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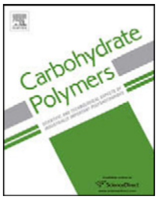

Adsorption kinetics of 4-nitrophenol onto a cellulosic material, mansonia wood sawdust and multistage batch adsorption process optimization

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ABSTRACT

The kinetics of 4-nitrophenol biosorption from aqueous solution using mansonia wood sawdust, a cellulosic material at different dose is probably a two step mechanism involving the adsorption of a hydrogen ion from solution onto the biosorbent surface followed by electrostatic attraction between the positive surface and the anionic adsorbate. The Wu's expression for the initial biosorption showed that limitations to intraparticle diffusion were higher for higher biosorbent dose. The switch of the rate-controlling step to intraparticle diffusion was observed in the pattern of the intraparticle diffusion plots as three distinct sections.

Multistage optimization studies suggested that 193.8 g of Mansonia wood sawdust, three countercurrent batch adsorption stages and 12 min 48 s are required for the removal of 99.5% of 120 mg dm^{-3} of 4-nitophenol from aqueous solution. The minimum contact time for removal of 4-nitrophenol in each stage is independent of the percentage removal for each stage.

1. Introduction

Environmental pollution emanating from the disposal of organic contaminants in industrial wastewater and from pesticide and herbicide residues in to the environment is fast becoming an issue in many industrialized nations. One class of organic contaminants of interest is the phenols and substituted phenols which have been classified as priority pollutants (Kumar, Kumar, Kumar, & Gupta, 2007), since they are known to be carcinogens and play important roles in the ecological balance of some of the compartments of soil and water. These compounds form part of effluents of many industries such as coal conversion, pharmaceutical, petroleum refining, petrochemicals, steel foundry, paper, pulp, textile, insecticides and herbicides industries and in agricultural applications (Kumar et al., 2007).

The chemical compound, 4-nitrophenol is one of such important organic compounds; it is a fine chemical intermediate, serving as a precursor of pharmaceuticals and pesticides (Boehncke, Koennecker, Mangelsdrof, & Wibbertmann, 2000). 4-Nitrophenol is known to be persistent, bioaccumulative and highly toxic (PBT) (US EPA, 2000). It can enter the human body through all routes and its toxic action is much like that of aniline. It aids the conversion of hemoglobin to methamoglobin, which is caused by the oxidation of iron (II) to iron (III) with the result that the hemoglobin can no longer transport oxygen in the body (Al-Asheh, Banat, & Masad, 2004). Therefore, the complete removal of 4-nitrophenol or in some cases reduction of its concentration in wastewaters to an acceptable level has become a major challenge. Many treatment technologies such as extraction (Peretti, Tompkins, Goodall, & Michaels, 2001), advanced oxidation processes (AOPs) (Gimeno, Carbajo, Beltran, & Rivas, 2005; Ksibi, Zemzemi, & Boukchina, 2003), adsorption, biological degradation and UV-oxidation (Kumar et al., 2007) have been developed to remove 4-nitrophenol from domestic and industrial wastewaters. Adsorption is widely used because of its simple design, easy operation and relatively simple regeneration.

Activated carbon is the most popularly used adsorbent for phenols and substituted phenols, but it has the usual disadvantage; it is expensive and non economical to regenerate (Kumar et al., 2007). It became necessary to look for cheap and readily available alternative for activated carbon. Mansonia wood sawdust is a readily available wood waste from the paper and furniture industry in West Africa, especially Nigeria and about 19,000 ton of Mansonia wood is used both by the paper and furniture industry per annum (FAO, 2003).

Several authors have shown that the kinetics of large organic compounds onto untreated sawdust may be limited by diffusion through micro and meso-pores. Hameed and Rahman (2008) showed that the intraparticle diffusion plots of the biosorption of

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Malachite green onto ratten sawdust showed multiple lines indicating diffusion into pores. Ahmad, Rafatullah, Sulaiman, Ibrahim, and Hashim (2009) also found that the intraparticle diffusion plots for the adsorption of methylene blue onto untreated meranti sawdust could be divided into three stages representing micro and meso-pore diffusion. Both authors however noted that pore diffusion was not the sole limiting step but was important in the biosorption kinetic process. Therefore, this study is aimed at investigating the diffusion limitation and mechanism of a low cost adsorbent, mansonia wood sawdust in its natural form for the removal of 4-nitrophenol from aqueous solution. Attempts will also be made to optimize first the number of biosorption stages and then optimize the contact time for the biosorption of 4-nitrophenol onto mansonia wood sawdust and the minimum contact time for the optimized number of stages reported.

2. Materials and methods

2.1. Materials

The Mansonia sawdust used was obtained from a local sawmill in Benin City, Edo State of Nigeria. The sawdust was washed several times with water to remove surface impurities, and this was followed by drying at 100 °C for 24 h. The sawdust was ground and sieved. Sawdust particles used was that retained between the set of sieves: 150–400 μm. The sieved sawdust was then stored in an airtight container.

The 4-nitrophenol was used purchased from BDH. The stock solution of 1000 mg dm^{-3} was prepared by dissolving the accurately weighed amount of 4-nitrophenol in 1000 ml distilled water. The experimental solution was prepared by diluting 12 ml of the stock solution with 88 ml of distilled water.

2.2. Methods

2.2.1. Analytical method

At alkaline pH, the phenolic proton dissociates, giving a phenolate anion with an intense yellow color that can be easily measured spectrophotometrically. Changing solution pH within the range of 11–12 will efficiently develop the color (Al-Asheh et al., 2004). The procedure for 4-nitrophenol analysis was adopted from the website Alpha, which involves adding equal volumes of the 4-nitrophenol sample and a 0.5 mol dm^{-3} sodium carbonate solution. The absorption of the resulting mixture was read at 400 nm wavelength using distilled water as a blank. Absorption was found to vary linearly with concentration up to 20 mg dm^{-3}; therefore, dilutions were undertaken when 20 mg dm^{-3} were exceeded.

2.2.2. Effect of solution pH on 4-nitrophenol biosorption

An accurately weighed amount (0.15 g) of Mansonia sawdust was added to nine 250 ml beakers containing 100 ml of 120 mg dm^{-3} of 4-nitrophenol solution each adjusted to pH of 2, 4, 6, 8 and 10 using either HCl or NaOH solutions. The solutions were stirred at 120 rpm for 2.5 h at 299 K. The mixture was centrifuged and the clear supernatant was analyzed for the residual concentration of 4-nitrophenol left in aqueous solution by a spectrophotometer at 400 nm.

