Intercept	n	$Ln K_F$	K_F	R^2
0.3126	4.3454	3.198976	4.3454	77.12288	0.9589

Fig. 4: A) Langmuir isotherm for adsorption of dye on mixed GAC and its parameters B) Freundlich adsorption isotherm for adsorption of MB on mixed GAC and its parameters

3.3.2. GAC, Particle Size ≥ 900 µm

The data extracted from Fig. 5-A elucidates the Langmuir adsorption isotherm and its parameters concerning the adsorption of Methylene Blue (MB) on large-size (GAC). Each parameter imparts specific insights into the adsorption behavior. The slope, indicative of the Langmuir constant associated with adsorption energy, is 0.004, suggesting a relatively low energy of adsorption. Meanwhile, the intercept, representing the equilibrium concentration of adsorbate molecules on the adsorbent surface, is 0.0105, indicating a small amount of adsorbate present at equilibrium. The maximum monolayer adsorption capacity (qm) of the large-size GAC is 250, indicating a moderate adsorption capacity for MB but less than the qm value for mixed GAC due to the larger particle size range.

KL, another Langmuir constant related to the rate of adsorption, has a value of 0.381, suggesting a moderate rate of adsorption. The RL value, indicating the separation factor, ranges from 0.026 to 0.226, signifying highly favorable adsorption of MB onto the large-size GAC. The coefficient of determination (R²) for the Langmuir model and the experimental data is 0.9889, indicating a strong correlation. This implies that the Langmuir isotherm effectively describes the adsorption behavior of MB on the large-

size GAC. To summarize, the Langmuir parameters demonstrate that the large-size GAC has a moderate adsorption capacity for MB, with highly favorable adsorption characteristics. The Langmuir isotherm model fits well with the experimental data, offering valuable insights for predicting and understanding the adsorption process to remove MB from wastewater using large-size GAC. Fig. 5-B, showcases the Freundlich adsorption isotherm and the associated parameters for MB adsorption on large-size (GAC). The slope, representing the adsorption intensity, is 0.3028, denoting a moderate adsorption intensity.

The intercept, indicative of adsorption capacity, is 4.3467, signifying a relatively high adsorption capacity for MB on the large-size GAC. The 'n' value, indicating adsorption behavior, is 3.30251, suggesting favorable adsorption behavior. The natural logarithm of KF and the value of KF highlight a relatively high adsorption capacity for MB on the large-size GAC. The coefficient of determination (R²) for the Freundlich model and the experimental data is 0.9544, suggesting a reasonably strong correlation. This indicates that the Freundlich isotherm is relatively suitable for predicting and describing the adsorption behavior of MB on large-size GAC. In essence, the Freundlich parameters imply moderate

adsorption intensity and a high adsorption capacity for MB with large-size GAC. The Freundlich isotherm model fits reasonably well with the experimental data, offering insights into the adsorption process to optimize MB removal from wastewater using large-size GAC.
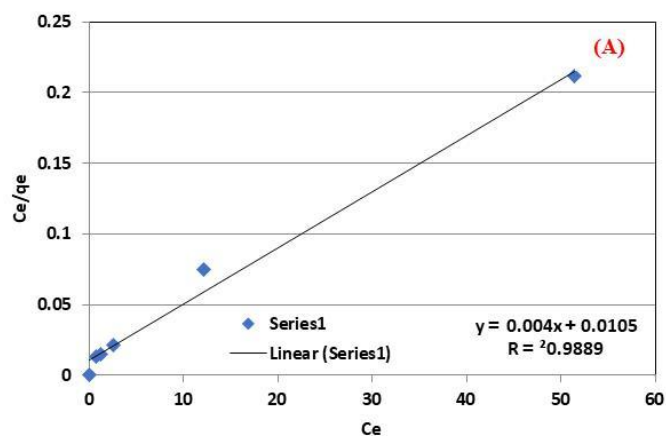
Slope	Intercept	q_m	K_L	R_L	R^2
0.004	0.0105	250	0.381	0.026-0.226	0.9889
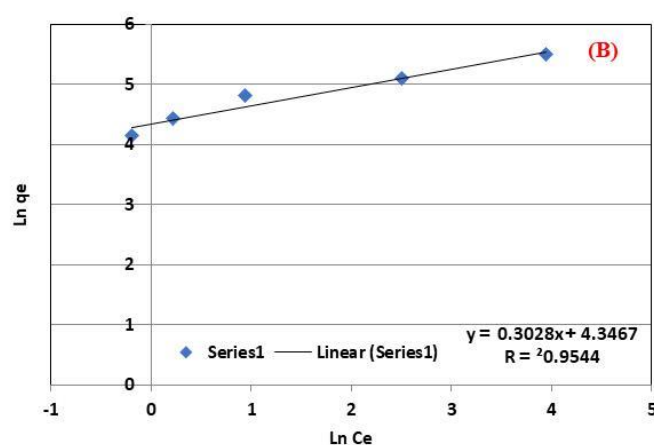
slope	Intercept	n	Ln K_F	K_F	R^2
0.3028	4.3467	3.30251	4.3467	77.22321	0.9544

Fig. 5: A) Langmuir adsorption isotherm for adsorption of dye on large-size GAC and its parameters B) Freundlich adsorption isotherm for adsorption of MB on large-size GAC and its parameters

