Environmental Technology

ISSN: (Print) (Online) Journal homepage: https://www.tandfonline.com/loi/tent20

Comparison of activated carbon and low-cost adsorbents for removal of 2,4-dichlorophenol from wastewater using Aspen Adsorption and response surface methodology

Hassnain A. Yasir, Sharif H. Zein, Mathew C. Holliday, Khalaf J. Jabbar, Usama Ahmed & A. A. Jalil

To cite this article: Hassnain A. Yasir, Sharif H. Zein, Mathew C. Holliday, Khalaf J. Jabbar, Usama Ahmed & A. A. Jalil (2023): Comparison of activated carbon and low-cost adsorbents for removal of 2,4-dichlorophenol from wastewater using Aspen Adsorption and response surface methodology, Environmental Technology, DOI: 10.1080/09593330.2023.2202829

To link to this article: https://doi.org/10.1080/09593330.2023.2202829

© 2023 The Author(s). Published by Informa UK Limited, trading as Taylor & Francis Group

Published online: 27 Apr 2023.

Submit your article to this journal

Article views: 1593

View related articles

View Crossmark data

Full Terms & Conditions of access and use can be found at
https://www.tandfonline.com/action/journalInformation?journalCode=tent20

ENVIRONMENTAL TECHNOLOGY
https://doi.org/10.1080/09593330.2023.2202829

Taylor & Francis
Taylor & Francis Group

OPEN ACCESS Check for updates

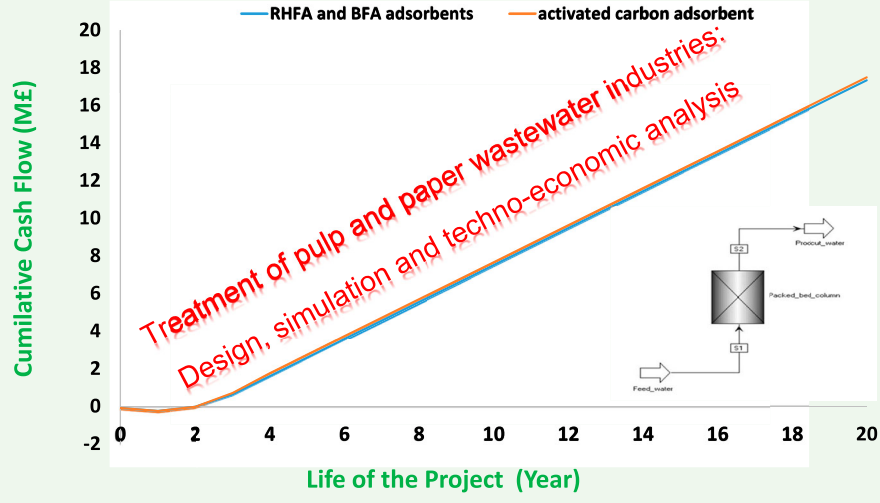
Comparison of activated carbon and low-cost adsorbents for removal of 2,4-dichlorophenol from wastewater using Aspen Adsorption and response surface methodology

Hassnain A. Yasir[a], Sharif H. Zein [a], Mathew C. Holliday[a,b], Khalaf J. Jabbar[a], Usama Ahmed [c,d] and A. A. Jalil [e,f]

[a]School of Engineering, Faculty of Science and Engineering, University of Hull, Kingston Upon Hull, UK; [b]Energy and Environment Institute, University of Hull, Kingston Upon Hull, UK; [c]Chemical Engineering Department, King Fahd University of Petroleum and Minerals, Dhahran, Saudi Arabia; [d]Interdisciplinary Research Center for Hydrogen and Energy Storage, King Fahd University of Petroleum & Minerals, Dhahran, Saudi Arabia; [e]Center of Hydrogen Energy, Institute of Future Energy, Universiti Teknologi Malaysia, UTM Johor Bahru, Johor, Malaysia; [f]Faculty of Chemical and Energy Engineering, Universiti Teknologi Malaysia, UTM Johor Bahru, Johor, Malaysia

ABSTRACT

In this paper, the adsorption of the chlorinated organic compound, 2,4-dichlorophenol, using activated carbon (AC), bagasse fly ash (BFA) and rice husk fly ash (RHFA) in a packed bed column was simulated using Aspen Adsorption software. The purpose of this study was to demonstrate the effectiveness of simulation software for identifying alternative low-cost adsorbents and optimising the adsorption process. The effect of process parameters such as initial concentration, bed height and inlet feed flow rate were evaluated using breakthrough curves. It was shown that the longest breakthrough times were at a higher bed height of 3 m and lower flow rate of 2 m^3/hr and concentration had no effect on breakthrough time. After optimisation using response surface methodology, the AC, BFA and RHFA had a breakthrough time of 534, 426 and 209 s, respectively. This shows the potential of BFA as a potential alternative for AC for the adsorption of 2,4-dichlorophenol and shows RHFA to be a relatively poor adsorbent in comparison. The economic evaluation illustrates that the overall cost of wastewater treatment with BFA and RHFA is lower than AC. The cost for the BFA and RHFA adsorbents is only a handling charge, but the cost for using AC adsorbent is £10,603/year. Therefore, the company can produce 17,520 m^3/year of fresh water from the adsorbent and save £87,600/year. Therefore, it was concluded that BFA had a slightly weaker adsorption efficiency than AC but was more cost effective, allowing it to be more affordable and increasing its availability.



ARTICLE HISTORY
Received 6 January 2023
Accepted 16 March 2023

KEYWORDS
Biomass; bagasse fly ash; rice husk fly ash economic evaluation breakthrough time; capital expenditure (CAPEX); operation expenditure (OPEX)

CONTACT Sharif H. Zein s.h.zein@hull.ac.uk School of Engineering, Faculty of Science and Engineering, University of Hull, HU6 7RX, Kingston Upon Hull, UK; Hassnain A. Yasir H.YASIR-2021@hull.ac.uk School of Engineering, Faculty of Science and Engineering, University of Hull, HU6 7RX, Kingston Upon Hull, UK

© 2023 The Author(s). Published by Informa UK Limited, trading as Taylor & Francis Group
This is an Open Access article distributed under the terms of the Creative Commons Attribution License (http://creativecommons.org/licenses/by/4.0/), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited. The terms on which this article has been published allow the posting of the Accepted Manuscript in a repository by the author(s) or with their consent.

1. Introduction

The quick increase in population and industrialisation to meet human needs, such as an increase in the demand for paper products, are having adverse impacts on the environment in the form of water and soil pollution. The pulp and paper mills are water-severe industries, and after the chemical and metals industries, they are ranked third in the world [1]. Paper industries are big consumers of fresh water and generate wastewater during the numerous stages of pulping and paper-making activities. The pulp and paper industry utilises 60–230 m^3 of fresh water per ton of paper production, and, as a result, a large amount of wastewater is produced [2]. For one ton of paper production, about 70 m^3 of wastewater is produced [3]. Pulp and paper industries are discharging diverse liquid and solid wastes [4]. The generated water has unfavourable impacts on humans and wildlife.

Bleached kraft pulp mill wastewater is one of the most challenging parts of the whole pulp industry. In the bleached pulp effluent, a wide variety of chlorinated organic compounds are present, starting from the lower molecular weight to the higher molecular weight of lignin derivative materials. Bleached pulp wastewater comprises numerous lignocellulosic compounds, tannins, cellulose, hemicelluloses and adsorbable organic halides compounds such as chlorophenols, dichlorophenols, tri-chlorophenols, etc. [5].

These chlorinated organic compounds are hazardous and toxic to numerous target organisms and human beings. So, it is essential to minimise their concentrations at safer values. When discharged into the receiving water body, these toxic compounds affect the ecological balance. Chlorinated organic compounds can display significant resistance to biological and chemical degradation. Therefore, reducing the concentration of chlorinated organic compounds, such as 2,4-dichlorophenol in bleached kraft pulp mill wastewater, is required before discharging to a receiving water body. Chlorophenols are toxic to human beings and aquatic life. They are a harmful compound proven toxic even at 0.1 ppm level for many water organisms. Additionally, it has a highly disagreeable taste and order in water even at 0.01 ppm level [5]. The permissible limit of 2,4-dichlorophenol in fish, water flea, and freshwater algae is in the range of 1.2–14 mg/L [6].

There are several methods for removing pollutants from wastewater including ultrafiltration, coagulation, flocculation, complexation, solvent extraction, flotation, reverse osmosis, ion exchange, precipitation, electrodialysis, membrane separation, ozonation and adsorption [7,8]. However, many of these methods are highly expensive, have a high energy requirement and are ineffective at low concentrations [7]. Adsorption is one of the most practical methods for removing pollutants from wastewater because of its low cost, high removal capacity, easy regeneration, the possibility of adsorbate recovery high surface area, high efficiency, ease of scaling up and use and comparatively lower secondary pollution all without toxic sludge generation [8–11]. The process of adsorption is the cleaning, deodorising, detoxifying, and separating of hazardous substances from aqueous solutions [12]. Solid adsorbents have broadly been used to eliminate pollutants such as dichlorophenols from wastewater [13–16]. The chosen adsorbent will significantly affect the adsorption process. To remove the dichlorophenols, the adsorbents that have been studied previously are chemically modified chitosan [17], coir pith carbon [18], organoclays [19], activated bamboo charcoal [20], modified plantain peel [13], bagasse fly ash (BFA) and rice husk fly ash (RHFA) [5]. Krishnaiah et al. [21] simulated phenol adsorption in a packed bed column by studying the physical and chemical properties of activated carbon (AC) and natural zeolite. AC is very porous, with a large particulate surface area [22]. It also effectively removes pollutants [23,24]. However, producing AC is costly and its regeneration in an aqueous solution requires elevated temperatures [25,26]. In a previous study, pea waste has successfully been used as a low-cost biosorbent of dye [27]. In a separate study, hydrochar was produced from different waste biomass with the assistance of microwaves but showed a low adsorption capacity and was not an effective alternative adsorbent [28]. BFA and RHFA are the cheapest adsorbents generated in large amounts by the sugar and rice mills, respectively [29,30]. Biosorbents are low-cost adsorbents made from waste biomass that has not been thermally treated; they are usually not as effective as AC but require minimal processing [27]. These adsorbents induced attention due to their ease of handling, cheapness and no disposal problems. Using agri-waste as a biosorbent not only helps solve the waste treatment problem, but it is also economical and eco-friendly [31]. Using waste material contributes to waste minimisation, recovery and reuse [8]. On the other hand, AC is a desirable adsorbent for removing dichlorophenol because of its exceptional properties, such as good surface area and pore volume. AC has been shown to outperform the adsorption capacity of biochar and carbon nanotubes [32]. Carbonisation will increase the value and application of waste biomass. Economic analysis has shown that the exploitation of biomass is economically feasible [33–35]. Pyrolysis is a common method for the production of biochar and AC. However, the process consumes

energy, with high activation energy and high costs, requiring high temperatures of 300–1000°C and an inert atmosphere [36–40]. When chemically activated, thorough washing to remove chemical agents is required and AC cannot be regenerated [9]. It is important to find a low-cost material comparable to AC in adsorption capacity but also economically viable and locally available. Therefore, this research has examined the suitability of BFA and RHFA as low-cost adsorbents for removing 2,4-dichlorophenol and their performance with AC compared using Aspen Adsorption [5,41].