2.2.3. Iodine number

In principle, 25 cm^3 of iodine solution of 0.05 mol dm^{-3} was added to flasks, which contained different amount of mansonia sawdust ranging from 0.031 to 0.500 g. The flasks were then shaken for 24 h to assure equilibrium adsorption of iodine onto pine cone powder. The iodine number (mg g^{-1}) (or adsorption capacity) was determined from the titration of the residual solution of 10 cm^3 with 0.10 mol dm^{-3} sodium thiosulfate in the presence of 1 cm^3 of 1.00 wt% starch solution as an indicator. The iodine adsorption capacity was determined from the adsorbed iodine/unit mass of the adsorbent at the residual iodine concentration.

2.2.4. Effect of sawdust dose on biosorption kinetics

The experiments were performed by agitating known weights (0.15, 0.20, 0.25, 0.30 and 0.35 g) of sawdust in 250 ml beakers containing 100 ml of 120 mg dm^{-3} solution at pH 4. The flasks were shaken at 200 rpm and 297 K for 2 h. Samples were withdrawn out at different time intervals, centrifuged and the concentration of 4-nitrophenol analyzed using UV spectrophotometer.

Adsorption kinetic models

The pseudo first order model (PFOM) is given as:

$$-\ln(q_e - q_t) + \ln q_e = k_1 t \tag{1}$$

Rearranging Eq. (1) we have

$$1 - \frac{q_t}{q_e} = \exp(-k_1 t) \tag{2}$$

The non-linear form of Eq. (2) when q_t is made the subject of the formula is:

$$q_t = q_e\,(1 - \exp(-k_1 t)) \tag{3}$$

The pseudo second order kinetic model (PSOM) is given by:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{4}$$

where q_e is the amount of 4-nitrophenol adsorbed at equilibrium (mg g^{-1}), q_t is the amount of 4-nitrophenl adsorbed at time t (min) in mg g^{-1} and k_2 is the rate constant of the PSOM for sorption of both metal ions.

The non-linear form of the PSOM is written as follows:

$$q_t = \frac{k q_e^2 t}{1 + k q_e t} \tag{5}$$

3. Result and discussion

3.1. Effect of mansonia sawdust dose on biosorption kinetics

The effect of mansonia wood sawdust dose, m_s, on the biosorption of 4-nitrophenol onto mansonia sawdust surface was studied by contacting different dose of mansonia sawdust, 0.15, 0.20, 0.25, 0.30 and 0.35 g dm^{-3} of mansonia sawdust with 100 ml of 120 mg dm^{-3} 4-nitrophenol solution agitated at 200 rpm for 120 min at pH 2.0 and temperature 299 K. The kinetic data obtained were plotted using both the pseudo-first and pseudo-second order kinetic models. The pseudo-first and pseudo-second order parameters were calculated and are given in Table 1. Fig. 1 shows the plot of the experimental data of the amount of 4-nitrophenol biosorbed per unit mass of mansonia sawdust against time along with the model values from the pseudo-first and pseudo-second order model.

From Fig. 1 it can be observed that both model lines were quite close to the experimental data at the initial biosorption period. After the first 5 min of biosorption the model lines of the pseudo-first order kinetic model deviated substantially from the experimental points. The observed deviation from the experimental data has been attributed to the sharp fall in concentration gradient after the initial rapid uptake 4-nitrophenol at the onset of the biosorption process due to large amount of vacant site for biosorption (Ofomaja, 2007, 2008). Within this time period, it is believed that there is a switch between mass transfer diffusion and pore diffusion control (Ofomaja, 2007, 2008). The pseudo-second order kinetic model lines on the order hand were found to be close to the experimental data all through the biosorption period.

Table 1
Kinetic models and parameters of 4-nitrophenol biosorption onto different dose of mansonia wood sawdust.

Model	0.15 g dm^{-3}	0.20 g dm^{-3}	0.25 g dm^{-3}	0.30 g dm^{-3}	0.35 g dm^{-3}
q_e (exp.) (mg g^{-1})	17.28	15.14	13.63	12.22	11.36
Pseudo-first order					
q_e (mg g^{-1})	16.07	14.03	12.09	11.07	10.12
k_1 (min^{-1})	0.140	0.147	0.154	0.166	0.173
r^2	0.993	0.993	0.994	0.990	0.989
Pseudo-second order					
q_e (mg g^{-1})	18.18	15.87	14.68	12.66	11.76
k_2 (g/mg min)	0.011	0.014	0.018	0.021	0.024
h (mg g^{-1} min)	3.64	3.55	3.52	3.37	3.31
r^2	0.998	0.999	0.999	0.999	0.999
Bangham diffusion					
k_o	0.0029	0.0028	0.0027	0.0025	0.0024
α	0.394	0.369	0.352	0.348	0.340
r^2	0.903	0.904	0.903	0.884	0.878

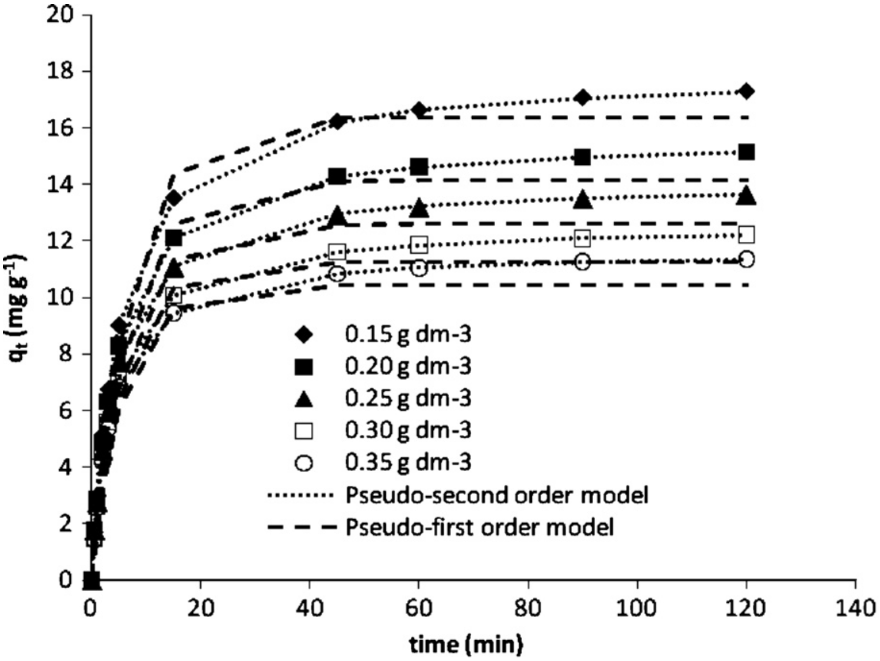

Fig. 1. Kinetic modeling of the effect of mansonia sawdust dose on the removal of 4-nitrophnoel from aqueous solution. Initial conc.: 120 mg/l; solution pH: 4.0; agitation speed: 120 rpm; temperature: 299 K.