3.3.3. GAC Particle Size < 900 μm

Fig. 6-A illustrates the Langmuir adsorption isotherm and its parameters for Methylene Blue (MB) adsorption on small-size (GAC). The slope, indicating relatively low adsorption energy, is 0.0037, while the intercept of 0.0114 suggests a small amount of adsorbate at equilibrium on the GAC's surface. The maximum monolayer adsorption capacity (qm) is 270.27, signifying a relatively high capacity for MB on the small-size GAC, which is higher compared to other GACs. KL, the Langmuir constant for the rate of adsorption, stands at 0.325, suggesting a moderate rate. RL values ranging from 0.03 to 0.255 indicate highly favorable adsorption of MB on the small-size GAC. With an R² value of 0.971, there's a strong correlation between the Langmuir model and the experimental data, showing the model's suitability for describing MB adsorption on the small-size GAC. The small-size GAC exhibits a notably high adsorption capacity for MB, coupled with highly favorable adsorption characteristics, according to the Langmuir parameters. The Langmuir isotherm effectively describes MB adsorption on the small-size GAC, offering valuable insights for optimizing MB removal from wastewater using this GAC size. In Fig. 6-B, the Freundlich parameters for MB adsorption on large-size (GAC) are outlined. The slope of 0.1846 indicates relatively low adsorption intensity, and the intercept of 4.6916 suggests a moderate adsorption capacity for MB on the large-size GAC. 'n,' the exponent in the Freundlich equation, stands at 5.417118, signaling relatively high adsorption intensity, surpassing the values observed for other GACs. Additionally, the Ln KF value of 4.6916 denotes moderate adsorption capacity, with KF at 109.0275, indicating a relatively high adsorption capacity for MB on the large-size GAC. The R² value of 0.8801 indicates a moderate correlation between the Freundlich model and the experimental data, implying the model's capacity to describe MB adsorption on the large-size GAC.

Overall, the Freundlich parameters illustrate a moderate adsorption capacity for MB and relatively low adsorption intensity of the adsorption isotherm on the large-size GAC. The Freundlich model fits reasonably well with the experimental data, shedding light on the adsorption process for MB removal using large-size GAC. However, further investigations might be necessary to enhance the model's predictive capabilities.

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slope	Intercept	n	Ln K_F	K_F	R²
0.3028	4.3467	3.30251	4.3467	77.22321	0.9544

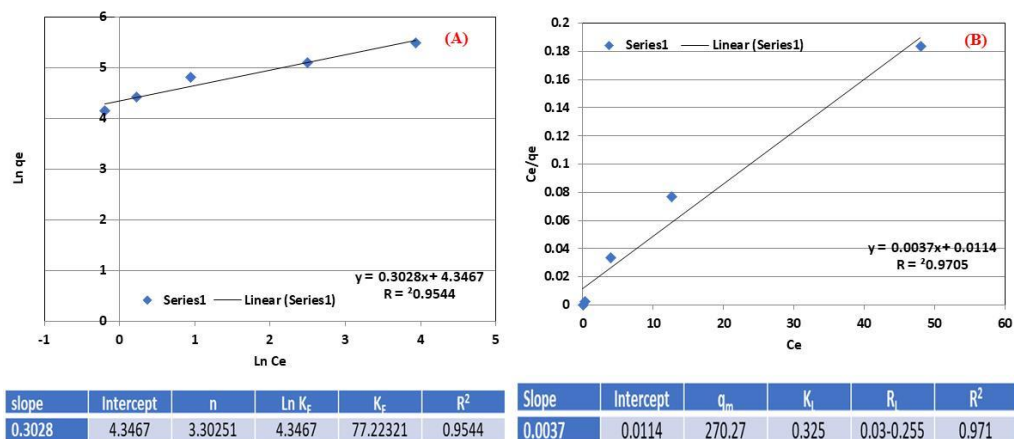| Slope	Intercept	q_m	K_l	R_l	R²
0.0037	0.0114	270.27	0.325	0.03-0.255	0.971

Fig. 6: A) Langmuir adsorption isotherm for adsorption of dye on small-size GAC and its parameters B) Freundlich adsorption isotherm for adsorption of MB on small-size GAC and its parameters

3.4. Continuous Experiments, Lab-Scale, Model Wastewater

Transferring the treatment process from batch to continuous had been achieved by utilizing a lab-scale plant containing an activated carbon filter unit (Fig. 1 B). The laminar flow existed when the flow rate did not exceed 250 ml/min. i.e. 0.015 m3/hr.

A = ∏ r2: r is the radius of the GAC column

A= 3.14 * (2.5)² ∴ A= 19.625 cm² =0.00196 m²∴ q = Q/A = 0.015 m³/hr ÷ 0.00196 m²

∴ q = 7.65 m/h

In the given equations, the A represents the cross-sectional area of the GAC column. In the equation A = ∏ r², A is calculated by multiplying the value of ∏ (pi, approximately 3.14) with the square of the radius (r) of the GAC column. The resulting value of A is 19.625 cm² or 0.00196 m². Q represents the flow rate of fluid passing through the GAC column. In this case, the given flow rate is 0.015 m³/hr, which is the amount of fluid passing through the column in one hour. q represents the superficial velocity or linear velocity of the fluid flowing through the GAC column. It is calculated by dividing the flow rate (Q) by the cross-sectional area (A) of the column. In this case, the value of Q is 0.015 m3/hr and the value of A is 0.00196 m2, which gives a value of q as 7.65 m/h (meters per hour). The cross-sectional area (A) of the GAC column is important for calculating the surface area available for adsorption and determining the efficiency of the adsorption process.

Flow rate (Q) is the rate at which the fluid passes through the column, and it determines the contact time between the fluid and the adsorbent material. It affects the adsorption kinetics and the overall efficiency of the process. Superficial velocity (q) represents the velocity at which the fluid moves through the column. It is an important parameter to consider for determining the residence time and the mass transfer rate during the adsorption process. Understanding and controlling these parameters is crucial in designing and optimizing GAC columns for effective adsorption processes.