Using simulation software is helpful because it saves cost and time and provides a suitable operating range by changing different parameters. Simulation provides an alternative method of analysing potential adsorbents without time-consuming experimental work. Though every real-life aspect can not be accounted for, the simulation and optimisation using computer software can predict the expected behaviour of a real industrial set-up, without having to make a small-scale plant. Response surface methodology (RSM) includes statistical and mathematical methods to optimise and analyse the interaction of factors under different conditions and remove the limit of experimental studies [32]. Design of experiment can optimise the limited resources to minimise time and ambiguity [31]. Aspen Adsorption can conduct different trials under many settings to govern the optimal parameters [41,42]. Successful optimisation using RSM of simulated adsorption data has been performed in other studies [11,28,41,43]. Packed bed systems are extensively used for the adsorption of organic solvents, toxic gases and water vapour. A simple packed bed system involves a single column encumbered with a specific adsorbent. In this research, for removing 2,4-dichlorophenol, a packed column was loaded with a selected adsorbent. Using simulation software can efficiently study the effect of numerous conditions, such as high concentrations and flow rates.

This research aimed to simulate the treatment of wastewater using the low-cost adsorbents BFA and RHFA and compare it with AC to economise the process. The following objectives were met to reach this aim: (1) Appropriate packed bed column size required to remove the 2,4-dichlororphenol from the pulp and paper mills wastewater is designed using Aspen Adsorption. (2) The suitability of BFA and RHFA as low-cost adsorbents for removing 2,4-dichlororphenol from wastewater will also be investigated. Different parameters such as flow rate, bed height, and initial concentration to determine the feasibility of the low-cost adsorbents for the pulp and paper wastewater treatment process will be evaluated using breakthrough curves [41]. (3) The results of the simulation were then optimised using Design Expert software and RSM to maximise breakthrough and saturation times. The relationship between initial concentration, bed height, flow rate and adsorbents was also investigated. (4) Using the optimised packed bed column, an economic analysis was produced, comparing the cost of using AC and biosorbents.

The novelty of this paper is to highlight how simulation software can be effectively used to compare different adsorbents and optimise the adsorption process. Using this information a detailed economic analysis could compare expensive AC with the cost of cheaper biosorbents and draw attention to the effectiveness of alternative adsorbents.

2. Materials and methodology

Adsorbents RHFA and BFA were collected from nearby rice and sugar mills, respectively. To use these adsorbents, the soluble impurities were removed by washing with distilled water and then drying them at 80 °C for 8 h [5]. The analytical grade of AC was used for economic evaluation and adsorption studies. Dynamic simulation of 2,4-dichlorophenol adsorption was conducted using Aspen Adsorption® V10 software and designed the packed bed column using the experimental data. For the application of RSM to optimise the breakthrough and saturation times and investigate the interaction of variables, Design Expert V13 software was used. Quadratic mathematical models were fitted with the simulation data to find the best-fitting Equation to describe the relationship of the variables, which could then be used for optimisation. The chemical and physical properties of 2,4-dichlorophenol are available in the Aspen Properties V10 software. Before the designing of the process flowsheet, the component 2,4-dichlorophenol was configured. The non-random two-liquid (NRTL) property model was used to calculate the liquid activity coefficients. NRTL property package is suggested for highly non-ideal chemical systems for both vapour–liquid and liquid–liquid equilibrium applications [44]. The process is isothermal, particles are packed uniformly into the bed column, and the fluid phase acts as the ideal condition.

The feed requirements, such as initial concentrations of 2,4-dichlorophenol ions (1.22×10^{-4} kmol/m^3, 6.13×10^{-4} kmol/m^3, 3.0×10^{-3} kmol/m^3, 6.13×10^{-3} kmol/m^3 and 1.2×10^{-2} kmol/m^3) and flow rates (2 m^3/hr, 4 m^3/hr, 6m^3/hr, 8 m^3/hr and 10 m^3/hr), are used as inputs for the feed water stream. The product concentration is set to 0 mol/L to determine the breakthrough time for the adsorption column [44]. The feed stream enters at 30 °C and a pressure of 3 atm. For the

process model type, the reversible model was chosen. The feed flow rate was set at the feed block for the uniform constant flow rate throughout the adsorption process. A packed bed column is used for the adsorption of 2,4- dichlorophenol from the pulp and paper mill wastewater as it can provide continuous contact between the vapour–liquid and liquid–solid phases. Packed bed columns are less expensive when handling corrosive liquids, give low-pressure drops, and are best for handling foaming systems than other options. Figure 1 displays the process flowsheet used in this research for the simulation runs. Table 1 gives theoretical assumptions for the modelling of 2,4-dichlorophenol adsorption, and Table 2 shows the adsorbent properties such as bulk density, average particle size, total pore volume, surface area and void ratio. These input parameters were used in the current simulation and fed into the simulation software to characterise the packed bed column.

The number of nodes and upwind differencing scheme-first order (UDS 1) was chosen under the general tab. In terms of stability, quick ion capability, accuracy and non-oscillatory in all possible situations, the UDS 1 is the best standard discretisation method. USD 1, the first-order convection term, is based on the Taylor expansion [11,44]. The accuracy can be increased by increasing the number of nodes. Hence, 20 were used in this simulation [11,44]. The film model assumption in this simulation was solid. This expresses the mass transfer driving force in terms of solid-phase concentrations of the components [11,44]. No pressure drop was assumed in this simulation [41]. The energy balance in this simulation was assumed to be isothermal [41]. In this research, convection with estimated dispersion is the material balance assumption selected under the material and momentum balance tab. This is the important assumption about material dispersion in the liquid phase for the ion exchange process. Convection with estimated dispersion is comprised of the material balance for the bed. In this condition, the dispersion coefficient varies along the length of the bed. The software is proficient in combining all resistances to an overall master transfer single component. Under the material and momentum balance tab, the pressure drop assumption selected none and the velocity assumption selected constant. This research selected solid phase loading as the mass transfer driving force [21]. The kinetic model assumption selected linear lumped resistance, the form of mass transfer coefficient (MTC) kept constant. The linear lumped resistance kinetic model assumes the driving force for the mass transfer of the components is a linear function of the component concentration in the liquid or solid phase [11,41,44]. Pseudo-first-order model, Pseudo-second-order model and Weber-Morris intra-particle diffusion model explain the 2,4-dichlorophenol adsorption process on AC, BFA and RHFA, respectively. Pseudo-first-order kinetics describe the adsorption process in other studies [31]. In this research, the mass transfer coefficients of 2,4-dichlorophenol using different adsorbents have been determined using the Lagergren first-order rate equation shown in equation 1 [48].

$$\frac{dqt}{dt}A = \ k1(qe - qt) \tag{1}$$

Where k1 (min-1) is the rate constant, q_t (mg/g) is the quantity of adsorbate adsorbed at a time 't', and q_e (mg/g) is the adsorption capacity in equilibrium. After integration and applying initial conditions at t = 0, q_t = 0, and at t = t, q_t = q_e, the Lagergren rate Equation (1) becomes [5]:

$$Log\ (q_e - q) = Log\ q_e - \frac{kad}{2.303}t \tag{2}$$

Where k_{ad} is the adsorption rate constant, q and qe are the quantities of 2,4-dichlorophenol adsorbed at

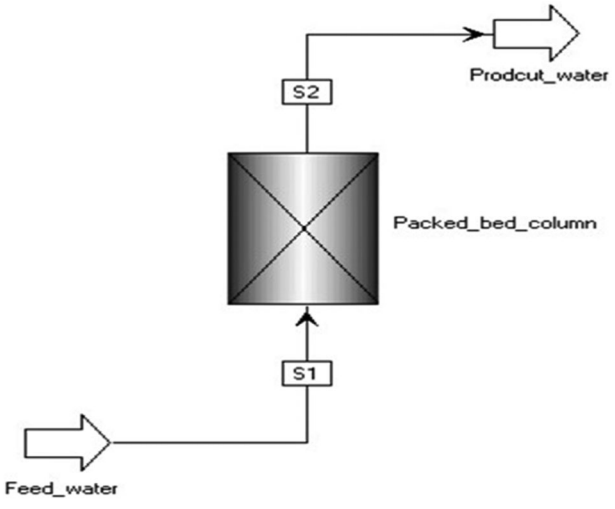


Figure 1. Process flowsheet of 2,4-dichlorophenol adsorption on Aspen Adsorption® V10.

Table 1. Theoretical assumptions for the modelling of 2,4-dichlorophenol adsorption.

Discretisation model: Upwind differencing scheme-first order (UDS 1)
Number of nodes: 20
Material/momentum balance: Convection with estimated dispersion
Pressure drop Assumption: None
Velocity assumption: Constant
Kinetic model assumption: Linear lumped resistance
Film model assumption: solid
Mass transfer coefficient: Constant
Isotherm model: Freundlich 1
Energy balance assumption: isothermal

Table 2. The characteristics of Bagasse fly ash characteristics (BFA), rice husk fly ash (RHFA) and activated carbon (AC) obtained from the sugar industry.

Adsorbent properties	Value	References
Bagasse fly ash characteristics		
Bulk density (kg/m^3)	270	[30]
Average particle size (μ)	167.35	[5]
Void ratio	0.79	[45]
Surface area (m^2/g)	440	[45]
Rice husk fly ash characteristics		
BET Surface area (m^2/g)	65.36	[46]
Total pore volume (cm^3/g)	0.039	[46]
Average particle size (μ)	412	[46]
Bulk density (kg/m^3)	175.3	[46]
Activated carbon characteristics		
Bulk density (kg/m^3)	617.5	[5]
Average particle size (m)	0.002	[5]
Total pore volume (cm^3/g)	0.55	[47]
BET Surface area (m^2/g)	847	[47]

time t on the unit weight of adsorbents at equilibrium. The values of the adsorption rate constant have been presented in Table 3.

At constant temperature, the quantity of solute adsorbed on the adsorbent and the solute concentration in the equilibrium solution is expressed as adsorption isotherm. Dynamic phase equilibrium is recognised between the adsorbent and adsorbate surface for the single component adsorption. The liquid phase concentration of adsorbate (C_e) and adsorbate loading on the adsorbent (q_e) are related to the adsorption equilibrium isotherm at a constant temperature. There are numerous isotherm models presented in the literature. However, the Freundlich model has been selected for the present study to remove the 2,4-dichloriorphenol by using different adsorbents such as BFA, RHFA and AC [5]. Freundlich has was presented as the best fitting model in other adsorption studies [31,32]. Freundlich isotherm model presented in the Equation (3) [49].

$$q_e = K_F C_e^{1/n} \tag{3}$$

where q_e and C_e are the equilibrium concentrations (mg/L), and n and K_F are Freundlich constants. The value of the Freundlich isotherm model has been recorded in Table 4 for removing 2,4-dichloriorphenol by using different adsorbents.

After identifying all the important parameters and finalising the bed configuration, the setup was organised to simulate. The adsorption of 2,4-dichlorophenol

Table 3. Values of mass transfer coefficient for the adsorption of 2,4-dichlorophenol by using different adsorbents [5].

Adsorbent	Adsorption rate constant k_{ad} (min^{-1})
RHFA	0.02047
BFA	0.02254
AC	0.01863

Table 4. Freundlich constants for the adsorption of 2,4-dichloriorphenol by using different adsorbents [5].