The correlation coefficients, r^2, values for the biosorption process were higher for the pseudo-second order kinetic model than for the pseudo-first order model as can be seen in Table 1. The equilibrium capacity values for the pseudo-second order model were higher than for the pseudo-first order kinetic models and both decreased with mansonia sawdust dose, m_s. The closeness to the pseudo-second order model equilibrium capacity to the experimentally determined equilibrium capacity indicates the ability of the pseudo-second order model to describe the kinetics of 4-nitrophenol uptake in the range of biosorbent dose examined.

The effect of solution pH on the removal of 4-nitrophenol was determined by varying the initial concentration of the solution and determining the amount of 4-nitrophenol adsorbed. The fact that 4-nitrophenol is moderately acidic (pK_a = 7.15) in aqueous and is water soluble makes the ionic form of 4-nitrophenol strongly pH dependent. At solution pH greater than 8, the sawdust surface is negatively charged and the 4-nitrophenol molecule dissociates to the anionic form (Tang, Zheng, Lin, Luan, & Zhang, 2007). This will generate repulsion between sorbate and adsorbent and the amount of 4-nitrophenol adsorbed will be very small (Fig. 2). As solution pH decreases, the magnitude of negative charge on the sawdust and 4-nitropheonol reduces, reducing the repulsion between sor-

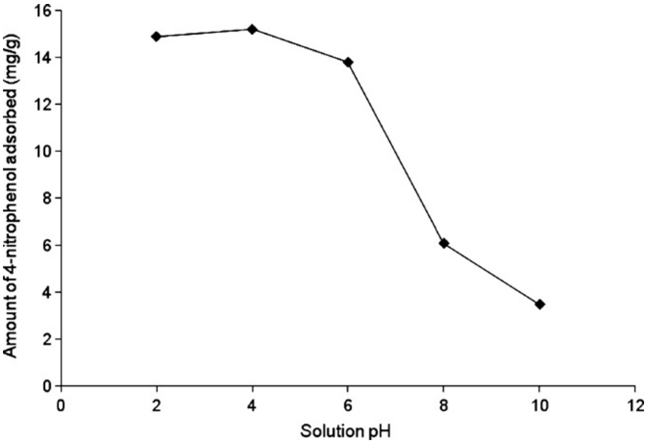

Fig. 2. Effect of solution pH on the uptake of 4-nitrophenol from aqueous solution by Mansonia sawdust. Initial conc.: 120 mg dm^{-3}; dose: 1.5 g dm^{-3}; solution vol.: 100 ml; agitation speed: 120 rpm; temperature = 26 ± 4 °C.

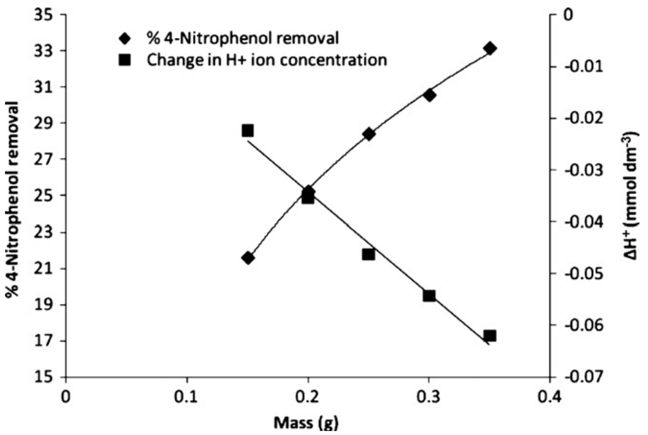

Fig. 3. Relationship between percentage 4-nitrophenol removal, change in H^+ ion concentration and mansonia sawdust dose.

bate and adsorbent and the amount of 4-nitrophenol adsorbed from solution begins to increase (Hameed & Rahman, 2008) As the solution pH approaches the pH at point zero charge of the sawdust, its net charge becomes almost zero and a large amount of 4-nitrophenol is removed from solution between pH 4 and 6. Above pH 4, there is a slight reduction in the amount of 4-nitrophenol adsorbed, this may be due to the fact that competition between 4-nitrophenol and H^+ ions for active sites occurs and there is electrostatic repulsion between sorbate and sorbent or repulsion between sorbate molecules. This observed behavior of the adsorption of 4-nitropheonl with varying solution pH has been reported several authors (Pei et al., 2006; Tang et al., 2007).

To establish the biosorption mechanism involved, the change in hydrogen ion concentration, ΔH^+, during the biosorption process at each biosorbent dose, m_s, was monitored by determining the initial and final solution pH for the kinetic study using each mansonia sawdust dose, m_s. The change in H^+ ion concentration, ΔH^+, is given by:

$$\Delta H^+ = H^+_{\text{initial}} - H^+_{\text{final}} \tag{6}$$

where ΔH^+ is the difference between the initial and final solution pH, $H^+{}_{\text{final}}$ is the pH before the biosorption reaction and $H^+{}_{\text{initial}}$ is the solution pH at the end of the biosorption.

Our previous studies revealed that biosorption of 4-nitrophenol is optimal at lower pH values below 6, and is biosorbed mostly as the phenolate ions at such pH values. Our previous studies (Ofomaja & Ho, 2008) also showed that the pH at point zero charge (pH_{PZC}) of mansonia sawdust is 6.91. Therefore, below pH 6.91, the mansonia sawdust surface is positively charged and associates with H^+ ions to attract the negatively charged phenolate ions. It was also observed from this study and our previous studies (Ofomaja & Ho, 2008) that at solution pH lower than 4, the biosorption capacity slightly decreased due to competition with H^+ ions and repulsion.