3.4.1. Adsorption Isotherm in Continuous Flow Conditions (At 6 mg/L MB 50 g WAC>0.9 mm in column using flow rate of (200 ±10) ml/min)

3.4.1.1. Thomas Model

Thomas's paradigm is the simple and generally utilized paradigm reported by many researchers **(Abdelfattah et al., 2022b; Abdelfattah et al., 2022c; Abdelfattah et al., 2022d; Abdelfattah et al., 2023)**. Thomas's model wasadapted from the kinetics of the first-order reaction of the adsorption model which is expressed inlinear form equation (3) as:

$$Ln\left[\left(\frac{C_0}{C_e}\right)-1\right] = \frac{K_{Th}Q_{max}\,M}{F} - K_{Th}C_0 t \quad (3)$$

Where k_{Th} is the Thomas model constant (L/mg.hr), Q_{max} is the maximum uptake of solute (mg/g), t is the time (minutes), M mass of biosorbent, and F is the flow rate ml/min. C_0 is the initial concentration of ammonia and Ce is the

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concentration of MB in effluent solution. A conspiracy of Ln $[(C_0 /C)-1]$ against t for a given flow rate of 120, 200, and 450 ml/min can be applied to calculate the model constants. Figs. (7-A, 7-B and 7-C) show the linear nature of the model yielding a virtuous fitting for the investigational results at all flow rates with high correlation coefficients (R^2). The limitations of the Thomas model evaluated at the four rates of flow were reported in Fig. 7-C which showed adsorption capacity diminished with growing flow rate. From the isotherm equation, the following parameters can be calculated as explained below:

Slope = $-K_{Th} C_0$ (4)

so, the K_{Th} = -slope/C_0 (5)

And the intercept = $K_{Th} * Q_{max} * M/F$ (6)

So, Q_{max}= Intercept * F/K_{Th} * M (7)

From the aforementioned equations, K_{Th} and Q_{max} can be calculated. The Thomas kinetic model parameters for varied flow rates are illustrated in Fig. 7-C. The flow rate, expressed in ml/min, denotes the speed of the liquid phase moving through the system. Fig. 7-C shows three distinct flow rates: 120 ml/min, 200 ml/min, and 450 ml/min. K_{Th}, the Thomas kinetic model constant (measured in L/mg.hr), signifies the adsorption rate, representing how swiftly the adsorption process transpires. The respective values in Fig. 7-C are 0.008117 L/mg.hr, 0.011133 L/mg.hr, and 0.020167 L/mg.hr for the corresponding flow rates.Q_{max}, denoting the maximum adsorption capacity of the adsorbent material (measured in mg/g), specifies the peak amount of adsorbate that the adsorbent can absorb per unit mass. The values in Fig. 7-C for Q_{max} are 457.3996 mg/g, 263.9712 mg/g, and 151.914 mg/g for the respective flow rates. R^2 is the coefficient of determination, indicating the fitness of the Thomas kinetic model to the actual data. The R^2 values in Fig. 7-C for the distinct flow rates are 0.9753, 0.9885, and 0.9731, respectively. These values reflect the degree of alignment between the experimental data and the model predictions.

The Thomas kinetic model parameters offer insights into the adsorption dynamics at various flow rates. As the flow rate escalates from 120 ml/min to 450 ml/min, the K_{Th} value increases from 0.008117 L/mg.hr to 0.020167 L/mg.hr, signifying a swifter adsorption pace at higher flow rates. Concurrently, Q_{max} values decrease from 457.3996 mg/g to 151.914 mg/g, indicating a reduction in maximum adsorption capacity as the flow rate rises. This suggests that at elevated flow rates, the adsorbent becomes less effective in capturing the adsorbate.

The R^2 values, reflective of the model's alignment with the actual data, maintain relatively high consistency across all flow rates, ranging from 0.9753 to 0.9885. This underscores the robust correlation between the model predictions and the experimental data, affirming the Thomas kinetic model's precise description of the adsorption behavior within the system.

In conclusion, the Thomas kinetic model parameters provide substantial insights into the adsorption process at varying flow rates, offering a means to fine-tune the adsorption system, comprehend its kinetics, and estimate the maximum adsorption capacity in different operational scenarios. Notably, the study highlights that higher flow rates lead to accelerated adsorption rates (higher K_{Th} values) but reduced maximum adsorption capacity (lower Q_{max} values).

Moreover, the model demonstrates a strong fit with the actual data across different flow rates, demonstrating its efficacy in describing adsorption behavior.

These findings offer valuable implications for refining adsorption processes and comprehending the impact of flow rates on adsorption efficiency.

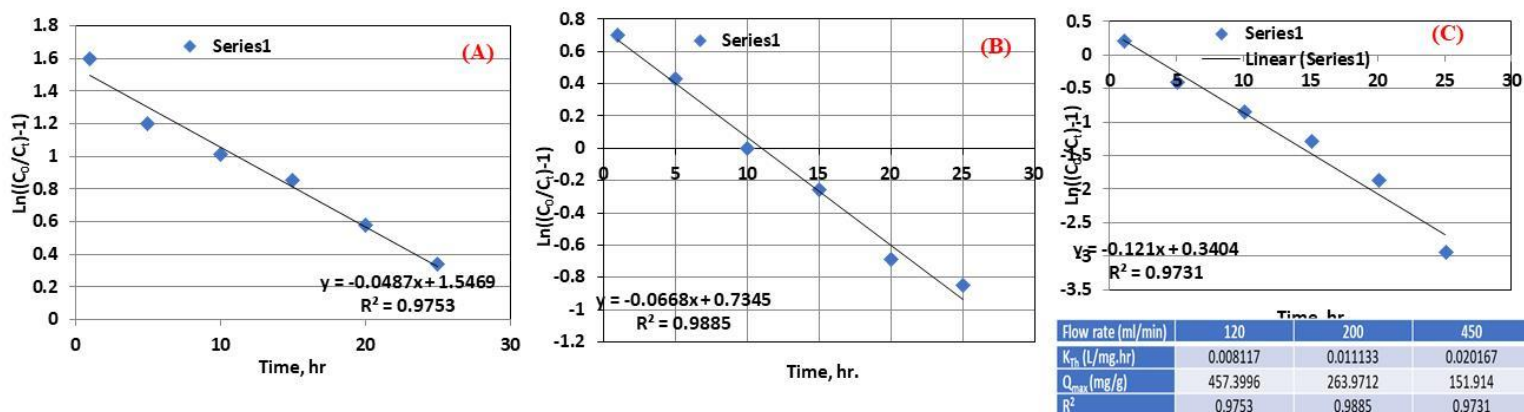| Flow rate (ml/min)	120	200	450
K_{Th} (L/mg.hr)	0.008117	0.011133	0.020167
Q_{max} (mg/g)	457.3996	263.9712	151.914
R^2	0.9753	0.9885	0.9731

Fig. 7: Plot Thomas's mathematical model for MB adsorption by bed column at different flow rates and their parameters A) 120 ml/min B) 200 ml/min C) 450 ml/min

3.4.1.2. Yoon and Nelson Model

This pattern estimates the possible decrease in the rate of adsorption which is directly proportional to its adsorption action; this model can be articulated as the following Equation (8):

$Ln[C_t/(C_0-C_t)] = K_{Y-N} t - K_{Y-N} t50$ (8)

Where C_0 (mg/L) is the initial load, C_e (mg/L) is the load at time t, k_{YN} (1/min) is the rate constant of velocity, and $t0.5$ (min) is the revolution band for 50% of ammonia being adsorbed by adsorbent Figs. (8-A and 8-B).