Freundlich isotherm	AC	BFA	RHFA
K_F((mg/g)/(mg/L)$^{1/n}$)	0.78886	0.52747	0.32337
N	2.74725	2.45942	1.91718

in a packed bed column was conducted on Aspen Adsorption software, as shown in Figure 1. There were three process constraints: initial 2,4-dichlorophenol concentration, bed height, and flow rate studied to check the effect of each constraint on the breakthrough curve. The simulation started by initialising the setup and then exchanged to dynamic mode. The breakthrough curve was created in the dynamic mode as time progressed. The initial concentration of the 2,4-dichlorophenol was altered at a constant flow rate (2 m^3/hr) and a bed height (2m). The initial concentrations of 2,4 dichlorophenol ions were 1.22×10^{-4} kmol/m^3, 6.13×10^{-4} kmol/m^3, 3.0×10^{-3} kmol/m^3, 6.13×10^{-3} kmol/m^3 and 1.2×10^{-2} kmol/m^3. The optimum initial concentration of 2,4 dichlorophenol ions was established by studying the breakthrough curves at these different concentrations and then choosing the concentration curve which generated the extended breakthrough time. After this, check the impact of bed height on the breakthrough curves by varying the heights of the bed, such as 1m, 1.50m, 2m, 2.5m, and 3.0m and keeping concentration at 3.0×10^{-3} kmol/m^3 and a flow rate of 2 m^3/hr. Lastly, studied the effects of different flow rates such as 2 m^3/hr, 4 m^3/hr, 6 m^3/hr, 8 m^3/hr and 10 m^3/hr were used in each trial while keeping the constant concentration of 2,4-dichlorophenol (6.13×10^{-4} kmol/m^3) and a bed height of 1.50 m to analyse the breakthrough curves of the packed bed column. These stages were carried out for the AC, followed by the BFA and RHFA. Then optimum-generated breakthrough curves were compared for the adsorbents such as AC, BFA and RHFA.

3. Results and discussion

The simulation of 2,4-dichlorophenol adsorption was conducted with 45 runs by changing the 2,4-dichlorophenol ion concentration, bed height and flow rate. It was completed using a trial-and-error technique, establishing that the selected constraint values were within the limit to generate an effective breakthrough curve. A longer breakthrough time provides a better adsorption capacity of adsorbents in the adsorption column [44]. The breakthrough time occurs when the outlet effluent concentration reaches 5% of the input concentration (Ce = 0.05 Co) [9]. The saturation time begins

when the outflow concentration reaches 95% of the inflow concentration, at which point the bed is saturated [9]. Despite being a valid indicator of an adsorbed bed column's performance, breakthrough time is also influenced by the bed's height, flow rate, temperature, pH, and material characteristics [9].

3.1. Effect of initial concentration

The effect of the initial 2,4-dichlorophenol concentration was determined by changing the concentrations such as 1.22×10^{-4} kmol/m^3, 6.13×10^{-4} kmol/m^3, 3.0×10^{-3} kmol/m^3, 6.13×10^{-3} kmol/m^3 and 1.2×10^{-2} kmol/m^3 at a constant bed height 2 m and a flow rate of 2 m^3/hr. Figure 2 (a-c) illustrate the breakthrough curves for the adsorbents AC, BFA and RHFA. The breakthrough curves were established by plotting the wastewater outlet concentration (C) divided by the 2,4-dichlorophenol initial concentration (Co) against time. It can be seen from Figure 2 that the outlet concentration of 2,4-dichlorophenol ultimately reached the inlet concentration value as the adsorption process proceeded.

Figure 2 shows that the initial concentration did not affect breakthrough and saturation time. For the concentration of 3.0×10^{-3} kmol/m^3, the breakthrough times were obtained as 333 s, 272 s and 140 s for adsorbents AC, BFA and RHFA, respectively. At the same concentration (3.0×10^{-3} kmol/m^3), the saturation time obtained for the adsorbents AC, BFA and RHFA were 1050 s, 804 s and 535 s, respectively. Hence, AC and BFA can be considered the better adsorbents because they have a longer breakthrough and saturation time.

Another study showed a similar trend as the present study, and it was concluded that the assumption of linear lumped resistance in the kinetic model might not fully characterise the adsorption mechanism [41]. It has been concluded in another work that since the lumped linear resistance kinetic model has been assumed in the work, which assumes that the rate of ion uptake is directly proportional to its concentration gradient, an increase in concentration would increase exhaustion capacity [11]. Other studies show mixed responses to changing initial concentration. A higher initial concentration has increased breakthrough and saturation times [50]. But in other studies, a lower initial concentration increased breakthrough and saturation times [44,51]. In other studies, adsorption efficiency decreased at higher initial concentrations [31,32]. A lower initial concentration should increase the adsorption capacity and thus lengthens the breakthrough and saturation time [9,44,52]. At higher concentrations, the number of empty adsorption sites decreases or are saturated by pollutant molecules, leaving the remaining sites not readily available, lowering adsorption efficiency [32]. The number of active sites were inefficient in adsorbing the pollutant [31].

3.2. Effect of bed height

The effect of bed height was determined by altering the bed heights such as 1.0 m, 1.50 m, 2.0 m, 2.5 m, and 3.0 m and fixing the concentration at 3.0×10^{-3} kmol/m^3 and a flow rate of 2 m3/hr. Figure 3 (a-c) displays the breakthrough curves observed from the column at different bed heights. The breakthrough times observed at a concentration of (3.0×10^{-3} kmol/m^3), a flow rate of (2 m^3/hr) and a bed height of (2.50m) for AC, BFA and RHFA were 425 s, 354 s and 132 s, respectively. Likewise, the saturation time observed for AC, BFA and RHFA at the same conditions were 1408 s, 1067 s and 615 s, respectively. The simulation results show that the breakthrough time increased as the bed height increased, and the breakthrough curve became less steep. So, removal efficiency can be increased with a higher bed height because there is a good retention time between the adsorbent and the removal component. So, as a result of this, there are more binding sites for the adsorption, increasing the available surface area and higher removal efficiency of 2,4-dichlorophenol.

While lower bed height directs that the bed has less ability to adsorb the component from the solution due to its less retention time and smaller surface area, which results in a faster breakthrough and exhaustion time. At a lower bed height, axial dispersion is considered the prominent mass transfer method, which reduces ion diffusion [44]. Furthermore, a lengthier breakthrough and saturation time is observed for the adsorbent's AC and BFA, which shows that they have good adsorption capacity. This indicates that AC and BFA are better adsorbents due to their higher adsorption capacity at the same conditions as RHFA. Similar results were seen in other studies [9,41,50,51]. A higher bed height means an increased adsorbent dosage, which increases absorption efficiency [31,32]. This is due to the increased availability of active sites [31,32]. At a lower bed height, the ion diffusion is reduced due to the prominent mass transfer method being axial dispersion [44]. When bed height increases, there is an increase in breakthrough time due to the diffusion mass transfer having a greater effect than axial dispersion [9].

3.3. Effect of flow rate

The effect of flow rate was studied by varying the flow rates at a constant bed height and initial concentration.

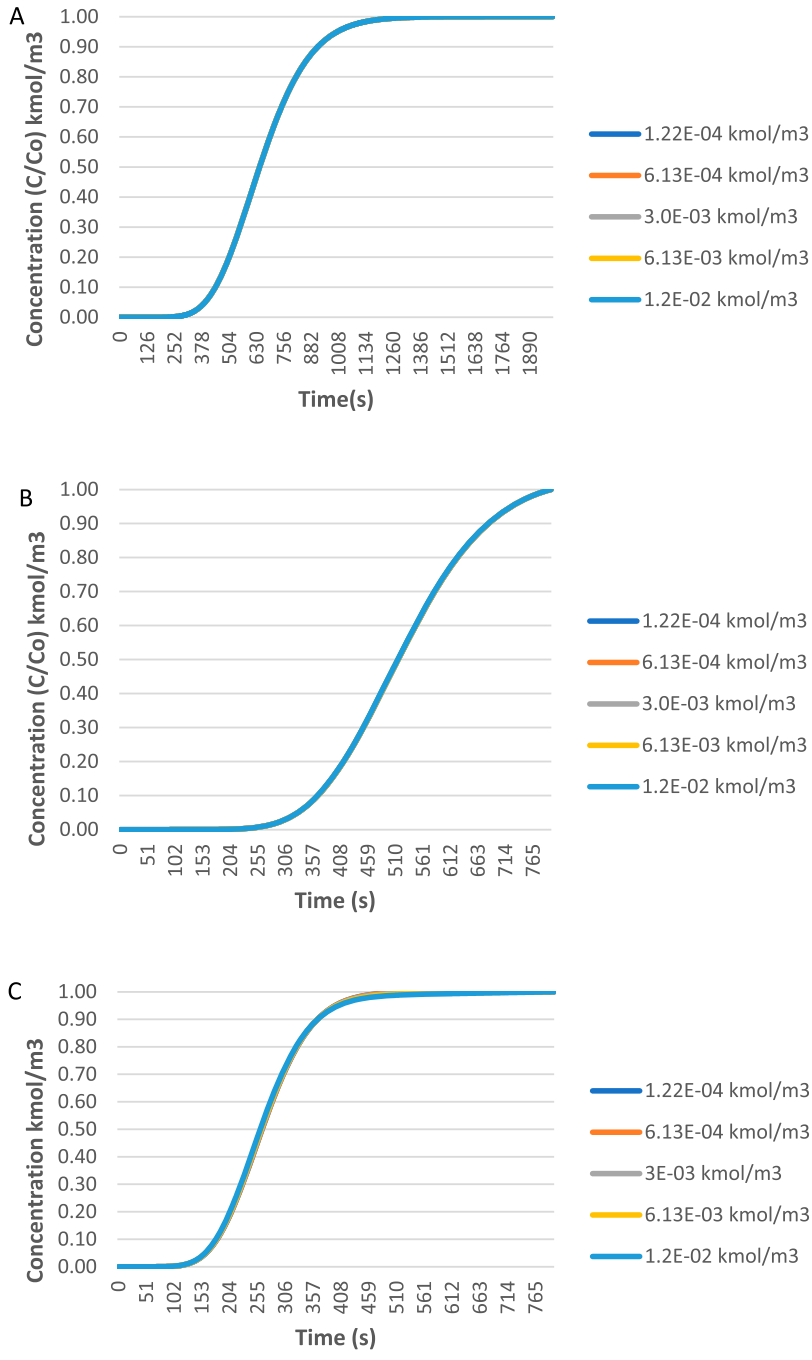


Figure 2. Effect of initial concentration on the breakthrough time and breakthrough curves of the column for (a) AC, (b) BFA and (c) RHFA.

