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The Economy of Adsorption Process: Factors of Equilibrium, Adsorbent Cost, Contact Time and Temperature

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Abstract: Economic factors are one of the determinants of the desirability and usability of wastewater treatment technology. Energy and time are indices of economic considerations in any industrial process. Therefore, to assess the implications of contact time, adsorbent dose, and temperature on cost, the batch adsorption process was conducted. Orthophosphoric activated carbon (OPAC) was prepared from *Daniellia oliveri* sawdust. The estimate for the preparation of 1 kg of OPAC was US$80.51. Pyrimethamine solutions were treated with OPAC. Contact times were varied between 0 and 200 (equilibrium time) minutes, and temperatures between 28°C (room temperature) and 50°C. At 30 and 200 minutes, 49.2 % and 54.3 % of pyrimethanie were removed, respectively. An approximately 100 % removal would be achieved through a 2-stage adsorption process for the two systems. If 30 minutes were chosen as contact time, 340 minutes would be saved. At 28°C and 50°C, 38.2 % and 43.8 % were removed, respectively. If room temperature were chosen for the adsorption, the cost of heating would be saved. Therefore, economic contact time, 30 minutes, and room temperature, 28°C, would be preferred against equilibrium time, 200 minutes, and heating at 50°C.

Keywords: economic-contact-time 2; pyrimethamine 3; equilibrium-contact-time 4; cost-of-heating 5; 2-stage-batch-adsorption-process 6; 3-stage-batch-adsorption-process.

1. Introduction

The generational consciousness has led to approaches to conserve natural resources [1]. This has given rise to research for developing new materials and emerging new industries and products [2]. New contaminants and pollutants have been generated and discharged into the environment [3]. Water bodies remain one of the main reservoirs of these unwanted substances. The world is experiencing dwindling usable and portable water resources while global south countries are the most hit [4]. Aside from water shortages, pollutants in water resources have been linked to daily deaths among the human population, mutation in exposed aquatic organisms, hormonal impairment, endocrine disruption, and loss of species [5-7].

There is a wide range of conventional wastewater treatment technologies: ion exchange, reverse osmosis, ultra-filtration, oxidation, electro-coagulation, precipitation, electro-dialysis, and adsorption [8-11]. These technologies are still evolving to enhance performance in terms of purification efficiency, non-toxic bye-product generation, and operation costs.

The adsorption process is one of the most appealing methods of wastewater treatment. The characteristics of the adsorption method are versatility, low cost, purification efficiency, and re-usability of adsorbent [12-16]. It is a surface phenomenon where adsorbate molecules are partitioned between the bulk and surface of a solid in contact. Various adsorbents have been used in adsorption, including activated carbon, biomass, nanoparticles, nanocomposites, clays, soil, resins, and agro-waste. The versatility of the adsorption method rests in the ability to remediate organic, inorganic, and many other substance-contaminated solutions [17,18].

In order to further reduce the cost of the adsorption process, the researchers are working to replace the expensive commercial adsorbents with cheaper and more efficient ones. The researchers have shifted attention towards converting agro-based wastes to competitive adsorbents for usage in wastewater remediation. Some of the agro-waste materials include sawdust, bagasse, fruit nuts shells, tree barks, leaves, tree stems, roots, animal dung, fruit peels, and animal bones [18,19]. These precursors were treated, modified, carbonized, and/or activated to make efficient and cheap adsorbents.

The effects of some experimental conditions are studied in the adsorption process. These include adsorbent dose, pH, temperature, contact time, and initial adsorbate concentration [20]. The effect of the adsorbent dose is studied to determine its mass, which would remove maximum adsorbate molecules from the adsorption system at equilibrium. The study of the effect of temperature enables researchers to know if the rise in temperature enhances the uptake of adsorbate. Also, contact time is studied to determine equilibrium time. Equilibrium time is reached when adsorbate molecules have completely occupied the adsorption sites on the surface of the adsorbent. These experimental conditions could significantly influence the cost of the adsorption process.

Therefore, contact time, adsorbent dose, and temperature in the adsorption process should be studied in the context of economy in addition to equilibrium to further reduce the cost of the adsorption process and wastewater remediation.

2. Materials and Methods

2.1. Materials.

Orthophosphoric acid (85%), 10% HCl, furnace (Carbolite AAF 1100), pH meter (Jenway 3520), sawdust of *Daniellia oliveri*, pyrimethamine (> 99.9%), distilled water, filter paper, ultraviolet-visible spectrometer (B-UV 1800PC).

2.2. Preparation of adsorbent.

In a crucible, RDS was soaked in 1 M H3PO4 (1 g:1 mL). This was subjected to the furnace at 800°C for 5 minutes. The activated carbon adsorbents prepared were washed using 10% HCl to remove surface ash, followed by washing with distilled water to neutral pH of the supernatant. The adsorbent was dried in an oven at 110°C overnight, sieved to have a regular particle size, and stored in an airtight container as H_3PO_4 activated carbon (OPAC) [9].