From the isotherm equation, the following parameters can be calculated as explained below:

Slope = k_{YN} (9)

and intercept = - k_{YN} t50   (10)

∴ t50 = - Intercept/k_{YN}(11)

From the aforementioned equations, K_{YN} and Q_{max} can be calculated.

Fig. 8-C exhibits the parameters of the Yoon and Nelson kinetic model for various flow rates. These flow rates represent the speed at which the liquid phase moves through the system. K_{YN} (1/min) denotes the rate constant of the Yoon and Nelson kinetic model, representing the speed of the adsorption process. The values in Fig. 8-C are 0.0489 1/min, 0.0665 1/min, and 0.121 1/min for the respective flow rates. t50 (min) signifies the time required for 50% of the adsorption to occur, essentially the half-life of the adsorption process. The values in Fig. 8-C are 31.67076 min, 10.96391 min, and 2.813223 min for the respective flow rates. $R2$,

indicating the coefficient of determination, measures the model's fit to the experimental data.

The values in Fig. 8-C are 0.9717, 0.9887, and 0.9717 for the respective flow rates. The Yoon and Nelson kinetic model parameters offer insights into the adsorption behavior at different flow rates. As the flow rate increases from 120 ml/min to 450 ml/min, the K_{YN} value also increases, signifying a swifter adsorption rate. This suggests that higher flow rates lead to more rapid adsorption kinetics. Concurrently, the t50 values decrease as the flow rate increases, indicating that at higher flow rates, it takes less time for 50% of the adsorption to occur. This implies that higher flow rates result in shorter durations to achieve a significant level of adsorption. The $R2$ values, indicative of the model's alignment with the experimental data, maintain relatively high consistency for all flow rates, suggesting a strong correlation between the model predictions and the actual data, affirming the accuracy of the Yoon and Nelson kinetic model in describing the system's adsorption behavior. In summary, the Yoon and Nelson kinetic model parameters reveal that higher flow rates lead to quicker adsorption rates and shorter durations required for adsorption to take place. The model aptly fits the experimental data, highlighting its capacity to delineate the adsorption behavior at varying flow rates. These findings can offer valuable insights into understanding and refining adsorption processes, particularly in predicting adsorption behavior under different flow rate conditions.
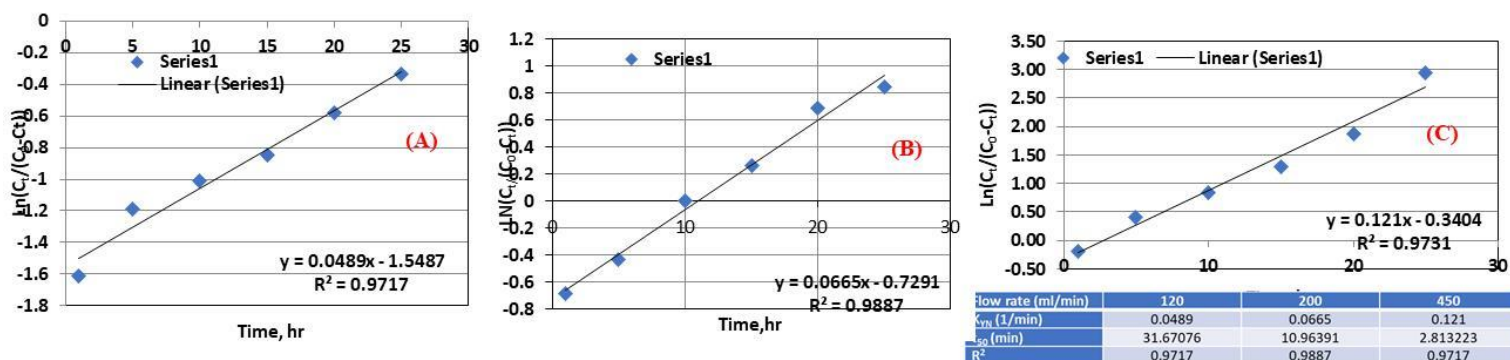
Fig. 8: Plot Yoon and Nelson's mathematical model for MB adsorption by bed column at different flow rates and their parameters A) 120 ml/min B) 200 ml/min C) 450 ml/min

3.4.1.3. Bohart-Adams Model

The Bohart-Adam model shows the adsorption rate is directly proportional to the adsorbent power and concentration used. The equation to the model is defined below:

$$Ln(C_t/C_0) = (K_{AB}\ C_0\ t) – K_{AB}\ N_0\ Z/U_0 \quad (12)$$

Where C_0 (mg/L) is the primary concentration, C_t (mg/L) is the concentration at time t, K_{AB} (L/mg.min) is constant of Borat-Adam kinetic, N_o (mg/L) is the saturation concentration, Z (cm) is the bed depth and U_0 (cm/min) is superficial velocity. see Figs. (9-A and 9-B).