The breakthrough curves were determined by varying the flow rates such as 2 m^3/hr, 4 m^3/hr, 6m^3/hr, 8m^3/hr and 10 m^3/hr at a constant concentration (6.13×10^{-4} kmol/m^3) and a bed height of 1.50 m. The breakthrough curves observed for the adsorption of 2,4-dichlorophenol at varying flow rates are shown in Figure 4 (a-c). Increasing the flow rate resulted in a steeper curve and the column saturated early. The observed breakthrough time for AC, BFA and RHFA at a flow rate of 4 m3/hr, concentration (6.13×10^{-4} kmol/m^3) and a bed height of (1.50m) were 104 s, 89 s and 38 s, respectively. Correspondingly, the saturation time observed for AC, BFA and RHFA at the same conditions was 497 s, 368 s and 213 s, respectively. These results show that the faster saturation of the adsorbent pores is due to the rapid fluid movement. As the flow rate increased, the interaction time between the adsorbent and 2,4-dichlorophenol ions also decreased, resulting in a shorter contact period. In other words, the faster saturation occurred at higher flow rates due to the formation of a thin film

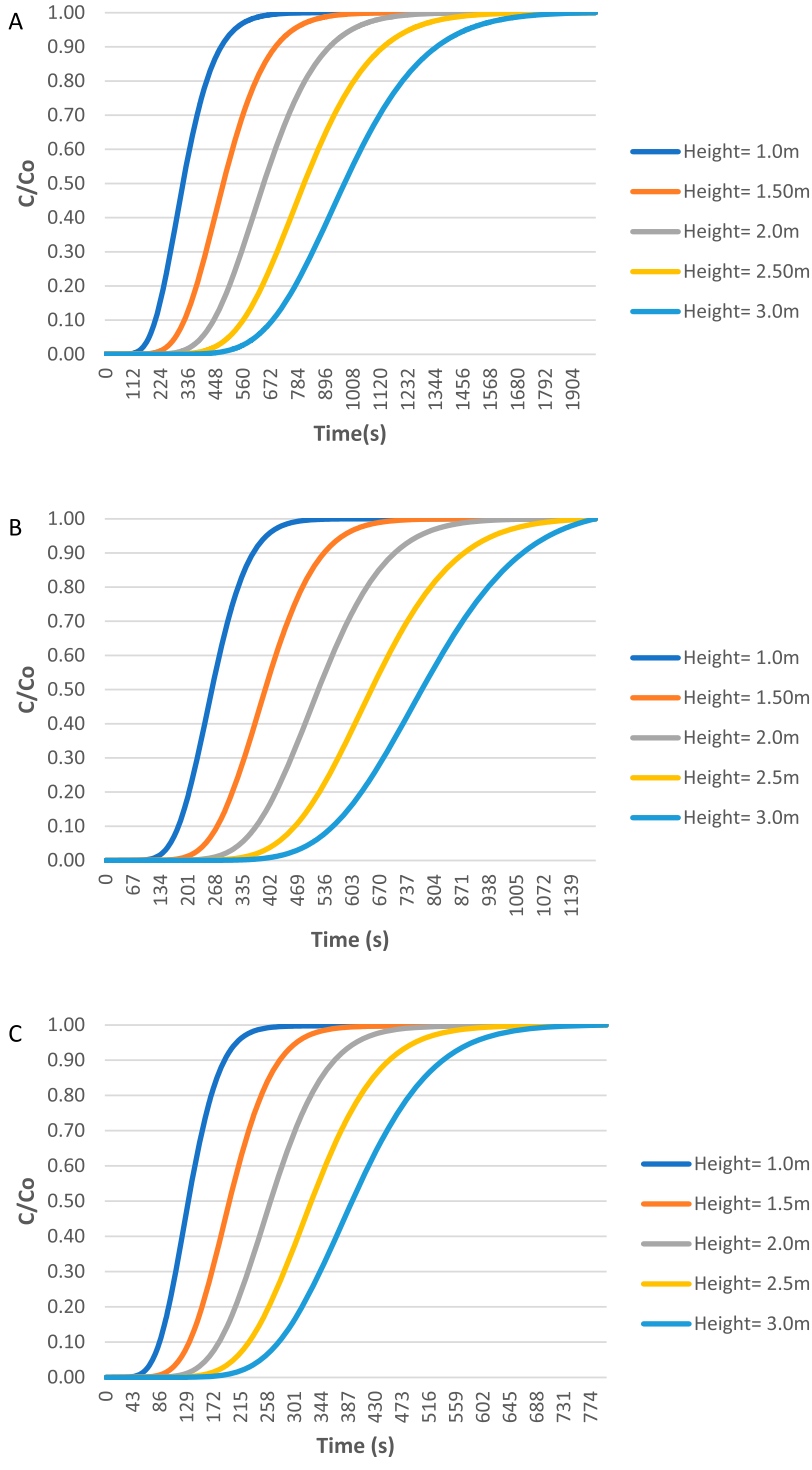


Figure 3. Effect of bed heights on the breakthrough time and breakthrough curves of the column for (a) AC, (b) BFA and (c) RHFA.

around the adsorbent which also causes the rate of mass transfer to increase [53]. A higher flow rate leads to the clogging of pores due to the increased movement of the fluid [44]. Moreover, If the retention time of the solute in the packed bed column is not extensive enough for the adsorption equilibrium to be achieved at a given flow rate, this results in a shorter saturation time [54]. A longer breakthrough and saturation time was observed for the adsorbent AC and BFA, as displayed in Figure 4 (a-c). This shows that AC and BFA are better adsorbents and have good adsorption capacity under the same conditions as RHFA.

Breakthrough times also observed for AC, BFA and RHFA adsorbents at a lower flow rate of 2 m^3/hr

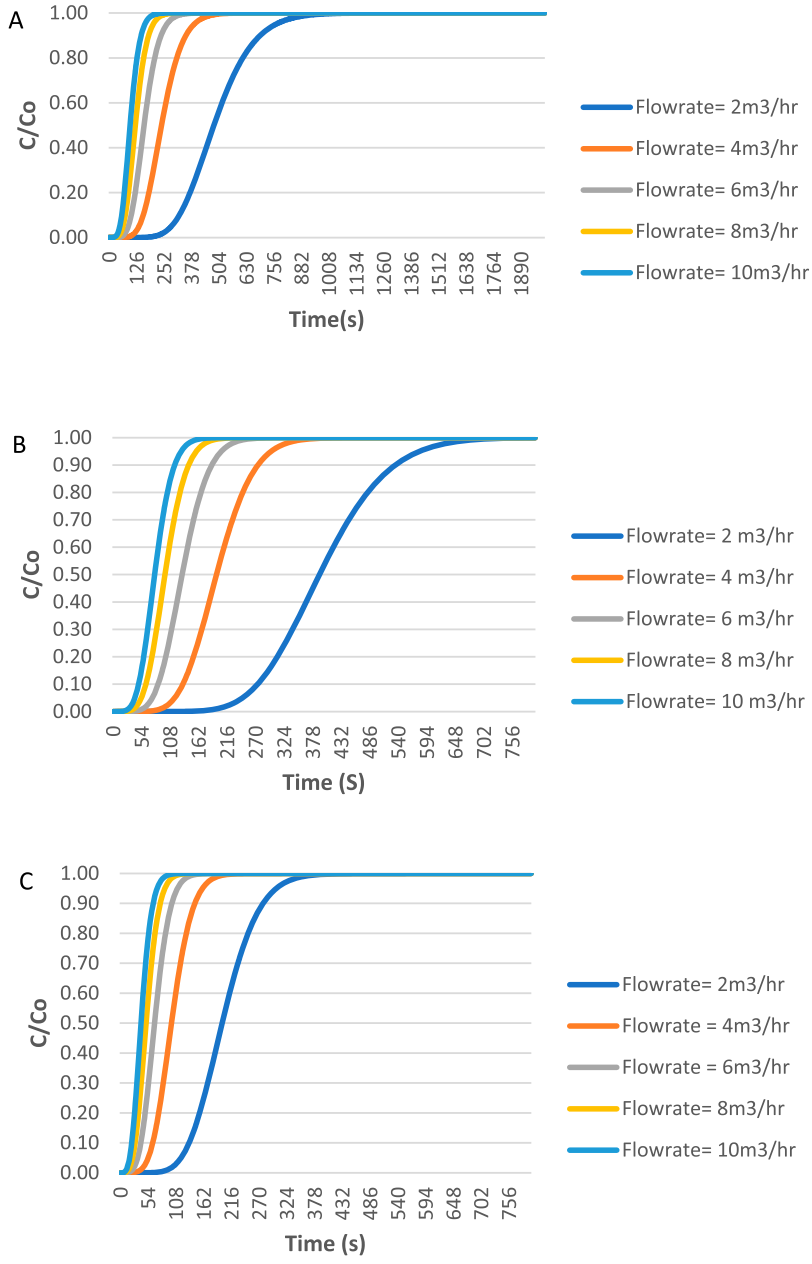


Figure 4. Effect of flow rates on the breakthrough time and breakthrough curves of the column for (a) AC, (b) BFA and (c) RHFA.

were 235 s, 206 sec and 97 s, respectively. This shows that at a low flow rate, the time required for the saturation and breakthrough time are also increased, resulting in a good adsorbent's adsorption capacity. So, this study shows that the optimum flow rate for removing 2,4-dichlorophenol from the wastewater was 2 m^3/hr. Similar results were seen in other studies [9,10,21,41,50,51]. There are fewer opportunities for the ions to reach the micro and mesopores of the adsorbent due to lower residence time [9]. An increase in the external film diffusion mass transfer resistance is the cause of the decrease in the slope at lower flow rates [9].

3.4. Optimisation of variables using response surface methodology

Design Expert software was used to optimise breakthrough and saturation time and identify the relationships between initial concentration, bed height, flow rate and adsorbent, which were given the terms A, B, C and D, respectively. A reduced quadratic model was used to describe how the variables affect breakthrough and saturation time. Terms that had a *p*-value over 0.1 were filtered out of the model. A *p*-value less than 0.05 indicates the term is statistically significant and values greater than 0.1 indicate the term is not significant [55]. The possible terms were A, B, C, D, AB, AC, AD,

BC, BD, CD, A^2, B^2 and C^2. A mathematical model was produced for each adsorbent's breakthrough and saturation time, which can be seen in Equations (4–9).

$$\begin{aligned}\text{AC Breakthrough time} &= 37.3 + 6790 \\ &\times \text{Initial Concentration} + 200 \\ &\times \text{Bed Height} - 67.3 \times \text{Flow rate} - 3650 \\ &\times \text{Initial Concentration} \times \text{Bed Height} + 3.62 \\ &\times \text{Flow rate}^2\end{aligned} \tag{4}$$

$$\begin{aligned}\text{BFA Breakthrough time} &= 69.1 + 6790 \\ &\times \text{Initial Concentration} + 157 \times \text{Bed Height} - 64.2 \\ &\times \text{Flow rate} - 3650 \times \text{Initial Concentration} \\ &\times \text{Bed Height} + 3.62 \times \text{Flow rate}^2\end{aligned} \tag{5}$$

$$\begin{aligned}\text{RHFA Breakthrough time} &= 60.3 + 6790 \\ &\times \text{Initial Concentration} + 79.9 \times \text{Bed Height} - 51.8 \\ &\times \text{Flow rate} - 3650 \times \text{Initial Concentration} \\ &\times \text{Bed Height} + 3.62 \times \text{Flow rate}^2\end{aligned} \tag{6}$$

$$\begin{aligned}\text{AC Saturation time} &= 530 + 528 \times \text{Bed Height} \\ &- 229 \times \text{Flow rate} + 11.4 \\ &\times \text{Flow rate}^2\end{aligned} \tag{7}$$

$$\begin{aligned}\text{BFA Saturation time} &= 416 + 376 \times \text{Bed Height} \\ &- 194 \times \text{Flow rate} + 11.4 \\ &\times \text{Flow rate}^2\end{aligned} \tag{8}$$

$$\begin{aligned}\text{RHFA Saturation time} &= 368 + 200 \times \text{Bed Height} \\ &- 167 \times \text{Flow rate} + 11.4 \\ &\times \text{Flow rate}^2\end{aligned} \tag{9}$$

The breakthrough and saturation time for the different adsorbents can be predicted using these equations. It can be seen from the equations that AC, AD, BC, A^2 and B^2 were deemed not significant terms in the breakthrough time model. The terms A, AB, AC, AD, BC, A2 and B2 were deemed insignificant in the saturation time model. The common non-significant term is the initial concentration of 2,4-dichlorophenol. To show the suitability of the models, the analysis of variance and fit statistics have also been presented. The analysis of variance for the two reduced quadratic models for breakthrough and saturation time can be seen in Table 5.

An F-value of 936.21 and 523.96 for breakthrough and saturation time, respectively, implies that the models are significant. A *p*-value less than 0.05 indicates that a term is significant [55]. This means all the terms except initial concentration and AB can be considered significant. The AB term was included in the model because its *p*-value of 0.0510 was low enough to pass the filter of 0.1. The initial flow rate term was included in the model as it was required to support the model hierarchy. A lack of fit F-value of 0.88 in saturation time implies the lack of fit is insignificant. This is good since the model wants to fit. However, A lack of fit F-value of 132.79 in breakthrough time implies the lack of fit is significant. This is not good since the model wants to fit. The fit statistics for the two reduced quadratic models for breakthrough and saturation time can be seen in Table 6.