A plot of percentage removal 4-nitrophenol and change in solution H^+ ion concentration was plotted against mansonia sawdust dose, m_s, so as to observe the biosorption relationship. Fig. 3 shows the observed trend between the percentage 4-nitrophenol removed, change in solution H^+ ion concentration and mansonia sawdust dose, m_s. From Fig. 3, it is observed that as mansonia sawdust dose increased, both percentage 4-nitrophenol removal and change in H^+ concentration in solution increased. We propose that the mechanism of the biosorption follows two steps:

$$\text{MS-OH} + H^+ \rightarrow \text{MS-OH}_2{}^+ \tag{7}$$

$$\text{MS-OH}_2{}^+ + {}^-\text{O-C}_6\text{H}_4\text{–NO}_2 \rightarrow \text{MS-OH}_2\cdots\text{O-C}_6\text{H}_4\text{–NO}_2 \tag{8}$$

where MS-OH can be a hydroxyl, phenolic or carboxylic group on the mansonia sawdust surface. It should be noted as well that the increase in the change in H^+ ion concentration is linear, while percentage 4-nitrophenol reduced slightly as dose of biosorbent increased to 0.30 and 0.35 g dm^{-3}. This will suggest that as dose increased at constant initial 4-nitrophenol concentration, the surface area for biosorption also increased and more H^+ ions were removed from solution onto the biosorbent surface which also increased the number of biosorption sites for 4-nitrophenol. The slight decrease with increased biosorbent dose may therefore be due to repulsion from 4-nitrophenol at the biosorbent surface from particle–particle interaction (Tang et al., 2007).

3.2. *Diffusion processes*

Since the pseudo-first order model deviated from the straight line after 5 min of biosorption, it is suspected that there is a switch in the rate-controlling step of the process or may become complex after 5 min. Therefore the rate determining step may be controlled by film or pore diffusion or a mixture of both. The Bangham's model can be used to determining the participation of diffusion processes in the rate determining step. The Bangham's model is given by:

$$\log\log\left[\frac{C_0}{C_0 - q_t m}\right] = \frac{\log k_0 m}{2.303V} + \alpha \log t \tag{9}$$

where C_0 is the initial concentration of adsorbate in solution (mg dm^{-3}), V the volume of solution (L), m the weight of sorbent used per dm^3 of solution (g dm^{-3}), q_t the amount of sorbate retained at time t (mg g^{-1}), α (<1) and k_0 are constant. The double logarithmic plots according to Eq. (9) did not yield perfect linear curves (figure not shown) showing that the diffusion of sorbate into the pores of the sorbent is also involved in the rate controlling step (Ütem, Apak, & Üńnal, 1998). The values of the constants α and k_0 as calculated from the slope and intercept showed that the values of both constants reduced with increasing mansonia sawdust dose, m_s (Table 1). It was observed from the values of correlation coefficient, r^2 that the lines at lower dose, m_s, were significantly linear with r^2 values of between 0.903 and 0.904, but as the dose increased to 0.3 g dm^{-3}, the linearity of the lines reduced with the r^2 values reducing to as low as 0.878. Therefore, it is expected that pore diffusion dominates the rate-controlling step at lower Mansonia sawdust dose but reduces in importance as the sole rate-controlling step with increasing mansonia sawdust dose. One possible explanation will be that as the mansonia sawdust dose increases, the external surface for biosorption increases for a constant concentration of 4-nitrophenol in solution leading to larger number of active sites and a reduction in concentration driving force.

3.3. *Intraparticle diffusion treatment*

The total surface area of an adsorbent is made up of both external and internal surface. The iodine number gives information on the internal surface of an adsorbent (Daifullah, Girgis, & Gad, 2003). Iodine number determination is complimentary to the N_2/77 K adsorption isotherms, and it is assumed to measure the surface area in micropores within pore sizes ≥10 Å (Ahmad, Usmani, & Mumtaz, 1991; Attia, Rashwan, & Khedr, 2006). The iodine molecule has an area of about 0.15–0.42 nm^2, therefore can fit into micropores of adsorbent particles providing information about the internal surface (Bota et al., 2007). In this study iodine number of Mansonia sawdust is obtained to be 260 mg g^{-1}, Martins, Cardoso, Stahl, and Diniz (2007) obtained are value of 179 mg g^{-1} for Eucalyptus sawdust. These values are only slightly lower than the iodine number for activated carbon produced from rubber wood sawdust (particle size 1.31 nm at 600 °C), which is 300 mg g^{-1} (Kumar, Shivakamy,

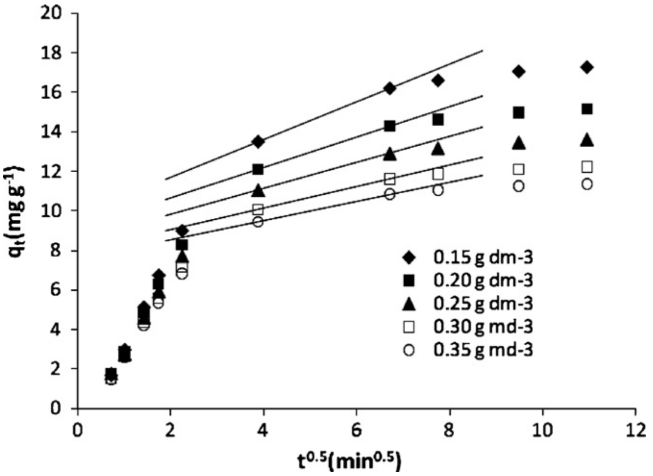

Fig. 4. Intraparticle diffusion modeling of the effect of mansonia sawdust dose on the removal of 4-nitrophnoel from aqueous solution. Initial conc.: 120 mg/l; solution pH: 4.0; agitation speed: 120 rpm; temperature: 299 K.

Miranda, & Velan, 2006). This suggests that mansonia sawdust may contain a level of micro and mesopores.