Ln(C_t/C_0) against t is plotted to find the constants

Slope = $K_{AB}\ C_0$ (13)

∴ K_{AB} = Slope/C_0 (14)

Intercept = - $K_{AB}\ N_0\ Z/U_0$ (15)

N_0 = -Intercept U_0 / K_{AB} Z, U_0 can obtained from the equation:

volumetric flow rate, F (cm3/min) = velocity, U_0 (cm/min) * cross section area, A (cm2) i.e., U_0 = F (cm3/min) / A (cm2)

Fig. 9-C displays the parameters of the Adam-Bohart kinetic model for various flow rates, with the data portraying three distinct flow rates: 120 ml/min, 200 ml/min, and 450 ml/min, representing the liquid phase's flow rate through the system. K_{AB} (L/mg.min) signifies the rate constant of the Adam-Bohart kinetic model, indicating the pace of the adsorption process. The values in Fig. 9-C are 0.005783 L/mg.min, 0.00525 L/mg.min, and 0.004817 L/mg.min for the respective flow rates. N_0 (mg/L) represents the initial concentration of the adsorbate in the liquid phase at the onset of the

adsorption process. The values in Fig. 9-C are 378.6413 mg/L, 261.0616 mg/L, and 189.4695 mg/L for the respective flow rates. R2 stands for the coefficient of determination, evaluating the alignment of the Adam-Bohart kinetic model with the experimental data. The values in Fig. 9-C are 0.9561, 0.963, and 0.9301 for the respective flow rates. Z (cm) symbolizes the bed height or the liquid phase's travel distance through the adsorption column, remaining constant at 8 cm across all flow rates. U_0 (F/A) (cm/min) stands for the linear velocity or the superficial velocity of the liquid phase passing through the column, maintaining a constant value of 10.19108 cm/min for all flow rates.

The Adam-Bohart kinetic model parameters offer insights into the system's adsorption behavior at varying flow rates. The K_{AB} values remain relatively similar across different flow rates, suggesting similar adsorption rates within the range of considered flow rates. The decline in N_0 values with increasing flow rates implies a dilution effect, where at higher flow rates, the initial concentration of the adsorbate in the liquid phase diminishes. This suggests that the target compound gets diluted due to the amplified flow rate. The strong R2 values imply a commendable alignment between the Adam-Bohart kinetic model predictions and the experimental data, affirming the model's adequacy in delineating the adsorption behavior in the system. The constant Z and U_0 values denote an unchanged column setup and consistent liquid phase velocity, signifying the uniformity in the column's height and the liquid phase's pace throughout the experiments. In summary, the Adam-Bohart kinetic model parameters disclose insights into the adsorption process at varying flow rates.

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The consistent KAB values suggest a relatively stable adsorption rate. The diminishing N0 values point to the dilution effects at higher flow rates. The robust R2 values suggest a favorable model fit with the experimental data. The steady Z and U0 values indicate a consistent column setup and liquid phase velocity, presenting crucial information for understanding and optimizing the adsorption process across different flow rate conditions.

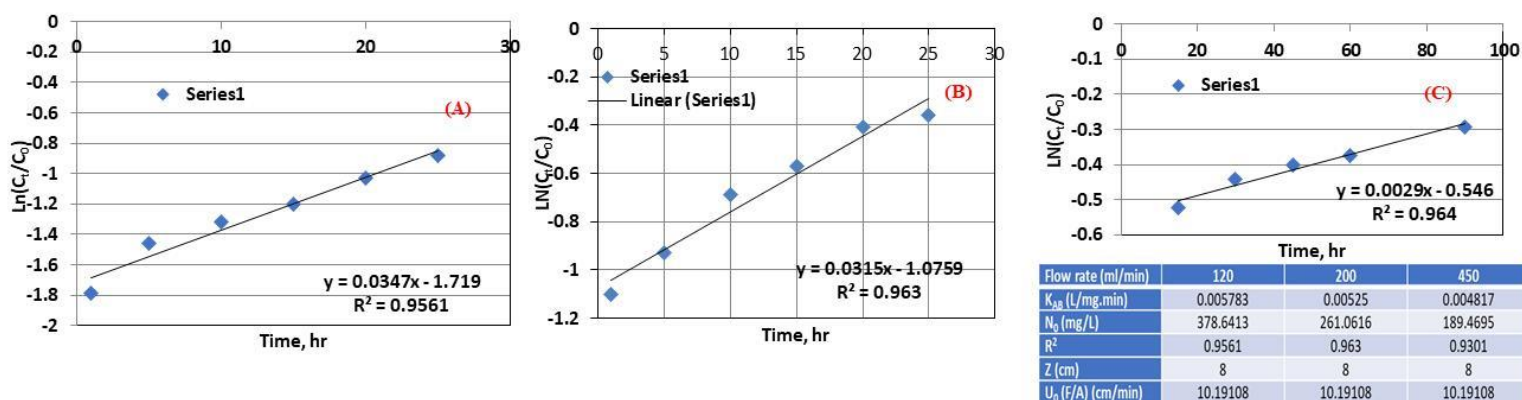| Flow rate (ml/min)	120	200	450
K_{AB} (L/mg.min)	0.005783	0.00525	0.004817
N_0 (mg/L)	378.6413	261.0616	189.4695
R^2	0.9561	0.963	0.9301
Z (cm)	8	8	8
U_0 (F/A) (cm/min)	10.19108	10.19108	10.19108

Fig. 9: Plot Bohart's mathematical model for MB adsorption by bed column at different flow rates and their parameters A) 120 ml/min B) 200 ml/min C) 450 ml/min

3.5. Continuous Experiments, Large-Scale, Real Application in Removal of Micropollutants

The treated effluent derived from the ISWA wastewater treatment plant in Stuttgart, Germany, has been subject to experiments to establish a correlation between Chemical Oxygen Demand (COD) and Specific Absorbance at 254 nm (SAC254). Fig. 10 exhibits this relationship, illustrating the connection between the measured COD, a gauge of the oxygen needed for oxidizing substances in wastewater, and the SAC254, which quantifies the absorption of UV light at 254 nm, serving as an indicator for organic matter concentration, particularly aromatic and conjugated organic compounds. The data from Fig. 10 delineates the link between COD and SAC254 values in the treated effluent of municipal wastewater. This relationship provides crucial insights into the presence of organic pollutants and specific organic compounds present in the wastewater treatment facility at ISWA in Stuttgart, Germany. Analyzing the patterns or trends visible in Fig. 10 allows for a deeper comprehension of the quality and constitution of the treated effluent. Such observations are instrumental in evaluating the efficacy of the wastewater treatment plant and gauging the elimination of organic pollutants from municipal wastewater. Moreover, SAC254 serves as a practical and reliable parameter that can potentially serve as an online alarm in municipal wastewater treatment plants. Fig. 11 depicts how varying flow rates affect the efficiency of removing Specific Absorbance at 254 nm (SAC) concerning its representation in terms of Chemical Oxygen Demand (COD). SAC, which measures ultraviolet (UV) light absorption at 254 nm, serves to estimate the concentration of organic matter, particularly aromatic and conjugated organic compounds. The graph in Fig. 11 shows the impact of different flow rates on the removal efficiency of SAC, denoted in terms of its reduction in COD. Flow rates refer to the speed at which a fluid, such as water or wastewater, moves through a system. By examining the data presented in Fig. 11, the correlation between distinct flow rates and the resultant efficiency in SAC removal, as measured by the decrease in COD, becomes evident. This data is instrumental in understanding the effect of flow rates on removing organic compounds and assists in identifying the optimal flow rate to achieve higher removal efficiencies.