Both models' predicted R2 and adjusted R2 are within the reasonable agreement, with a difference of less than 0.2 [55]. The R^2, predicted R^2, and adjusted R^2 values of both models were found to be very close to 1, indicating that the suggested models can be good predictors of the experiment results [11]. 'Adeq precision' measures the signal-to-noise ratio, a ratio greater than 4 is desirable [55]. A ratio of 113.8829 and 85.2643 for breakthrough and saturation time, respectively, indicate an adequate signal. The 2-D model graphs for the two reduced quadratic models for breakthrough and saturation time can be seen in Figure 5.

Figure 5A, B and C show that initial concentration had little effect on the breakthrough time for all three adsorbents. It can be seen that the colour gradient does not change as the Initial concentration varies. However, the colour gradient changes as bed height varies, with a longer breakthrough time favouring a taller bed height. In another study, initial concentration and dosage were found to be significant influencers of adsorption efficiency [31]. AC showed the longest breakthrough times, and RHFA showed the shortest. Figure 5D shows the effect of flow rate and adsorbent on breakthrough time. A lower flow rate and AC are preferred for a longer time. Figure 5E shows the effect of bed height and adsorbent on saturation time. A higher bed height and AC is preferred for a longer time. Figure 5F shows the effect of flow rate and adsorbent on saturation time. A lower flow rate and AC are preferred for a longer time. All the adsorbents show similar trends in all graphs, with AC performing best and RHFA performing worst. The optimum parameters are, therefore, a flow rate of 1.22×10^{-4} kmol/m^3, a bed height of 3.0 m and a flow rate of 2 m^3/hr.

3.5. Optimisation and comparison performance between adsorbents

The optimisation results show that the most optimum conditions found to be the initial concentration of 2,4-dichlorophenol are 1.22×10^{-4} kmol/m^3 with 3.0 m bed

Table 5. Analysis of variance for the reduced quadratic model.

	Breakthrough Time			Saturation Time		
	F-value	*p*-value	Significance	F-value	*p*-value	Significance
Model	936.21	<0.0001	Significant	523.96	<0.0001	Significant
A – Initial Concentration	**1.56**	**0.2194**	**Not significant**	**n/a**	**n/a**	
B – Bed Height	2453.51	<0.0001	Significant	867.60	<0.0001	Significant
C – Flow Rate	766.16	<0.0001	Significant	692.27	<0.0001	Significant
D – Adsorbent	1299.34	<0.0001	Significant	774.16	<0.0001	Significant
AB	4.07	0.0510		n/a	n/a	
BD	179.69	<0.0001	Significant	59.97	<0.0001	Significant
CD	66.57	<0.0001	Significant	45.10	<0.0001	Significant
C2	128.27	<0.0001	Significant	68	<0.0001	Significant
Lack of fit	132.79	0.0009	Significant	0.8790	0.6527	Not significant

height and 2 m^3/hr flow rate. This was the case for these three adsorbents: AC, BFA and RHFA. Figure 6 shows the breakthrough curves of these adsorbents to relate to their breakthrough time at optimum conditions.

Figure 6 shows that the breakthrough time observed for AC, BFA and RHFA was 534, 426 and 209 s, respectively. Similarly, the saturation time observed for AC, BFA and RHFA was 1627, 1242 and 650 s, respectively. These results show that a long time is needed for AC and BFA to be saturated with 2,4-dichlorophenol. This indicates that AC and BFA are better adsorbents to adsorb the 2,4-dichlorophenol from the wastewater at these optimum conditions.

4. Economic evaluation

This section aims to investigate and study the economic analysis of a small project Figure 7 in a water filtering system as shown in Figure 7. Once all the other project plans are completed, a decision needs to be taken to highlight the economic analysis section. Economic analysis is one of the essential key objectives that must be considered in a project's conceptual design. Economic analysis is a great technique or tool that involves assessing and examining various issues related to a project's economic viability [56]. Economic analysis is applied to value a project or a company that needs to understand that project spending on costs such as raw materials and profits. It is also used to understand how the project performs. Therefore, the main aim of the economic analysis presented in this paper is to indicate how changes in the broader economy will affect the present or future of the project performance [57]. Furthermore, when economic analysis is conducted, several economic factors need to be considered, as some of them directly or indirectly may influence the production performance of the project. The economic evaluation presented in this paper estimate capital expenditure (CAPEX) and operation expenditure (OPEX) [2]. It is also adjusted to estimate the sum investment value because it is the most important key objective in the conceptual design of a project.

Table 6. Fit Statistics for the two reduced quadratic models.

	Breakthrough Time	Saturation Time
R2	0.9965	0.9920
Adjusted R2	0.9955	0.9901
Predicted R2	0.9904	0.9837
Adeq Precision	113.8829	85.2643

4.1. Estimated Capital Cost (CAPEX)

CAPEX is a key element for this project that need to be considered to determine its overall economic analysis and visibility to display costing analysis that is required to be spent on purchasing designing, technological equipment, physical assets, building, etc. [57]. The Capital cost (CAPEX) is divided into main categories: i) Fixed capital investment (CAPES) and ii) Working capital investment (WCI).

4.1.1. Fixed capital investment (FCI)

Fixed capital investment is considered one of the most important economic aspects. It is applied to estimate the sum of money that needs to be spent on purchasing anything related to the plant construction [2]. This section of economic analysis is comprised of four essential categories:

1- Inside Battery Limit (ISBL) refers to the total initial cost of the direct field and indirect field of the plant that needs to be spent on purchasing all the essential equipment installation and components such as process equipment, shipping costs of equipment, and piping land costs. Therefore, to find out (ISBL) for this project or addition unit, Equation (10) [58] is used:

$$Ce = a + bS^n \tag{10}$$

Where:

Ce = Cost of the equipment based on the US Gulf Coast.

a & b = Constant values for a pacific parameter obtained from Sinnott and Towler [58].

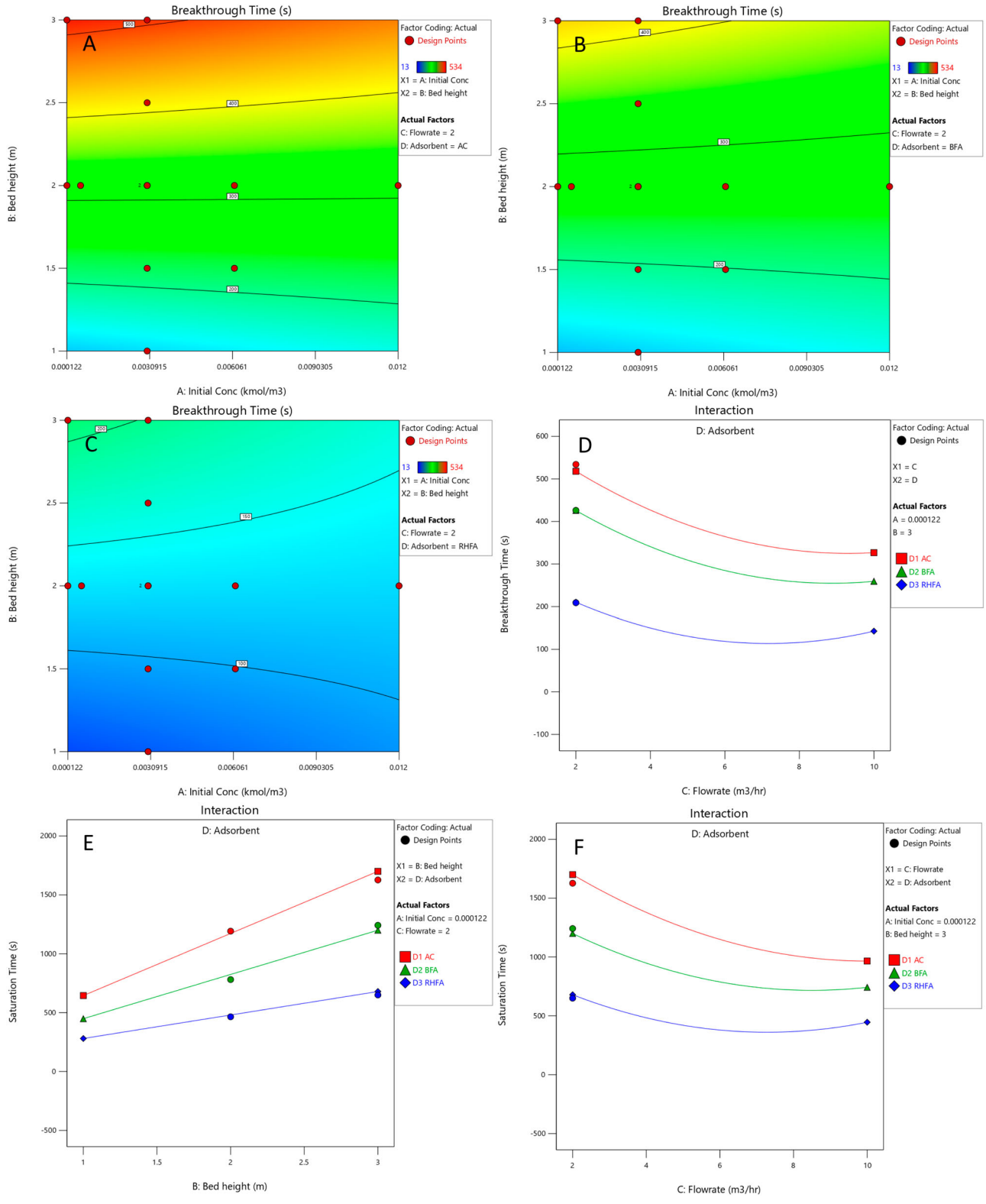


Figure 5. Model graphs for A) the effect of bed height and initial concentration on AC breakthrough time, B) the effect of bed height and initial concentration on BFA breakthrough time, C) the effect of bed height and initial concentration on RHFA breakthrough time, D) effect of flow rate and adsorbent on breakthrough time, E) the effect of bed height and adsorbent on saturation time and F) the effect of flow rate and adsorbent on saturation time.

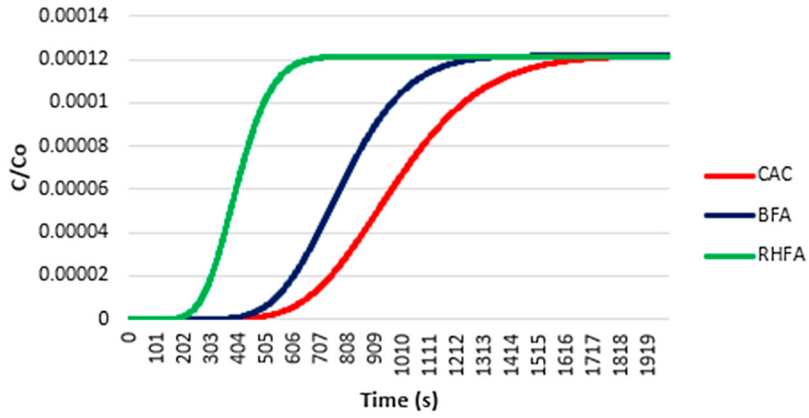


Figure 6. Effect of flow rates on the breakthrough time and breakthrough curves of the column for (a) AC, (b) BFA and (c) RHFA.

S = Size parameter

n = Denotes the exponent for the types of equipment.