A functional relationship common to most treatments of intraparticle diffusion is that uptake varies almost proportionally with the half-power of time, $t^{0.5}$, rather than t. A nearly linear variation in the quantity biosorbed with $t^{0.5}$ is predicted for a large initial fraction of reactions controlled by rates of intraparticle diffusion. Good linearization of the data is observed for the initial phase of the reaction in accordance with expected behavior if intraparticle diffusion is the rate-limiting step (Weber & Morris, 1963).

$$q_t = k_i t^{0.5} + C \tag{10}$$

The plot of q_t versus $t^{0.5}$ for the kinetic data of the effect of mansonia sawdust dose, m_s, is shown in Fig. 4. It will be observed that the curve can be divided in to three sections; the first, sharper stage can be attributed to the diffusion of biosorbate through the solution to the external surface of the biosorbent or the boundary layer diffusion of the biosorbate molecules. The second stage describes the gradual biosorption, where intraparticle diffusion is rate limiting and the third stage is attributed to the final equilibrium for which the intraparticle diffusion starts to slow down due to extremely low biosorbate concentration left in solution. The three stages in the plot suggest that the biosorption process occurs by surface biosorption and intraparticle diffusion (meso- and micropores). The intraparticle diffusion rate constant obtained from the slope of the second portion of Fig. 4 are given in Table 2. From Table 2, it is observed that the intraparticle diffusion rate constant decreased with increasing sawdust dose from 0.15 to 0.35 g dm^{-3}. The intraparticle diffusion rate constants were found to decrease with increasing adsorbent dose, perhaps due to the increased external surface for adsorption, leading to a rapid fall in 4-nitrophenol concentration in solution and consequent reduction in the concentration difference driving force for the mass transfer. The constant, C, which represents the boundary layer diffusion were obtained from the curve as the intercept of the second portion in Fig. 4 and are shown in Table 2. These values were also found to decrease with increasing sorbent dose from 0.15 to 0.35 g dm^{-3}. These values decreased due to increased surface area of the biosorbent with increasing biosorbent dose, m_s, at a constant biosorbate concentration.

Table 2
Intraparticle rate parameters and diffusion coefficients at different Mansonia sawdust dose.

Dose (g dm^{-3})	Intraparticle diffusion		R_i	C/q_{ref}
	k_i (mg g^{-1} min$^{0.5}$)	C		
1.50	0.952	9.821	0.43	0.57
2.00	0.769	9.122	0.40	0.60
2.50	0.656	8.519	0.30	0.63
3.00	0.639	6.429	0.35	0.65
3.50	0.587	6.557	0.33	0.67

The initial biosorption behavior of the biosorption system is important in the determination of the rate-controlling since it has been observed that a switch in biosorption mechanism occurred at a point in the biosorption process. According to (Wu, Tseng, & Juang, 2009), to determine the initial biosorption behavior, the following equations can be deduced. Eq. (10) can be written as:

$$q_{ref} = k_i + C \tag{11}$$

where t_{ref} is the longest time in the biosorption process and q_{ref} is the solid phase concentration at time $t = t_{ref}$ for a biosorption system. Subtracting Eq. (10) from Eq. (11), we have

$$q_{ref} - q_t = k_i(t_{ref}^{0.5} - t^{0.5}) \tag{12}$$

Rearrangement of Eq. (12) yields

$$\left(\frac{q_t}{q_{ref}}\right) = 1 - R_i\left[1 - \left(\frac{t}{t_{ref}}\right)^{0.5}\right] \tag{13}$$

where $R_i = (k_i t_{ref}^{0.5}/q_{ref})$, which is defined as the initial biosorption factor of the intraparticle diffusion model.

The so-called characteristics curve based on the intraparticle diffusion model can be defined from Eq. (13). R_i is expressed as

$$R_i = \frac{q_{ref} - C}{q_{ref}} = 1 - \left(\frac{C}{q_{ref}}\right) \tag{14}$$

Therefore, Eq. (14) indicates the R_i can be represented in terms of the ratio of the initial biosorption amount (C) to the final biosorption amount (q_{ref}). Table 2 shows the values of R_i and C/q_{ref} calculated for the effect of mansonia sawdust dose on the biosorption of 4-nitrophenol onto mansonia sawdust. The values of R_i were found to range from 0.43 to 0.33 and C/q_{ref} values were between 0.57 and 0.67, which falls within zone 3 in Table 3. These values indicate strong initial biosorption during the removal of 4-nitrophenol from solution in the biosorbent dose range of 1.50–3.50 g dm^{-3} and intraparticle diffusion rate becomes slower.

The results from the intraparticle diffusion modeling can be further explained by calculating out the R_i values at each time, t, during the biosorption process. The relationship between operating time,

Table 3
Initial adsorption factor (R_i) and kinetic behavior based on intraparticle diffusion model.

R_i	Initial point of kinetic curve (C/q_{ref})	Initial biosorption behavior	Zone
$R_i = 1$	$C/q_{ref} = 0$	No initial biosorption	0
$1 > R_i > 0.9$	$0 < C/q_{ref} < 0.1$	Weak initial biosorption	1
$0.9 > R_i > 0.5$	$0.1 < C/q_{ref} < 0.5$	Intermediate initial biosorption	2
$0.5 > R_i > 0.1$	$0.5 < C/q_{ref} < 0.9$	Strong initial biosorption	3
$R_i < 0.1$	$C/q_{ref} > 0.9$	Approaching complete initial biosorption	4

t, and amount of biosorption can be obtained from Eq. (15) (Wu et al., 2009):

$$\left(\frac{t}{t_{ref}}\right) = \left[1 - \frac{1}{R_i}\left(1 - \frac{q_t}{q_{ref}}\right)\right]^2 \tag{15}$$

It is therefore possible to calculate the value of R_i at any time, t, using the corresponding amount of 4-nitrophenol biosorbed per unit mass, q_t. At the initial 0.5 min of 4-nitrophenol biosorption, the values for R_i were 0.90, 0.88, 0.87, 0.87 and 0.87 for mansonia sawdust dose, m_s, of 0.15, 0.20, 0.25, 0.30 and 0.35 g dm^{-3} samples. These values fall within zone 2, indicating intermediate initial biosorption. Notice that the higher mansonia sawdust dose, m_s, had slightly lower R_i values. At 3 min of contact the R_i values had dropped to 0.61, 0.58, 0.56, 0.54 and 0.53 respective and by 5 min of contact the values are now below 0.50 indicating a change from the intermediate initial biosorption process to strong initial biosorption which implies weak intraparticle diffusion. At 15 min of biosorption there was a further reduction of R_i values to 0.22, 0.20, 0.20, 0.18 and 0.17, respectively. It is observed here that for mansonia sawdust dose, m_s, 0.30 and 0.35 g dm^{-3}, the R_i values became less than 1.0 (zone 4) which means that the system is approaching total initial biosorption and that intraparticle diffusion is extremely slow were as the R_i values of the 0.10, 0.15, 0.20 and 0.25 g dm^{-3} samples are still within zone 3. This accounts for the low values of intraparticle diffusion observed for the higher mansonia dose and for the lower adsorption capacities obtained for these dosages compared with lower dosages. Above 15 min of biosorption R_i values for all systems drops below 0.10.