The findings derived from this analysis offer insights into how flow rates influence the treatment process's efficacy in eliminating SAC. It aids in the evaluation of different flow rate scenarios' efficiency and helps in determining appropriate flow rates to attain desired levels of removal efficiency for organic pollutants, as indicated by SAC/COD.

4. Conclusions

This research delves into the efficacy of granular activated carbon (GAC) for the elimination of

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micropollutants from the effluent of municipal wastewater treatment plants, using methylene blue as a representative organic compound. The study offers valuable insights into the mechanisms governing efficient micropollutant removal and provides a comprehensive understanding of the factors influencing this process. Batch experiments conducted with GAC filters demonstrate remarkable removal efficiency, showcasing an impressive absorption capacity of 349.3 mg/g.

The study systematically examines the impact of key variables, including contact time, initial dye concentration, GAC particle size, and pH levels ranging from 2 to 11. Notably, the study finds that pH minimally affects the absorption process, emphasizing the robustness of GAC in diverse pH environments. The kinetics of micropollutant removal are thoroughly analyzed through Langmuir and Freundlich models, offering a detailed perspective on the adsorption behavior. In continuous flow experiments with lab-scale GAC filters, sustained high removal efficiency is observed across various flow rates. However, scalability considerations reveal a reduction in removal

percentages from 93.9% to 88.8% as flow rates increase from 1 m3/h to 5 m3/h.

These findings are of paramount importance in devising effective strategies to address the potential dangers posed by micropollutants in wastewater. The research contributes to the broader understanding of GAC as a promising tool for micropollutant removal, laying the groundwork for further exploration and application of this technology in real-world wastewater treatment scenarios. As environmental concerns related to micropollutants continue to grow, the insights gained from this study offer a pathway toward sustainable and efficient water treatment practices.

In practical terms, the research outcomes suggest avenues for designing and implementing GAC-based filtration systems that can contribute to the continuous improvement of water quality. As we move forward, further research and application-oriented studies can build upon these findings to develop sustainable and effective strategies for micropollutant removal, addressing environmental and public health concerns associated with wastewater contamination.
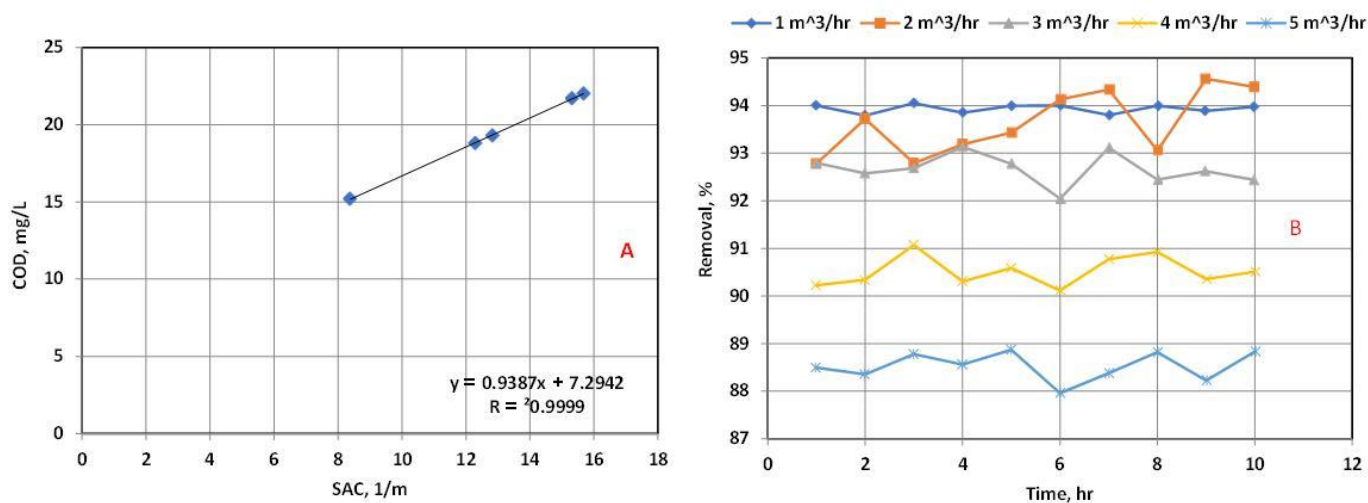

Fig. 10: (A) Relation between COD and SAC254 for municipal wastewater treated effluent, ISWA, Stuttgart, Germany (B): Effect of different flow rates in removal efficiency of SAC in the form of COD

Conflicts of interest

The authors declare that they have no known competing financial interests or personal

relationships that could have appeared to influence the work reported in this paper

Credit Authorship Contribution Statement

Methodology, validation, formal analysis, experimental section, and investigations, writing original draft, writing review, and editing, visualization was carried out by Ibrahim Abdelfattah. P. Maurer is concerned with providing ways and facilities to complete research work and participate in experimental discussions. G. Duelli provides facilities to complete research work and revisions. Ashraf M El-Shamy participated in writing the original draft, writing reviews, editing, and publishing.