2.3. Percentage yield of adsorbent.

$$Yield\ of\ adsorbent\ (\%) = \frac{weight\ of\ adsorbent}{weight\ of\ precursor\ (raw\ material)} \times 100 \qquad (1)$$

2.4. Determination of cost of adsorbent.

Cost of adsorbent per unit mass of adsorbate adsorbed (US$/$_{adsorbate}$) =

$$\frac{Chemical\ purchase\ cost\ \left(\frac{US\$}{g}\right) + Energy\ cost\left(\frac{US\$}{g}\right)kWh}{Adsorption\ capacity\ \left(\frac{mg}{g}\right) \times 10^{-3}\left(\frac{mg}{g}\right)} \qquad [21]$$

2.5. Adsorption experiments.

The batch adsorption studies were conducted to determine the effects of contact time, temperature, and adsorbent dose in 100 mL adsorption bottles containing 25 mL of 20 ppm of pyrimethamine. The adsorbent-adsorbate systems were oscillated on a mechanical shaker operating at 160 rpm. After the adsorption, the mixtures were filtered, and the absorbances of the filtrates were determined with an ultraviolet-visible (UV) spectrometer to determine the amount of un-adsorbed adsorbates in solutions. The amount of equilibrium uptake of adsorbate was determined using:

$$q_e = \frac{(C_i - C_e)V}{m}$$

$$\%\ removal = \frac{(C_i - C_e)}{C_i}$$

Where q_e, C_i, C_e, m, and V are the amount of adsorbate taken up by the adsorbent at equilibrium (mg/g); the initial adsorbate concentration (mg/L); the adsorbate concentration at equilibrium (mg/L); the mass of the adsorbent (g) and the volume of the solution (mL) respectively.

3. Results and Discussion

3.1. Cost of OPAC.

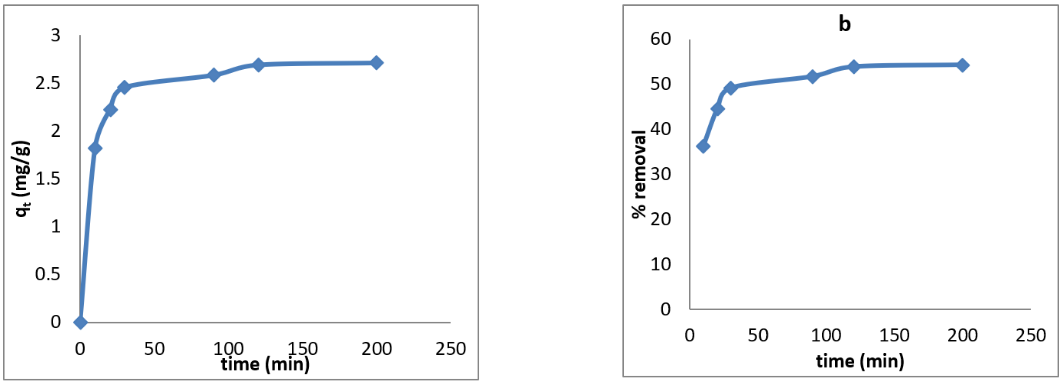
The percentage yield of the adsorbent was 18.26 %. A 68 mL of concentrated H_3PO_4 (85%) was diluted and needed for the preparation of 182.6 g of OPAC, while 372.4 mL was needed for 1 kg. The sawdust was obtained freely. It could be deduced from Table 1 that the cost for preparation of 1 g of OPAC was US$0.081.

Table 1. Cost estimate of OPAC preparation.

Material	**Price (US$)/kg of OPAC**
Sawdust	--
H_3PO_4	29.80
Furnace	10.89
10% HCl	23.49
Distilled water	1.09
pH meter usage	2.17
Oven	1.09
Sieve	1.09
Transportation	10.89
Total	80.51

3.2. Comparing economic contact time with equilibrium contact time.

Pyrimethamine was rapidly removed from the solution in the first 30 minutes. At 30 minutes, 2.46 mg of pyrimethamine had been adsorbed by a unit gram of OPAC. This implied that OPAC worth US$0.081 was expended in removing 2.46 mg of the adsorbate. At a later stage of the process and till the attainment of equilibrium at 200 minutes (2.71 mg adsorbed), the adsorption rate slowed down due to exhaustion of active adsorption sites on the adsorbent. A 0.25 mg of pyrimethamine was adsorbed over the last 170 minutes (between 30 and 200 minutes) (Figure 1a). Figure 1b shows the extent (in percentage) of purity of the contaminant (pyrimethamine) solution. The 2.46 mg of pyrimethamine adsorbed at 30 minutes was equivalent to 49.2 % removal, while 2.71 mg adsorbed at 200 minutes amounted to 54.3%.