3.4. *Multistage batch adsorption design*

For multistage batch adsorption design the minimum amount of adsorbent for the purification is given as:

$$M_1 = M_2 = \left[\frac{V}{k}\left(\frac{C_o}{C_e}\right)^{0.5} - 1\right] \tag{16}$$

For a multistage process involving N stages the general result for a linear isotherm is:

$$\sum (M_1 + M_2 + M_3 ... M_N) = \frac{NV}{K}\left[\left(\frac{C_o}{C_e}\right)^{1/N} - 1\right] \tag{17}$$

where M is mass of adsorbent, N is the number of adsorption stages, V is volume of adsorbate solution and C_o, C_e and K are langmuir parameters. Mathematical description of these equations has been given in Unuabonah, Adie, Onah, and Adeyemi (2009). Comparing Eq. (16) with Eq. (17) when $N = 2$ suggest that by splitting the adsorbent into two equal amounts the total amount of adsorbent required for the given purification is reduced from that required when all the adsorbent is used in one stage. Table 4 shows the total amount of Mansonia wood sawdust adsorbent required for the adsorption of 99.5% 4-nitrophenol from 120 mg dm^{-3} of the adsorbate in various volumes of aqueous solution.

Let us consider the optimization of the number of adsorption stages for the batch adsorption of 120 mg dm^{-3} of 4-nitrophenol from known volumes of the aqueous solution and the amount of Mansonia wood sawdust required for each stage if $M_1 = M_2 ... = M_N$ using Eq. (17). Thus, from Eq. (17), using experimental data, the optimum amount of mansonia wood sawdust and the optimum number of countercurrent adsorption stages were determined for the adsorption of 99.5% of 120 mg dm^{-3} 4-nitrophenol. Plots showing the optimum amount of adsorbent dose and the corresponding optimum adsorption stages required for the removal of 99.5% of 4-nitrophenol from various volumes of influent containing 120 mg dm^{-3} of 4-nitrophenol are shown in Fig. 6. From Table 4 it

Table 4
Optimized total weights of Mansonia wood sawdust obtained from theoretical prediction for batch adsorption stages to remove 99.5% of 120 mg dm^{-3} 4-nitrophenol from various volumes of aqueous solution.

No of stages	Volume of 120 mg dm^{-3} 4-nitrophenol												
	0.5 dm^3	1 dm^3	2.5 dm^3	5 dm^3	10 dm^3	50 dm^3	100 dm^3	500 dm^3	1000 dm^3	1500 dm^3	2000 dm^3	2500 dm^3	10,000 dm^3
Total weights (g) of adsorbent required to remove 99.5% of 120 mg dm^{-3} 4-nitrophenol for various volumes of adsorbate													
2	0.14	0.29	0.72	1.43	2.86	14.31	28.62	143.10	286.21	429.31	572.41	715.52	2862.07
3	0.12	0.23	0.58	1.16	2.33	11.63	23.25	116.27	232.54	348.81	465.08	581.34	2325.37
4	0.12	0.24	0.60	1.20	2.40	12.03	24.05	120.24	240.48	360.72	480.96	601.20	2404.79
5	0.13	0.26	0.64	1.28	2.57	12.83	25.66	128.31	256.62	384.94	513.25	641.56	2566.24
6	0.14	0.28	0.70	1.39	2.79	13.94	27.88	139.41	278.82	418.23	557.64	697.05	2788.19
7	0.15	0.30	0.76	1.51	3.02	15.12	30.23	151.17	302.33	453.50	604.67	755.83	3023.33
8	0.16	0.33	0.82	1.64	3.27	16.36	32.73	163.63	327.27	490.90	654.54	818.17	3272.69
9	0.18	0.35	0.88	1.77	3.53	17.65	35.31	176.53	353.06	529.59	706.12	882.65	3530.59
10	0.19	0.38	0.95	1.90	3.80	19.02	38.04	190.19	380.37	570.56	760.75	950.94	3803.74
11	0.20	0.41	1.02	2.04	4.08	20.41	40.81	204.07	408.14	612.22	816.29	1020.36	4081.44
12	0.22	0.43	1.08	2.17	4.33	21.65	43.30	216.52	433.03	649.55	866.06	1082.58	4330.30
13	0.23	0.46	1.16	2.31	4.63	23.14	46.28	231.39	462.78	694.17	925.57	1156.96	4627.85
14	0.25	0.49	1.23	2.45	4.91	24.53	49.07	245.33	490.66	735.9	981.32	1226.65	4906.58
15	0.26	0.52	1.30	2.60	5.19	25.96	51.93	259.64	519.27	778.91	1038.55	1298.19	5192.74

was observed that increasing volume of influent requires increasing adsorbent dosage. The optimum number of stages of adsorption was found to remain the same even with increasing volume of effluent (Table 4). However, with increasing number of adsorption stages smaller amount of adsorbent is required for each stage of adsorption (Table 5). For example, the optimized number of stages for the adsorption of 99.5% of 120 mg dm^{-3} 4-nitrophenol from a 2.5 m^3 aqueous solution is three (3). A total of 581.3 g of Mansonia wood sawdust adsorbent is required for the removal of 99.5% of 120 mg dm^{-3} 4-nitrophenol present in 2.5 m^3 of aqueous solution. Each stage of adsorption requires 193.8 g of Mansonia wood sawdust adsorbent. For 10,000 dm^3 (10 m^3), three (3) adsorption stages and adsorbent dose of 77.51 g for each of the three stages (Table 5) are required to remove 99.5% of 120 mg dm^{-3} 4-nitrophenol from the aqueous solution.