References

Abdelfattah, I., Abdelwahab, W., El-Shamy, A. M. (2022a). Environmental Remediation of Contaminated Wastewater with Ammonium Using Clay-Based Adsorbents, Journal of Environmental Management, 351: 119614. https://doi.org/10.1016/j.jenvman.2023.119614

Abdelfattah, I., El-Shamy, A. M. (2024). Review on the escalating imperative of zero liquid discharge (ZLD) technology for sustainable water management and environmental resilience, Journal of Environmental Management, 21(4): 1971-1982. https://doi.org/10.46488/NEPT.2022.v21i04.052

Abdelfattah, I., El-Saied, F. A., Almedolab, A. A., El-Shamy, A. M. (2022b). Biosorption as a Perfect Technique for Purification of Wastewater Contaminated with Ammonia, Applied Biochemistry, and Biotechnology, 194(9): 4105–4134. https://doi.org/10.1007/s12010-021-03794-4

Abdelfattah, I., El-Shamy, A. M. (2022c). Chitosan as Potential De-coloring Agent for Synthetic and Textile Industrial Wastewater, Journal of Environmental Accounting and Management, 10(3): 305–319. DOI:10.5890/JEAM.2022.09.008

Abdelfattah, I., Abdelwahab, W., El-Shamy, A. M. (2022d). Montmorilonitic clay as a Cost-Effective, Eco Friendly and Sustainable Adsorbent for Physicochemical Treatment of Contaminated Water, Egyptian Journal of Chemistry, 65(2): 687-694. DOI: 10.21608/ejchem.2021.92320.4378

Abdelfattah, I., Abuarab, M. E., Mostafa, E., El Awady, M. H., Aboelghait, K. M., El Shamy, A. M. (2023). Integrated system for recycling and treatment of hazardous pharmaceutical wastewater,

International Journal of Environmental Science and Technology, 20(4): 4101–4110. https://doi.org/10.1007/s13762-022-04269-7

Ahammad, S. Z., Ong, S. L., Ng, H. Y. (2019). Micropollutants in wastewater: Fate, effects, and treatment. In: Micropollutants and Pharmaceuticals 39-69. Springer, Singapore.

Arévalo, J., Constantino, A. A., Silva, J, Alcántara, R., Schmalz, V., Calvo, L., D'Antonio, M. (2019). Micropollutant removal in granular activated carbon filters: Influence of the operating conditions. Chemical Engineering Journal, 361: 1086-94.

Baker, R. W., Lonsdale, H. K. (1991). Gas separation membrane materials: A perspective. Macromolecules, 24(6): 1513-21.

Benner, J., Helbling, D. E., Kohler, H. P., Wittebol, J. (2013). Micropollutants in biologically treated wastewater: current challenges in microbial ecotoxicology and future research trends. Journal of Hazardous Materials, 262: 685-706

Bhatnagar, A., Kaczala, F., Hogland, W., Marques, M. (2018). Granular activated carbon adsorption for wastewater treatment. In: Industrial and Hazardous Wastes. Springer, Cham.

Boehler, M., Zwickenpflug, B., Hollender, J., Ternes, T. A., Joss, A., Siegrist, H. (2012). Removal of micropollutants in municipal wastewater treatment plants by powder-activated carbon. Water Research, 46(14): 4281-91.

Bohart, G. S., Adams, E. Q. (1920). Some aspects of the behavior of charcoal concerning chlorine. J. of the American Chemical Society, 42(3): 523-44.

Chen, H., et al. (2021). Characterization of biochars and activated carbons derived from spent mushroom substrates and their potential for heavy metal removal. Journal of Environmental Management, 289: 112456.

Disanto A.R., Wagner J.G. (1972) Pharmacokinetics of Highly Ionized Drugs I: Methylene Blue—Whole Blood, Urine, and Tissue Assays, J. Pharma. Sci., 61(4) 598-602. https://doi.org/10.1002/jps.2600610422

Dong, Huiyu, Xiangjuan Yuan, Weidong Wang, and ZhiminQiang. 2016. Occurrence and Removal of Antibiotics in Ecological and Conventional Wastewater Treatment Processes: A Field Study." J. Environ. Manage., 178 (August): 11–19. https://doi.org/10.1016/j.jenvman.2016.04.037.

El-Kashef, E., El-Shamy, A. M., Abdo, A., Gad, E. A. M., Gado, A. A. (2019). Effect of Magnetic

Treatment of Potable Water in Looped and Dead-End Water Networks, Egypt. J. Chem., 62(8), 1467-1481. DOI: 10.21608/ejchem.2019.7268.1595

El-Shamy, A. M., Abdelfattah, I., Elshafie, O. I., Shehata, M. F. (2018). Potential removal of organic loads from petroleum wastewater and its effect on the corrosion behavior of municipal networks, J. Environ. Management, 219: 325-331. https://doi.org/10.1016/j.jenvman.2018.04.074

Eusebi, A. L., Soares, A., Esteves, V. I. (2019). A critical review on the removal of micropollutants from wastewater: Upgrading wastewater treatment plants with advanced oxidation processes. Journal of Environmental Management, 245: 180-95.

Falås, P., Longree, P., la Cour Jansen, J., Siegrist, H. (2015). The fate of micropollutants during municipal wastewater treatment processes. Environ.Sci.Technol., 49(4): 2138-46.

Flindt, M. R., Kjeldsen, P., Christensen, T. (2007). Microbial changes and pesticide removal in bio-purification systems treating pesticide-contaminated surface water. Wat. Res., 41(16): 3640-50.

Freundlich, H. (1906). Über die Adsorption in Lösungen. ZeitschriftfürphysikalischeChemie (Leipzig), 57: 385-470.

Garcia-Ivars, Jorge, Lucia Martella, ManueleMassella, Carlos Carbonell-Alcaina, Maria-Isabel Alcaina598 Miranda, and Maria-Isabel Iborra-Clar. 2017. "Nanofiltration as Tertiary Treatment Method for Removing Trace Pharmaceutically Active Compounds in Wastewater from Wastewater 600 Treatment Plants." Water Research 125 (November): 360–73. 601 https://doi.org/10.1016/j.watres.2017.08.070.