The costs for the packed bed column would be:

$$Ce = 53,000 + 28,000 \times (5.30)^{0.7} = \mathbf{\$159,311.13}$$

Tanks used as storage for receiving raw materials and storing products:

$$Ce = 5000 + 1400 \times (10)^{0.7} = \mathbf{\$12,016.62} \quad (11)$$

Therefore, two tanks need to be installed as displayed in Figure 7:

$$Ce = 2 \times \$12,016.62 = \$24,033.24$$

$$Total\ Ce = ISBL = Cost\ of\ packed\ bed\ column + cost\ of\ both\ tanks \quad (12)$$

Due to the related present costs to past costs being based on data for material, energy and labour costs, therefore, the cost value of the project obtained needs to be converted from US Gulf Cost basis 2013 into US Gulf Cost 2021 by manipulating the data discovered from the Economic Indicators published in government statistical digests for Chemical engineering plant cost index (CEPCI) for the year 2021 [59].

ISBL value with inflation:

Equation (13) Sinnott and Towler [58] is manipulated to find out the cost of the unit for the year 2021:

$$Cost\ of\ present\ plant\ in\ (2021) = Cost\ plant_{2013} \times \left(\frac{Cost\ plant\ index\ 2021}{Cost\ plant\ index\ 2013}\right) = \$183,344.37 \times \left(\frac{677.7}{567.3}\right) = \$219,024.29 \text{ with US Gulf Cost Basis} \quad (13)$$

ISBL with location factor:

Equation (14) is applied to convert the obtained value from the US Gulf Cost Basis into the UK basis location factor [58]. The UK basis location factor value is (1.02) [58].

$$UK\ basis\ location\ factor = Obtained\ value\ in\ US\$ \times \left(\frac{UK\ location\ factor}{USGC\ location\ factor}\right) = \$219,024.29 \times \left(\frac{1.02}{1}\right) = \$223,404.78\ as\ the\ UK\ basis\ in\ 2021. \quad (14)$$

ISBL value with exchange rate:

Then the obtained ISBL value needs to be converted and changed from the US currency ($) to the UK currency (£). The exchange rate is approximated as (0.77) by the Bank of England [60] and used in Equation (15) [58].

$$ISBL = \$223,404.78 \times 0.77 = \mathbf{£172,021.68}\ \text{on the UK basis in}\ 2021 \quad (15)$$

2- Outside Battery Limits (OSBL) is calculated in Equation (15) [58] as (40%) of the obtained ISBL value from Equation (16).

$$\text{OSBL value} = 40\%\ X\ \text{ISBL} = 40\%\ X\ £172,021.68 = \mathbf{£68,808.67} \quad (16)$$

3- Contingency costs are another portion of fixed capital investment that needs to be considered by the company. It is approximated as (10%) of the sum of (ISBL+OSBL) as calculated in Equation (17) [58].

$$\text{Contingency Cost} = 10\%\ \text{of (ISBL} + \text{OSBL)} = \mathbf{£24,083.04} \quad (17)$$

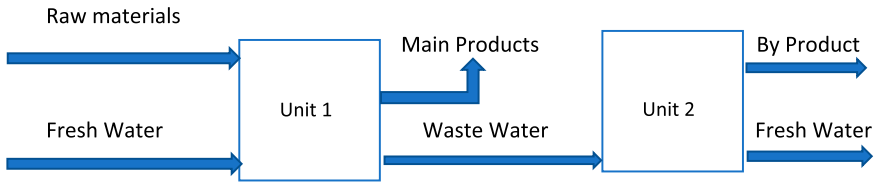


Figure 7. Schematic diagram of a water filtering system.

4- Design and engineering costs are approximated as (20%) of the sum of (ISBL+OSBL) value. It is the design and engineering costs related to structures either inside or outside the project, and it is also calculated in Equation(18) [58].

$$\text{Engineering cost} = 20\% \text{ of (ISBL} + \text{OSBL)} = \pounds\mathbf{48, 166.07} \quad (18)$$

$$\text{Therefore, the total fixied capital investment (FCI)} = \text{ISBL} + \text{OSBL} + \text{Contingency costs} + \text{Design and engineering costs}$$
$$(FCI) = \pounds\mathbf{313, 079.46} \quad (19)$$

4.1.2. Working capital investment

According to Sinnott and Tower [58], the working capital value is approximated based on the size of the project. For a small project like this, estimated as (5%) of the sum (ISBL+OSBL) value and Equation (20) is applied to calculate the value:

$$\text{Working Capital Investment} = 5\% \text{ of (ISBL} + \text{OSBL)} = \pounds\mathbf{12, 041.52} \quad (20)$$

$$\text{Therefore, CAPEXcost will be the fixed capital investment cost} + \text{working capital} = \pounds 606, 582.72 + \pounds 23, 330.10 = \pounds 32, 5120.98 \quad (21)$$

4.2. Operation Expenditure (OPEX)

4.2.1. Fixed costs of production

Sinnott & Towler [58] stated that the operating labour cost is $60,000 US per annum:

$$\$60, 000 \text{ based on the USGulf Cost (2013)}$$

Then the inflation rate of (2.9% per annum) Sinnott and Towler [58] is applied to the obtained value by using Equation (22) for conversion from 2013 to 2021 (8 years):

$$\$60,000 \times (1.029)^8 = \$\mathbf{75,417.87} \text{ per annum on (USGC) basis (2021)} \quad (22)$$

The UK location factor of (1.02) is applied in Equation (23) [61]:

$$\$75, 417.87 \times 1.02 = \mathbf{\$76, 926.22} \text{ as the UK basis } (\mathbf{2021}) \quad (23)$$

Finally, the exchange currency of (0.77) [60] is applied to the value in the UK£ by using Equation (24):

$$\$76, 926.22 \times (0.77) = \pounds 59, 233.19 \text{ (UK) basis } (2021) \quad (24)$$

Therefore, the total fixed costs of production for this process is £64393.84 as displayed in Table 7.

4.2.2. Variable Cost of Products (VCOP) (Raw materials)

The economic evaluation for three different adsorption techniques of wastewater treatment from pulp and paper processes as solid adsorbents are broadly investigated, as shown in Figure 7. These adsorptions are used to eliminate particular pollutants from the pulp and paper wastewater, including dichlorophenols [16]. In the first and second techniques of the wastewater treatment process, Rice husk fly ash (RHFA) and Bagasse fly ash (BFA) as adsorbents were applied, and the economic evaluation for these two adsorbents was studied as shown in Table 8. In the third technique, activated carbon (AC) as an adsorbent was applied, and the cost was evaluated as 900–1200 USD/ton in Table 8 [62].

The amount of adsorbent used in the packed bed column for the adsorption of 2,4-dichlororphenol can be calculated by Equation (22) [51].

$$m_b = 1/4D^2H_b\rho_b \quad (25)$$

Table 7. Fixed Costs of Production of the water treatment unit.

Fixed Costs of Production	Equations	Costs
Labour Cost	–	£59233.19
Maintenance	3%×(ISBL)	£5160.65
Total	–	£64393.84

where: m_b = denotes the mass of the adsorbent in the bed (kg); D = the diameter of the column (m); H_b = the height of the bed in the column (m) and ρ_b = show the density of the adsorbent used (kg/m^3).

$$m_b = \frac{1}{4} \times \pi \times (1.5)^2(m) \times 0.50(m) \times 500\left(\frac{\text{kg}}{m^3}\right) = 441.79 \text{ kg is placed in the bed column.}$$

The volume of the packed column:

$$V_{column} = \pi \times (r)^2 \times h = \pi \times (0.75)^2(m) \times 3(m) = 5.30\ \boldsymbol{m^3} \quad (26)$$

Where:

(v) is the volume of the column in (m^3), (r) is the radius of the column in (m) and (h) is the height of the column in (m).

The volume of the bed in the packed column:

$$V_{\text{carbon bed}} = \rho_{\text{carbon}} \times m_{\text{carbon}} = 500\left(\frac{kg}{m^3}\right) \times 441.79 = 0.88(m)^3 \quad (27)$$

out of the packed columne

The volumetric flow rate of water $= 2\ m^3/hr$

The volumetric rate of water on one day

$$= 24hr \times 2\frac{m^3}{hr} = 48\ \frac{m^3}{day} \quad (28)$$

The total volumetric flow rate of fresh water from this process could be obtained as calculated in Equation (29):

$$Fresh\ water = 365\ day \times 48\ \frac{m^3}{day} = 17520\ \frac{m^3}{year} \quad (29)$$

The price of freshwater [63] is estimated as £5/m^3: Therefore,

$$17,520\ \frac{m^3}{year} \times \frac{£5}{m^3} = £\mathbf{87, 600\ per\ year} \quad (30)$$

For a period of 20 years, the company can save £1,752,000 from this unit.

Table 8. The cost of the adsorbent used in this study [62].

Adsorbents	Cost of adsorbent
Rice husk fly ash	Handling charges
Bagasse fly ash	Handling charges
Activated carbon	900–1200 USD/Ton

4.3. Gross profits, discount factor and discounted cash flow calculations

Financial elements and calculations are of essential section in every business to determine the cost of revenue, products' costs and profitability. As soon as a modern chemical (process) engineer begins to produce products, it requires a start-up schedule because it does not make products at full capacity for a number of years. Table 9 is a typical start-up schedule for the engineering process provided by Sinnott and Towler [58]. The cost (cash flow) of this project was calculated as 30% of fixed capital investment which is £93,923.84 in the first year and 50% of fixed capital investment which is 156,539.73 in the second year. Therefore, this project has zero revenue and minuses gross profits for the first two years. The gross profit values from year 5 to year 20 for this are calculated and shown in the Equations in Table 9 are derived from Sinnott and Towler [58].

To find out depreciation and taxable income values, the scrap value needs to be found using Equation (31) [58]:

$$\text{Scrap} = 5\% \text{ of (ISBL} + \text{OSBL)} = (0.05) \times (£172,021.68 + £68,808.67) = £12,041.52 \quad (31)$$

The scrap value is then used in Equation (32) to find the depreciation value [57]:

$$\text{Depreciation value at year 2} = \frac{\text{FCI} - \text{Scrap value}}{\text{Plant life}} \quad (32)$$

And the tax paid values will be found by Equation (33) [57]:

$$\text{Tax paid at year 2} = (20\%) \text{ of taxable income} \quad (33)$$

To find cash flow in the second year of the project, the following Equation (28) is used:

$$\text{Cash Flow at year 2} = \text{Gross profit} - \text{Tax paid} \quad (34)$$

Equation (35) is used to determine the discount factor for every year, assuming the discount rate for the next 20 years of the plant is 2% [58].

$$\text{Discount factor at year 2} = (1 + i)^{-n} \quad (35)$$

Where:

i = representing the discounted cash flow rate of return (Percent/100).

n = representing the life period of the project in a year.

Table 9. Start-up schedule of gross profits for RHFA, BFA and AC adsorbents.

		RHFA and BFA Adsorbents		AC Adsorbent	
Year	Equations &Costs (£)	Revenues (£)	Gross Profits (£)	Revenues (£)	Gross Profits (£)
0	30% of (FCI) = 93,923.84	0	Revenue − Cost = − 93,923.84	0	Revenue − Cost = − 93,923.84
1st	50% of (FCI) = 156,539.73	0	Revenue − Cost = − 156,539.73	0	Revenue − Cost = −156,539.73
2nd	(20% of FCI) +(WCI) + FCOP + (30% of VCOP)	30% of Design basis = 420,000	Revenue − Cost = 280,948.75	30% of Design basis =420,000	Revenue − Cost = 277,767.86
3rd	(70% of VCOP) + FCOP	70% of Design basis = 980,000	Revenue − Cost = 808,182.32	70% of Design basis = 980,000	Revenue − Cost = 908,184.09
4th	FCOP + VCOP	100% of Design basis = 14,000,000	Revenue − Cost = 1,228,182.32	100% of Design basis = 1,400,000	Revenue − Cost = 1,325,003.20

* Design basis = total price of the obtained water from the process.