(a) (b)

Figure 1. Effect of contact time on adsorption capacity of OPAC for pyrimethamine in **(a)** mg/g; **(b)** %.

Consequently, there is a need for further treatment of the pyrimethamine solution to achieve 100 % purity. Approximately 100 % purification could be achieved by either treating the solution with the same quantity of OPAC at 30 minutes or 200 minutes in a 2-stage batch adsorption process (Figure 2). This implied that 60 minutes would be enough if 30 minutes were considered in a 2-stage batch adsorption system, while 400 minutes were required if 200 minutes were considered. There would be a difference of 340 minutes between the operation times of the two systems. Factoring economy into this discussion, there would be an economic time of 30 minutes and an equilibrium time of 200 minutes. It is, therefore, imperative to note that the two systems would meet the environmental consideration of purifying wastewater before discharge with the same quantity of OPAC used but with lesser economic contact time.

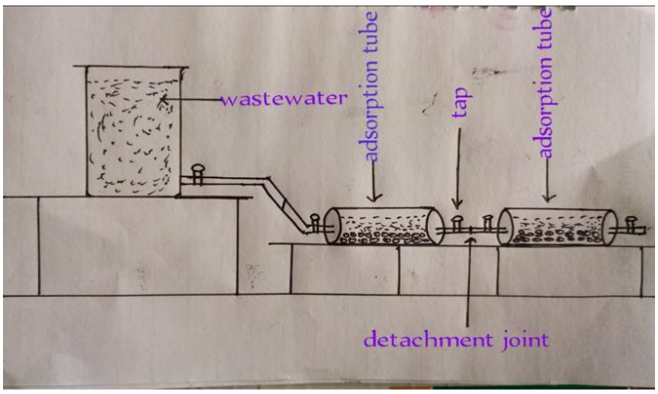
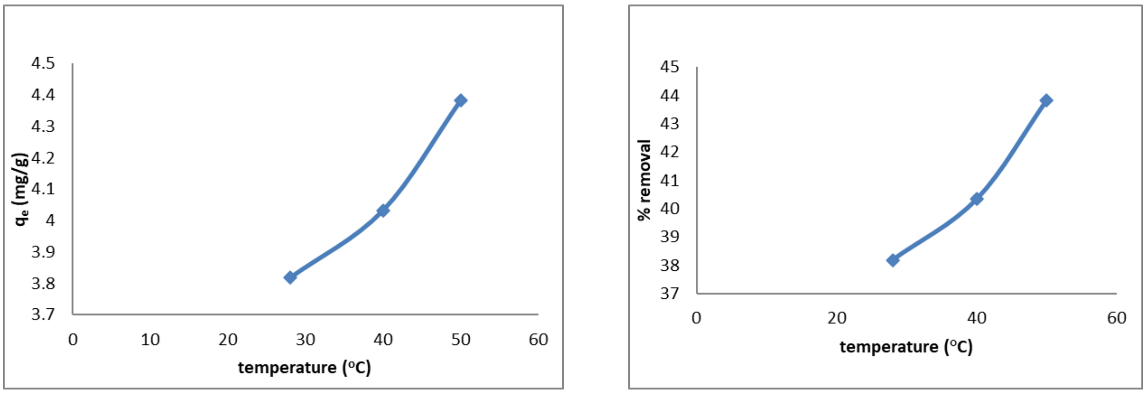


Figure 2. 2-stage batch adsorption process set up.

3.3. Effect of temperature on the cost of adsorption.

At room temperature of 28°C, 3.82 mg of pyrimethamine was adsorbed per unit gram of OPAC. This amounted to 38.2 % removal. At 40 and 50°C, 4.03 mg (40.3 %) and 4.38 mg (43.8 %) of the adsorbate were adsorbed (Figure 3). For 100 % purification of pyrimethamine solutions to be achieved at all the tested temperatures, a 3-stage batch adsorption process (Figure 4) would be necessary using the same quantity of OPAC (0.1 g) in each stage. At room temperature, no power cost was incurred as a result of the temperature effect, but at 40°C and 50°C, heating costs were incurred according to Table 2.



(a) **(b)**

Figure 3. Effect of temperature on adsorption capacity of OPAC for pyrimethamine in **(a)** mg/g; **(b)** %.

Table 2. Cost of adsorbent and heating (at 25 mL of pyrimethamine solution, assuming a specific density of water (solution) is 1 g/mL).