3.5. *Optimization of contact time for a multistage batch adsorption process*

The total amount of 4-nitrophenol removal can be calculated analytically as follows.

$$\sum_{n=1}^{N} C_{n-1} - C_n = \sum_{n=1}^{N} \frac{100Skq_e^2 t_i}{LC_o(1+kq_e t_i)} \tag{18}$$

where i is the adsorption system number ($i = 1, 2, 3, 4\ldots N$)

The mathematical descriptions of Eq. (18) have been well discussed by Ho and McKay (1998). The 4-nitrophenol removal, R_i, in each batch stage can be evaluated from the equation as follows:

$$R_n = \frac{100(C_{n-1} - C_n)}{C_o} = \frac{100Skq_e^2 t_i}{LC_o(1+kq_e t_i)} \tag{19}$$

The total removal of 4-nitrophenol can be calculated analytically as follows:

$$\sum_{n=1}^{N} R_n = \frac{100S}{LC_o} \sum_{n=1}^{N} \frac{kq_e^2 t_i}{1+kq_e t_i} \tag{20}$$

Therefore it is useful for process design purposes if q_e and k can be expressed as a function of C_o for adsorption of 4-nitrophenol onto Mansonia wood sawdust adsorbent as follows:

$$q_e = X_{q_e} C_o^{Yq} \tag{21}$$

$$k = X_k C_o^{Y_k} \tag{22}$$

Substituting the values of q_e and k from Eqs. (21) and (22) into Eq. (20) gives:

$$R_n = \frac{100S(X_k C_{n-1}^{Y_k})(X_q C_{n-1}^{Yq})^2 t_i}{LC_o[1 + (X_k C_{n-1}^{Yq})t_i]} \tag{23}$$

$$\sum_{n=1}^{N} R_n = \frac{100S}{LC_o} \sum_{n=1}^{N} \frac{(X_k C_{n-1}^{Y_k})(X_q C_{n-1}^{Yq})^2 t_i}{[1 + (X_k C_{n-1}^{Y_k})(X_q C_{n-1}^{Yq})^2 t_i]} \tag{24}$$

Eqs. (23) and (24) can be used to predict the removal of 4-nitrophenol at any given initial concentration and the reaction time for any multi-stage system. When data of q_e and k against initial 4-nitrophenol concentration, C_o, were regressed the following equations were obtained:

$$298\,\mathrm{K}\; q_e = 1.7739 C_p^{0.4903} \quad r^2 = 0.9887 \tag{25}$$

$$298\,\mathrm{K}\; k = 1.7103 C_0^{-1.0556} \quad r^2 = 0.9861 \tag{26}$$

Table 5
Optimized weights of Mansonia wood sawdust obtained from theoretical prediction in each batch adsorption stage to remove 99.5% of 120 mg dm^{-3} 4-nitrophenol from various volumes of aqueous solution.

Volume (L)	Weights of adsorbent (g) required in each stage to remove 99.5% of 120 mg/l 4-nitrophenol from various volumes of solution													
	2 stages	3 stages	4 stages	5 stages	6 stages	7 stages	8 stages	9 stages	10 stages	11 stages	12 stages	13 stages	14 stages	15 stages
0.5	0.07	0.04	0.03	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	17.80	0.02	0.02
1	0.14	0.08	0.06	0.05	0.05	0.05	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.03
2.5	0.36	0.20	0.15	0.13	0.12	0.11	0.10	0.10	0.10	0.09	0.09	0.09	0.09	0.09
5	0.72	0.39	0.30	0.26	0.23	0.22	0.20	0.20	0.19	0.19	0.18	0.18	0.18	0.17
10	1.43	0.78	0.60	0.51	0.46	0.43	0.41	0.39	0.38	0.37	0.36	0.36	0.35	0.35
50	7.16	3.88	3.01	2.57	2.32	2.16	2.05	1.96	1.90	1.86	1.80	1.78	1.75	1.73
100	14.31	7.75	6.01	5.13	4.65	4.32	4.09	3.92	3.80	3.71	3.61	3.56	3.50	3.46
500	71.55	38.77	30.06	25.66	23.23	21.60	20.46	19.61	19.02	18.55	18.04	17.80	17.52	17.31
1000	143.10	77.51	60.12	51.32	46.47	43.19	40.91	39.23	38.04	37.10	36.09	35.60	35.05	34.62
1500	214.65	116.27	90.18	76.99	69.70	64.79	61.36	58.84	57.06	55.66	54.13	53.40	52.57	51.93
2000	286.21	155.02	120.24	102.65	92.94	86.38	81.82	78.46	76.07	74.21	72.17	71.20	70.09	69.24
2500	357.76	193.78	150.30	128.31	116.17	107.98	102.27	98.07	95.09	92.76	90.21	89.00	87.62	86.55
10,000	1431.03	775.12	601.20	513.25	464.70	431.90	409.09	392.29	380.37	371.04	360.86	355.99	350.47	346.18

Table 6
Optimized minimum contact time data (min) obtained from theoretical prediction for the adsorption of 120 mg dm^{-3} of 4-nitrophenol from 2.5 m^3 aqueous solution onto 193.8 g Mansonia wood sawdust adsorbent in a 3-stage countercurrent batch adsorption process at various percentage removal.

Percentage removal mode for stages 1, 2 & 3, respectively	System no.	Stage 1	Stage 2	Stage 3	Total
4.53%, 35.47%, 59.5%	9	4.5	3.1	5.2	12.8
4.53%, 45.47%, 49.5%	9	4.5	4.0	4.3	12.8
4.53%, 55.47%, 39.5%	9	4.5	4.9	3.5	12.9
4.53%, 65.47%, 29.5%	9	4.5	5.7	2.6	12.8

When Eqs. (25) and (26) were incorporated into Eq. (24) at 298 K the model equation becomes

$$\sum_{n=1}^{N} R_n = \frac{100S}{LC_o} \sum_{n=1}^{N} \frac{(1.7103C_o^{-1.0556})(1.7739C_o^{0.4903})^2 t_i}{1 + (1.7103C_o^{-1.0556})(1.7739C_o^{0.4903}) t_i} \tag{27}$$

Eq. (27) is a valid mathematical model for the calculation of contact time for the second, and third stages in a three-stage batch adsorption of 4-nitrophenol from aqueous solution onto Mansonia wood sawdust adsorbent.