Finally, to figure out the discount cash flow, the following Equation (36) is applied:

$$\text{Discount Cash Flow at year 2} = \text{Net Cash flow} \times \text{Discount factor} = -£156,539.73 \times 0.98 = -£153408.94 \quad (36)$$

Tables 10 and 11 contains all the values and calculation methods of gross profit, discounted cash flow and cumulative net cash flow for (RHFA and BFA adsorbents) as scenario 1 and (AC) as scenario 2 for a period of 20 years. In scenario 1, the cumulative cash flow applied in this project from year 1 to year 8 are (-£93923.84), (-£250463.57), (-£25,702), (£620,847), (£1,603,395), (£2,585,944), (£3,568,49), (£4,551,041), respectively. By adding them all together, a cumulative cash flow for year 8 is obtained, which is equal to (£9347986.59). The cumulative cash flow for both scenarios is quite close to each other andare calculated as £161,135,073 and 163,843,513, respectively, over 20 years. The fresh water production capacity of this unit is estimated as 17,520 m^3/year to remove the 2,4-dichlorophenol ions from the pulp and paper mill effluent. Therefore, economic analysis for RHFA, BFA and AC as absorbents have been done to meet the higher performance and lower cost. The cost value for RHFA and BFA is only the handling charge but for AC adsorbent is £10602.96 per year with better performance with a volumetric flow rate of 2 m^3/hr, and the NPVs for all processes were obtained. Therefore, the company can save £87,600 per year with the AC absorbent. The cumulative cash flow for both scenarios is presented and the cumulative cash flow for the second scenario is better according to obtained results. For example, the cumulative cash flow for scenarios 1 & 2 are calculated as £161,135,073 and 163,843,513, respectively, over twenty years. The advantage of using simulation software is it gives responses cheaper and faster than a physical process. It allows responses from scenarios that would be unsafe or expensive to operate. With the correct data, the responses can be very accurate. The limitations and cons of this method of research are the simulation software

Table 10. Gross profit, discounted cash flow and cumulative net cash flow for RHFA and BFA Adsorbents.

Year	Gross Profit (MM£)-	Depreciation Change (£)	Taxable Income (£)	Taxes Paid (£)	Net Cash Flow (£)	Discount Factor	Present Value of Cash Flow (£)	Cumulative Net Cash Flow (£)
0	−93,923.84	0	0	0	−93,923.84	1	−93,923.84	−93923.84
1	−156,539.73	0	0	0	−156,539.73	0.98	−153408.9354	−250463.57
2	280,948.75	13.31	280,935	56187.08	224,762	0.96	215771.1961	−25,702
3	808,182.32	13.31	808,169	161633.80	646,549	0.94	607755.6075	620,847
4	1,228,182.32	13.31	1,228,169	245633.80	982,549	0.92	903944.6371	1,603,395
5	1,228,182.32	13.31	1,228,169	245633.80	982,549	0.91	894119.1519	2,585,944
6	1,228,182.32	13.31	1,228,169	245633.80	982,549	0.89	874468.1816	3,568,492
7	1,228,182.32	13.31	1,228,169	245633.80	982,549	0.87	854817.2112	4,551,041
8	1,228,182.32	13.31	1,228,169	245633.80	982,549	0.85	835166.2408	5,533,589
9	1,228,182.32	13.31	1,228,169	245633.80	982,549	0.84	825340.7556	6,516,138
10	1,228,182.32	13.31	1,228,169	245633.80	982,549	0.82	805689.7853	7,498,686
11	1,228,182.32	13.31	1,228,169	245633.80	982,549	0.8	786038.8149	8,481,235
12	1,228,182.32	13.31	1,228,169	245633.80	982,549	0.79	776213.3297	9,463,783
13	1,228,182.32	13.31	1,228,169	245633.80	982,549	0.77	756562.3593	10,446,332
14	1,228,182.32	13.31	1,228,169	245633.80	982,549	0.76	746736.8741	11,428,880
15	1,228,182.32	13.31	1,228,169	245633.80	982,549	0.74	727085.9038	12,411,429
16	1,228,182.32	13.31	1,228,169	245633.80	982,549	0.73	717260.4186	13,393,977
17	1,228,182.32	13.31	1,228,169	245633.80	982,549	0.71	697609.4482	14,376,526
18	1,228,182.32	13.31	1,228,169	245633.80	982,549	0.7	687783.963	15,359,074
19	1,228,182.32	13.31	1,228,169	245633.80	982,549	0.69	677958.4778	16,341,623
20	1,228,182.32	13.31	1,228,169	245633.80	982,549	0.67	658307.5075	17,324,171
							NPV = 13801297.09	161135073

Gross profit, discounted cash flow & cumulative net cash flow for RHFA and BFA adsorbents

Table 11. Gross Profits, discounted cash flow & cumulative cash flow for activated carbon adsorbent.

Year	Gross Profit (£)	Depreciation Change (£)	Taxable Income (£)	Taxes Paid (£)	Net Cash Flow (£)	Discount Factor	Present Value of Cash Flow (£)	Cumulative Net Cash Flow (£)
0	−93,923.84	0	0	0	−93,923.84	1	−93,923.84	−93923.84
1	−156,539.73	0	0	0	−156,539.73	0.98	−153408.935	−250463.57
2	277,767.86	13.313	277,755	55550.9094	222,217	0.96	213328.2726	−28,247
3	908,184.09	13.313	908,171	181634.1554	726,550	0.94	682956.9385	698,303
4	1,325,003.20	13.313	1,324,990	264997.9774	1,060,005	0.92	975204.8048	1,758,309
5	1,228,182.32	13.313	1,228,169	245633.8014	982,549	0.91	894119.1519	2,740,857
6	1,228,182.32	13.313	1,228,169	245633.8014	982,549	0.89	874468.1816	3,723,406
7	1,228,182.32	13.313	1,228,169	245633.8014	982,549	0.87	854817.2112	4,705,954
8	1,228,182.32	13.313	1,228,169	245633.8014	982,549	0.85	835166.2408	5,688,503
9	1,228,182.32	13.313	1,228,169	245633.8014	982,549	0.84	825340.7556	6,671,051
10	1,228,182.32	13.313	1,228,169	245633.8014	982,549	0.82	805689.7853	7,653,600
11	1,228,182.32	13.313	1,228,169	245633.8014	982,549	0.8	786038.8149	8,636,148
12	1,228,182.32	13.313	1,228,169	245633.8014	982,549	0.79	776213.3297	9,618,697
13	1,228,182.32	13.313	1,228,169	245633.8014	982,549	0.77	756562.3593	10,601,245
14	1,228,182.32	13.313	1,228,169	245633.8014	982,549	0.76	746736.8741	11,583,794
15	1,228,182.32	13.313	1,228,169	245633.8014	982,549	0.74	727085.9038	12,566,342
16	1,228,182.32	13.313	1,228,169	245633.8014	982,549	0.73	717260.4186	13,548,891
17	1,228,182.32	13.313	1,228,169	245633.8014	982,549	0.71	697609.4482	14,531,439
18	1,228,182.32	13.313	1,228,169	245633.8014	982,549	0.7	687783.963	15,513,988
19	1,228,182.32	13.313	1,228,169	245633.8014	982,549	0.69	677958.4778	16,496,536
20	1,228,182.32	13.313	1,228,169	245633.8014	982,549	0.67	658307.5075	17,479,085
							NPV = 13945315.66	163843513

assumes perfect conditions and does not account for all factors and scenarios. The simulation is only as effective as the input data and skill of the user.

5. Conclusion

In this research, the adsorption process of 2,4-dichlorophenol ions from the pulp and paper wastewater was simulated using Aspen Adsorption with a packed bed column of AC, BFA, and RHFA adsorbents. The effect of the parameters of initial 2,4-dichlorophenol concentration, bed height and feed flow rate on the adsorption process were investigated. Based on the simulation results, the initial 2,4-dichlorophenol concentration did not affect the breakthrough and saturation time at the set parameters. Increasing the flow rate reduced the contact time between the adsorbent and contaminant, and as a result, adsorbents saturated faster, reducing breakthrough and saturation time. Increasing the bed height resulted in more adsorption binding sites, hence a longer breakthrough time and saturation time. Using RSM, the parameters were optimised. The optimum parameters were an initial 2,4-dichlorophenol concentration of 1.22×10^{-4} kmol/m^3, a flow rate of 2 m^3/hr and a bed height of 3.0 m, the longest breakthrough time was 534 s for AC, 426 s for BFA and 209 s for RHFA. The simulation results show that the performance of AC and BFA were better adsorbents than RHFA. The production capacity of this unit is estimated as 17,520 m^3/year to remove the 2,4-dichlorophenol ions from the pulp and paper mill effluent. Therefore, economic analysis for RHFA, BFA and AC as absorbents have been done to meet the higher performance and lower cost. the NPVs for all processes were obtained with better performance. The cumulative cash flow for scenarios 1 & 2 are calculated as £161,135,073 and 163,843,513, respectively, over twenty years. The company can save £87,600 per year with the AC absorbent. The advantage of using simulation software is it gives responses cheaper and faster than a physical process. It allows responses from scenarios that would be unsafe or expensive to operate. With the correct data, the responses can be very accurate. The limitations and cons of this method of research are the simulation software assumes perfect conditions and does not account for all factors and scenarios. The simulation is only as effective as the input data and skill of the user. Future work would include Investigating other factors such as bed diameter and temperature,the adsorption of mixed pollutants; the simulation of adsorption columns in series and pilot-scale studies.

Disclosure statement

No potential conflict of interest was reported by the author(s).

Data availability statement

The authors confirm that the data supporting the findings of this study are available within the article.

ORCID

Sharif H. Zein http://orcid.org/0000-0002-8863-1450
Usama Ahmed http://orcid.org/0000-0001-7199-600X
A. A. Jalil http://orcid.org/0000-0003-0811-3168

References

[1] Kallas J, Munter R. Post-Treatment of pulp and paper industry wastewaters using Oxidation and Adsorption processes. Water Sci Technol. 1994;29(5–6):259–272.

[2] Buyukkamaci N, Koken E. Economic evaluation of alternative wastewater treatment plant options for pulp and paper industry. Sci Total Environ. 2010;408(24):6070–6078.

[3] Latorre A, Malmqvist A, Lacorte S, et al. Evaluation of the treatment efficiencies of paper mill whitewaters in terms of organic composition and toxicity. Environ Pollut. 2007;147(3):648–655.

[4] Ali M, Sreekrishnan TR. Aquatic toxicity from pulp and paper mill effluents: a review. Adv Environ Res. 2001;5:175–196.

[5] Mall ID, Singh D, Singh AK, et al. Detoxification of bleach plant effluent using low cost adsorbents: removal of 2,4 dichlorophenol. Indian Pulp and Paper Technology Association (IPPTA). 2001;13(4).

[6] Thermofisher Scientific. Safety data sheet. 2,4-Dichlorophenol; 2020. [cited 2023 Mar 08]. https://www.fishersci.pt/chemicalProductData_uk/wercs?itemCode=10427540&lang=EN.

[7] Dawodu FA, Akpan BM, Akpomie KG. Sequestered capture and desorption of hexavalent chromium from solution and textile wastewater onto low cost heinsia crinita seed coat biomass. Appl Water Sci. 2020;10(1):1–15.

[8] Priyadharshini MR. Removal of chromium (VI) from textile waste water by using activated carbon prepared from neem leaves and garlic husk. Middle East J Appl Sci Technol. 2021;4:19–28. DOI:10.46431/mejast.2021.4303

[9] Agarwal A, Upadhyay U, Sreedhar I, et al. Simulation studies of Cu(II) removal from aqueous solution using olive stone. Cleaner Mater. 2022;5:100128.