Gogoi, Anindita, PayalMazumder, Vinay Kumar Tyagi, G. G. TusharaChaminda, Alicia Kyoungjin An, Manish Kumar, (2018) Occurrence and Fate of Emerging Contaminants in Water Environment: A Review, Groundwater for Sustainable Development 6 (March): 169–80. https://doi.org/10.1016/j.gsd.2017.12.009

Gogoi, Anindita, PayalMazumder, Vinay Kumar Tyagi, G. G. TusharaChaminda, Alicia Kyoungjin An, Manish Kumar, (2018) Occurrence and Fate of Emerging Contaminants in Water Environment: A Review, Groundwater for Sustainable Development 6 (March): 169–80. https://doi.org/10.1016/j.gsd.2017.12.009

Golovko O., Anton L., Cascone C., Ahrens L., Lavonen E., Koehler S. (2020) Sorption characteristics and removal efficiency of organic micropollutants in drinking water using granular activated carbon (GAC) in pilot-scale and full-scale tests, Water, 12, 2053.

Gu, B., Chang, A. C. (2003). Kinetic modeling of adsorption for the removal of trace organic compounds in wastewater by powdered activated carbon. Water Research, 37(3): 386-400.

Karsten, R., Burkhard, K., Serghei, B., Katrin, W. P., Olaf, B. J. T., Martin, S., Peter, H., Helmut, R., Karsten, R., Kristine, R., Maren, D., Marco, M., Lothar, P., Kurt, F. (2013). Reservoirs as sentinels of catchments: the Rappbode Reservoir Observatory (Harz Mountains, Germany), Environ Earth Sci., 69: 523–536. DOI 10.1007/s12665-013-2464-2

Kasprzyk-Hordern, B., Dinsdale, R. M., Guwy, A. J. (2009). The removal of pharmaceuticals, personal care products, endocrine disruptors, and illicit drugs during wastewater treatment and its impact on the quality of receiving waters. Wat. Res., 43(2): 363-80.

Kümmerer, K. (2013). Pharmaceuticals in the environment: sources fate, effects, and risks. Springer Science & Business Media.

Langmuir, I. (1918). The adsorption of gases on plane surfaces of glass, mica, and platinum. Journal of the American Chemical Society, 40(9): 1361-403.

Li, X., Xu, L., Shi, H., Su, J., Liu, Y., Li, A. (2019). Granular activated carbon for the removal of emerging organic micropollutants from municipal wastewater: A review. Science of the Total Environment, 662: 414-427.

Li, X, Zhang, J., Wang, Y., Liu, H., Li, A. (2020). Removal of micropollutants from wastewater using advanced oxidation processes: a review. Journal of Environmental Sciences, 87: 225-41.

Li, Y., Zhang, L., Zhou, Q., Xie, Y., Yu, S., Zhang, Y. (2020). Removal of antibiotics and antibiotic resistance genes from wastewater using granular activated carbon: A comprehensive review. Chemosphere, 242: 125168.

Omran, M., Ahmed, M. B., Selima, N. B., Abdel-Fattah, T. M., Ahmed, I. T. (2020). Pharmaceuticals in municipal wastewater and their removal using granular activated carbon. Environmental Technology & Innovation, 17: 100494.

Radjenović, J., Petrović, M., Barceló, D. (2009). Fate, and distribution of pharmaceuticals in wastewater and sewage sludge of the conventional activated sludge (CAS) and advanced membrane bioreactor (MBR) treatment. Water Research, 43(15): 831-41.

_____

Schepers, V., Verliefde, A. R., Cornelissen, E. R., Quanrud, D. M., Amy, G. L. (2011). Contaminant adsorption in nanofiltration-rejection and fouling mechanisms. Journal of Membrane Science, 366(1-2): 167-74.

Shon, H. K., Vigneswaran, S., Snyder, S. A. (2006). Effluent organic matter (EfOM) in wastewater: constituents, effects, and treatment. Critical Reviews in Environmental Science and Technology, 36(5): 327-78.

Sörengård M., Campos-Pereira H., Ullberg M., Lai F.Y., Golovko O., Ahrens L., (2019) Mass loads, source apportionment, and risk estimation of organigmicropollutants from hosbital and municipal wastewater in recipient catchments. Chemosphere, 234, 931-941.

Tang, J., Zhang, S., Chen, H., Jiang, W. (2019). Removal of pharmaceuticals and personal care products (PPCPs) from wastewater: a review. Journal of Environmental Management, 230: 215-34.

Thomas, H. C. (1944). Heterogeneous ion exchange in a flowing system. Journal of the American Chemical Society, 66(8): 1664-6.

Verlicchi, P., Galletti, A., Petrovic, M., Barceló, D. (2010). Hospital effluents as a source of emerging pollutants: an overview of micropollutants and sustainable treatment options. Journal of Hydrology, 389(3-4): 416-28.

Yacouba Z. A., Mendret J., Lesage G., Zaviska F., Brosillon S., (2021) Removal of organic micropollutants from domestic wastewater: The effect of ozone- based advanced oxidation process on nanofiltration, Journal of Water Process Engineering, 39, 101869.

Yao, M., Zhang, Y., Yang, L., Zhou, L., Chen, Z., Chen, J., Liang, S., Zeng, G. (2017). Application of membrane technology for the removal of pharmaceuticals and personal care products from wastewater: a review. Reviews in Environmental Science and Bio/Technology, 16(1): 67-88.

Yoon, Y. H., Nelson, J. H. (1984). Application of gas adsorption kinetics. I. A theoretical model for respirator cartridge service life. American Industrial Hygiene Association Journal, 45(9): 609-16.

Yu, Z., Zhang, L., Wu L., Guo, W., Wang, S., Zhang, Y. (2021). Removal of organic micropollutants from wastewater by powdered activated carbon adsorption: A review. Journal of Environmental Sciences, 103: 22-36.

Zapater-Pereyra, M., Kumar, R., Wood, F., Pikaar, I., Yuan, Z., Batstone, D. J. (2017). Granular activated carbon adsorption kinetics for water and wastewater treatment: A critical review. Water Research, 117: 178-97.

Zhang, S., Li, B., He, Y., Zhang, X., Wang, H., Lin, H. (2014). Removal of micropollutants from water by activated carbon adsorption: A review. Chemical Engineering Journal, 253: 1-18

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