However, from data available from the optimization of number of adsorption stages and amount of adsorbent dose initially carried out suggested that 193.8 g of the Mansonia wood sawdust adsorbent is required in each stage in a three stage removal of 99.5% of 120 mg dm^{-3} 4-nitrophenol from a 2.5 m^3 aqueous solution.

Thus, let us assume that the first stage of the adsorption process has fixed contact times. For this study, a series of contact times from 0.5 min up to 20 min in a 0.5 min increment has been considered in stage one of a five-stage adsorption system for the adsorption of 4-nitrophenol. In the first adsorber, for example, system number 10 implies that the first adsorber contact time is 0.5 min + (10 − 1) 0.5 min = 5 min since system number 1 represents 0.5 min contact time in adsorber number 1. Thus, the contact time in the second adsorber, t_2, is the time, T min, required to achieve a fixed total percentage of 4-nitrophenol removal minus the contact time in the first adsorber stage t_1, therefore:

$$T = t_1 + t_2$$

For N systems, t_n, becomes

$$t_1 = 2 + (N - 1)2 \ldots \text{min}$$

The total batch contact time, T, is

$$T = 2 + (N - 1)2 + t_2 \ldots t_n$$

where N is number of stages.

With a known percentage removal in stage 1 (4.53%) calculated using Eq. (27), let us assume that the percentage removal in stage two is 35.47% and stage three is 59.5%, in a 99.5% removal of 120 mg dm^{-3} 4-nitrophenol from 2.5 m^3 aqueous solutions by 193.8 g of Mansonia wood sawdust adsorbent in a three stage adsorption process. The various minimum contact times for the various system numbers for each batch adsorption stage are shown Table 5. Fig. 6 shows the plot of contact time and the equivalent system number and Fig. 5 shows the variation of the adsorbent weight to number of adsorption stages for the adsorption of 99.5% 4-nitrophenol from 120 mg dm^{-3} of the adsorbate solute at 4.53%, 35.47% and 59.5% for stages 1, 2 and 3, respectively. From the table it can be seen that optimum contact time (as shown in system number 9) for the adsorption of 99.5% removal of 120 mg dm^{-3} 4-nitrophenol from 2.5 m^3 aqueous solution by Mansonia wood sawdust adsorbent is 12.8 min with stage one 4.5 min, stage two 3.1 min and stage three 5.2 min. Other varieties of percentage removal for the various stages were further used for optimization. For example, 4.53%, 45.47%, and 49.5%; 4.53%, 55.47% and 39.5%; and 4.53%, 65.47%, and 29.5%, 4-nitrophenol removal for stages 1, 2, and 3, respectively. They all gave same optimum contact times

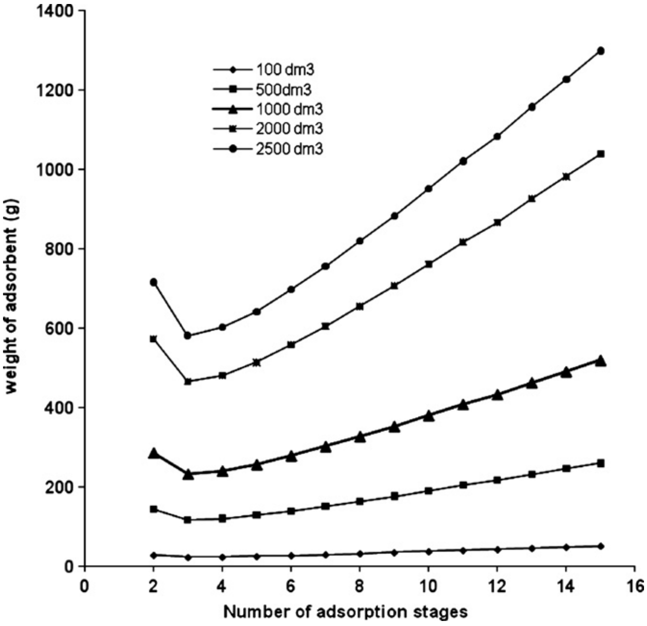

Fig. 5. Plots of optimization data contact time and number of adsorption stages for the adsorption of 99.5% of 120 mg dm^{-3} 4-nitrophenol onto Mansonia wood sawdust adsorbent from various volumes.

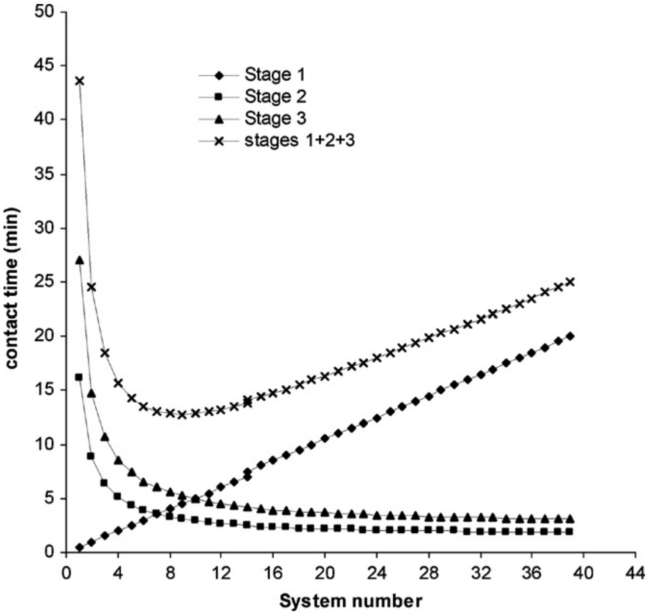

Fig. 6. Comparison of 95.5% 4-nitrophenol removal time of each stage in a three-stage countercurrent batch adsorption process.

for the various stages (Table 6). Similar results were obtained by Unuabonah et al. (2009).

4. Conclusion

Biosorption of 4-nitrophenol onto mansonia sawdust is characterized by a switch of rate-controlling step after the first 5 min. The biosorption mechanism is probably a two step mechanism involving the adsorption of a hydrogen ion from solution onto the biosorbent surface followed by electrostatic attraction between the positive surface and the anionic adsorbate.

Optimization of experimental data for the removal occurred in three batch adsorption stages, and a total of 12 min 48 s is required for the adsorption process. Minimum contact time is not dependent of the percentage removal of the adsorbate in each stage of the adsorption process.

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