[10] Gonzalez-Delgado A, Tejada-Tovar C, Villabona-Ortiz A. Computer-aided modeling and evaluation of a packed bed for chromium (vi) removal using residual biomass of theobroma cacao L. Chem Eng Trans. 2022;92:517–522.

[11] Upadhyay U, Gupta S, Agarwal A, et al. Adsorptive removal of Cd2+ ions using dolochar at an industrial-scale process optimization by response surface methodology. Environ Sci Pollut Res. 2021. doi:10.1007/s11356-021-17216-9.

[12] Crini G, Lichtfouse E. Advantages and disadvantages of techniques used for wastewater treatment. Environ Chem Lett. 2019;17(1):145–155.

[13] Agarry S, Owabor C, Ajani A. Modified plantain peel as cellulose-based low-cost adsorbent for the removal of 2,6-dichlorophenol from aqueous solution: adsorption isotherms,: kinetic modelling and thermodynamic studies. Chem Eng Commun. 2013;200(8):1121–1147.

[14] Ding H, Li X, Wang J, et al. Adsorption of chlorophenols from aqueous solutions by pristine and surface functionalised single-walled carbon nanotubes. J Environ Sci. 2016;43:187–198.

[15] Garba Z, Rahim A. Evaluation of optimal activated carbon from an agricultural waste for the removal of para-chlorophenol and 2,4-dichlorophenol. Process Saf Environ Prot. 2016;102:54–63.

[16] Ren L, Zhang J, Li Y, et al. Preparation and evaluation of cattail fiber-based activated carbon for 2,4-dichlorophenol and 2,4,6-trichlorophenol removal. Chem Eng J. 2011;168(2):553–561.

[17] Zhou L, Meng X, Fu J, et al. Highly efficient adsorption of chlorophenols onto chemically modified chitosan. Appl Surf Sci. 2014;292:735–741.

[18] Namasivayam C, Kavitha D. Adsorptive removal of 2,4-dichlorophenol from aqueous solution by Low-cost carbon from an agricultural solid waste: coconut coir pith. Sep Sci Technol. 2005;39(6):1407–1425.

[19] Huang L, Zhou Y, Guo X, et al. Simultaneous removal of 2,4-dichlorophenol and Pb(II) from aqueous solution using organoclays: isotherm,: kinetics and mechanism. J Ind Eng Chem. 2014;22:280–287.

[20] Ma J, Wang H, Wang F, et al. Adsorption of 2,4-dichlorophenol from aqueous solution by a New Low-cost adsorbent – Activated bamboo charcoal. Sep Sci Technol. 2010;45(16):2329–2336.

[21] Krishnaiah D, Anisuzzama S, Joseph C, et al. Simulation of phenol adsorption in a packed Bed column. J Appl Sci. 2014;14(23):3249–3255.

[22] Praveen S, Jegan J, Bhagavathi Pushpa T, et al. Biochar for removal of dyes in contaminated water: an overview. Biochar. 2022;4(1):10.

[23] Biswal BK, Vijayaraghavan K, Tsen-Tieng DL, et al. Biochar-based bioretention systems for removal of chemical and microbial pollutants from stormwater: A critical review. J Hazard Mater. 2022;422:126886.

[24] Mohamed BA, Huang C, Mok N, et al. A comparative life-cycle assessment and cost analysis of biofilters amended with sludge-based activated carbon and commercial activated carbon for stormwater treatment. J Hazard Mater. 2023;445:130632.

[25] Mohamed BA, Li LY, Hamid H, et al. Sludge-based activated carbon and its application in the removal of perfluoroalkyl substances: a feasible approach towards a circular economy. Chemosphere. 2022;294:133707.

[26] Mu'azu ND, Jarrah N, Zubair M, et al. Removal of phenolic compounds from water using sewage sludge-based activated carbon adsorption: a review. Int J Environ Res Public Health. 2017;14(10):1094.

[27] Holliday MC, Parsons DR, Zein SH. Agricultural Pea waste as a Low-Cost pollutant biosorbent for methylene blue removal: adsorption kinetics, isotherm and thermodynamic studies. Biomass Conv Bioref. 2022a. doi:10.1007/s13399-022-02865-8

[28] Holliday MC, Parsons DR, Zein SH. Microwave-Assisted hydrothermal carbonisation of waste biomass: The effect of process conditions on hydrochar properties. Processes. 2022b;10:1756. doi:10.3390/pr10091756.

[29] Allwar A, Syamsurizal S. Removal of 2-chlorophenol using rice husk activated carbon prepared by zncl2/h3po4 activation. Orient J Chem. 2022;33(5):2386–2393. DOI:10.13005/ojc/330531

[30] Srivastava V, Swamy M, Mall I, et al. Adsorptive removal of phenol by bagasse fly ash and activated carbon: equilibrium,: kinetics and thermodynamics. Colloids Surf, A. 2006;272(1–2):89–104.

[31] Lingamdinne LP, Karri RR, Khan MR, et al. Evaluation of surface phenomena of magnetic biomass for dye removal via surface modeling. J Environ Chem Eng. 2021;9:105953.

[32] Amiri MJ, Bahrami M, Beigzadeh B, et al. A response surface methodology for optimization of 2,4-dichlorophenoxyacetic acid removal from synthetic and drainage water: a comparative study. Environ Sci Pollut Res. 2018;25:34277–34293.
[33] Thoppil Y, Zein SH. Techno-economic analysis and feasibility of industrial-scale biodiesel production from spent coffee grounds. J Clean Prod. 2021;307:127113.
[34] Waudby H, Zein SH. A circular economy approach for industrial scale biodiesel production from palm oil mill effluent using microwave heating: design,: simulation, techno-economic analysis and location comparison. Process Saf Environ Prot. 2021;148:1006–1018.
[35] Zein SH, Antony A. Techno-Economic analysis and feasibility of industrial-scale activated carbon production from agricultural Pea waste using microwave-assisted pyrolysis: a circular economy approach. Processes. 2022;10:1702. doi:10.3390/pr10091702.
[36] Chen N, Cao S, Zhang L, et al. Structural dependent Cr(VI) adsorption and reduction of biochar: hydrochar versus pyrochar. Sci Total Environ. 2021;783:147084.
[37] Hibbert S, Welham K, Zein SH. An innovative method of extraction of coffee oil using an advanced microwave system: In comparison with conventional soxhlet extraction method. SN Appl Sci. 2019;1:1467.
[38] Li X, Wang R, Shao C, et al. Biochar and hydrochar from agricultural residues for soil conditioning: Life Cycle Assessment and Microbially mediated C and N cycles. ACS Sustain Chem Eng. 2022;10:3574–3583.
[39] Touhami D, Zhu Z, Balan WS, et al. Characterization of rice husk-based catalyst prepared via conventional and microwave carbonisation. J Environ Chem Eng. 2017;5:2388–2394.
[40] Zein SH, Gyamera BA, Skoulou VK. Nanocarbons from acid pretreated waste coffee grounds using microwave radiation. Mater Lett. 2017;193:46–49.
[41] Anisuzzaman S, Bono A, Krishnaiah D, et al. A study on dynamic simulation of phenol adsorption in activated carbon packed bed column. J King Saud Univ - Eng Sci. 2016;28(1):47–55.
[42] Hameed A, Hameed B, Almomani F, et al. Dynamic simulation of lead(II) metal adsorption from water on activated carbons in a packed-bed column. Biomass Convers Biorefinery. 2022. DOI:10.1007/s13399-022-03079-8
[43] Sutradhar P, Maity P, Kar S, et al. Modelling and optimization of PSA (pressure swing adsorption) unit by using aspen Plus® and design expert ®. Int J Innovative Technol Exploring Eng. 2019;8:64–69.
[44] Nieva A, Garcia R, Ped R. Simulated biosorption of Cr6+ using peels of litchi chinensis sonn by aspen adsorption® V8.4. Int J Environ Sci Dev. 2019;10(10):331–337.
[45] Shah B, Shah A, Patel H, et al. High-value Zeolitic material from bagasse Fly Ash: utilisation for Dye elimination. Water Environ Res. 2013;85(6):558–567.
[46] Ahmaruzzaman M, Gupta V. Rice husk and Its Ash as Low-cost adsorbents in water and wastewater treatment. Ind Eng Chem Res. 2011;50(24):13589–13613.
[47] Polaert I, Wilhelm A, Delmas H. Phenol wastewater treatment by a two-step adsorption–oxidation process on activated carbon. Chem Eng Sci. 2002;57(9):1585–1590.
[48] Liu Q, Zheng T, Wang P, et al. Adsorption isotherm,: kinetic and mechanism studies of some substituted phenols on activated carbon fibers. Chem Eng J. 2010;157(2–3):348–356.
[49] Kumar S, Zafar M, Prajapati J, et al. Modeling studies on simultaneous adsorption of phenol and resorcinol onto granular activated carbon from simulated aqueous solution. J Hazard Mater. 2011;185(1):287–294.
[50] Patrick UA, Cosmas U. Studying and modelling dynamic adsorption of lead (II) ion onto fixed bed column of activated carbon of plantain peels and bamboo. Science J Environ Eng Res. 2016. DOI: 10.7237/sjeer/115
[51] Adornado A, Soriano A, Orfiana O, et al. Simulated Biosorption of Cd(II) and Cu(II) in single and binary metal systems by water hyacinth (Eichhornia crassipes) using Aspen adsorption. ASEAN J Chem Eng. 2017;16(2):21.
[52] Zhang YP, Adi VSK, Huang H, et al. Adsorption of metal ions with biochars derived from biomass wastes in a fixed column: adsorption isotherm and process simulation. J Ind Eng Chem (Seoul, Korea). 2019;76:240–244.
[53] Samarghandi M, Hadi M, McKay G. Breakthrough curve analysis for fixed-Bed adsorption of Azo dyes using Novel Pine Cone—Derived active carbon. Adsorpt Sci Technol. 2014;32(10):791–806.
[54] Simate G, Ndlovu S. The removal of heavy metals in a packed bed column using immobilised cassava peel waste biomass. J Ind Eng Chem. 2015;21:635–643.
[55] Stat-Ease. Design-Expert Help [PDF guide]; 2021.
[56] Chen W, Horan NJ. The treatment of a high strength pulp and paper mill effluent for wastewater re-use. Environ Technol. 1998;19(2):173–182. doi:10.1080/09593331908616669.
[57] Garratt D, Guest J, Jones E, et al. Economic for business: investment and the employment of capital. 8th ed Harlow: Pearson Education Limited; 2019.
[58] Sinnott T, Towler G. Chemical engineering design: principles, practice and economics of plant and process design. 3rd ed Oxford: Elsevier Ltd; 2021.
[59] ChemicalEngineering. Economic Indicators; 2021.
[60] Bank of England. Daily spot exchange rate against Euro; 2021. Available from: https://www.bankofengland.co.uk/boeapps/database/Rates.asp?Travel=NIxAZx&into=EUR [cited 2022 Nov 10].
[61] Sinnott T, Towler G. Chemical engineering design: principles,: practice and economics of plant and process design. Oxford: Elsevier Ltd; 2009.
[62] Alibaba.com. Top Rated Efficient price of activated carbon per ton At Luring Offers - Alibaba.com. [online].; 2022. Available from: <https://www.alibaba.com/showroom/price-of-activated-carbon-per-ton.html> [cited 2022 Sep 3].
[63] Thameswater. How to calculate your water bill; 2022. Available from: file:///C:/Users/Dell/Downloads/Documents/how-we-calculate-metered-bills-2020-21.pdf [cited 2022 Dec 19].