Temperature (°C)	Energy (kJ)	Power (kWh)	Cost of heating[1] (US$)	Cost of adsorbent (US$/$g_{adsorbate}$)
28 (room temperature)	2.9302	0.00081	0	0.0173
40	4.1860	0.00116	0.000094	0.0233
50	5.2323	0.00145	0.000116	0.0268

1 cost of 1 kWh of electricity in Nigeria as of June 2022 was ≌ US$ 0.08 [22].

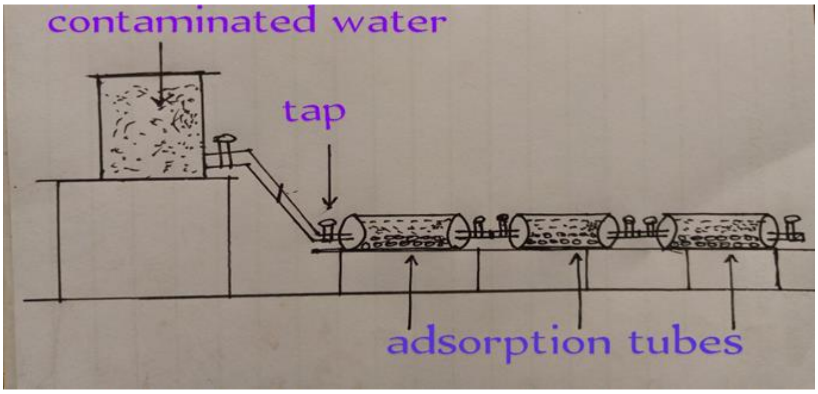


Figure 4. 3-stage batch adsorption set-up.

There was a cost of heating as temperatures of the systems were raised, as presented in Table 2. The important parameter of concern was approximately 100 % purification, which could be achieved at the same stage and simultaneously at all the working temperatures. However, scaling up could drastically change the economic implications of heating. The volume of adsorption solution would increase the power usage and invariably the cost. Also, cooling the system before the eventual discharge of purified water could attract a significant cost or require lengthy time for natural cooling to be attained. Therefore, the room temperature would be preferred for this study considering economic factors.

3.4. Cost implication of adsorbent dose.

As the mass of OPAC increased from 0.1 to 1 g, the OPAC capacity for pyrimethamine dropped from 3 to 0.16 mg/g at equilibrium (Figure 5). An increased OPAC dose increased adsorption sites per unit of adsorbate concentration. There was less competition among the adsorbate molecules for adsorption sites as the mass of adsorbent increased. It is important to note that 0.1 g is 10 % of 1 g, and the capacity of OPAC dipped by about 95 % (3 – 0.16 mg/g).

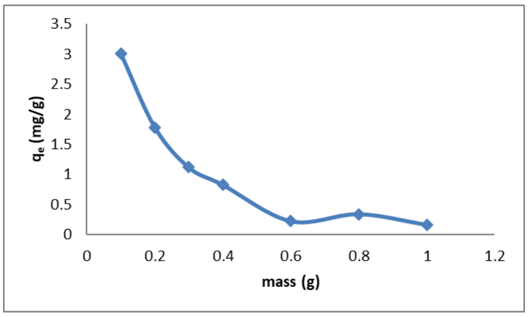


Figure 5. Effect of dose of OPAC on adsorption of pyrimethamine.

A 1 g of OPAC costs US$0.081 (Table 2), while 0.1 g costs US$0.0081. It means that US$0.081 worth of adsorbent removed 0.16 mg (0.00016 mg/g) while much lower US$0.0081 worth of OPAC adsorbed far higher 3 mg (0.003 mg/g) of pyrimethamine. The cost of OPAC ($US\$/g_{adsorbate}$) (considering room temperature for preparation) was 0.0173. For 1 g, the cost was $US\$2.768 \times 10^{-6}$ (0.00016 × 0.0173) and for 0.1 g, $US\$5.19 \times 10^{-5}$. There was a difference of $US\$4.91 \times 10^{-5}$. This implied that the capacity of OPAC for pyrimethamine at 0.1 g worth in value by $US\$4.91 \times 10^{-5}$ than that of 1 g at an industrial scale, which will translate into a huge operation cost implication. However, the level of purification of the contaminated/polluted water is a factor in determining the optimum adsorbent dose in the adsorption process. Attention should be paid to cost for the sake of scaling up strategies. The sections above have shown that the multiple-stage adsorption procedure could be an economical way out of the status quo equilibrium adsorption study.

4. Conclusions

Purity and economy are two of the major factors considered in determining the viability of the adsorption process for water and wastewater treatment. Contact time of the adsorption process, temperature, and dose of adsorbent are indices of economy, while equilibrium is a process characteristic. The multi-stage adsorption process is a strategy to achieve both purification and economic demands. An economically friendly contact time, temperature, and adsorbent can be identified and explored through a multi-stage process.

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Conflicts of Interest

The authors declare no conflict of interest.

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