



## Kinetics and pseudo-isotherm studies of 4-nitrophenol adsorption onto mansonia wood sawdust

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### ABSTRACT

Kinetic models alone are usually applied to describe adsorption onto porous materials, but little attention is given to the fact that diffusion of pollutants especially large organic pollutant molecules may also control the reaction rates. In this investigation, the kinetics and pseudo-isotherm studies of an organic pollutant, 4-nitrophenol from aqueous solution on mansonia sawdust was examined. The intraparticle diffusion particle plots revealed three distinct sections representing sorption into external diffusion, intraparticle diffusion and diffusion to a biosorption site within the particles. The fractional removal of pollutant versus square root of time plots further revealed three sectional straight lines whose slope may represent the rates of pollutant sorption into macro-, meso- and micropores.

The equilibrium capacities determined using four forms of the Ho's pseudo-second order model and the Type-1 pseudo second-order expression was also used to evaluate equilibrium concentrations and pseudo-isotherms were obtained by changing initial concentration,  $C_0$ .

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### 1. Introduction

Biosorption as a separation technique for pollutant removal from wastewater has become a very popular and widely studied method in recent years. In the design of an efficient treatment plant, the biosorption kinetics and factors that affect the biosorption process are of utmost importance to study. Biosorption kinetics involves the study of the rate at which pollutants are removed from aqueous solution onto biosorbent surface, which in turn controls the residence time of the biosorbate uptake at the solid–solution interface. Diffusion of biosorbate molecules across the liquid film on the biosorbent surface and through the pores within a porous biosorbent also plays a significant role in biosorption studies since diffusion can also control the rate of biosorbate uptake. System variables such as pollutant concentration, temperature, agitation speed and solution pH may also affect the rate of pollutant uptake.

Several kinetic models are available to describe reaction order of biosorption processes; pseudo-first order (Lagergren, 1898); first order (Sobkowsk and Czerwiński, 1974); second order (Blanchard et al., 1984) and pseudo-second order (Ho, 1995). The pseudo-

second order kinetic expression described by Ho (1995) is by far the most widely applied kinetic model for sorption systems in recent years. This kinetic expression was initially used to model bi-metal/solutions (Ho et al., 1996). The application of Ho's expression to several adsorption systems have been documented in literature; metal adsorption (Ho, 2003; Ho and McKay, 2000; Ho and Ofomaja, 2005, 2006a,b), dye adsorption (Ho and McKay, 1998a,b, 1999a; Ho et al., 2005; Ofomaja and Ho, 2007a,b; Ofomaja, 2007a,b) and organic pollutants adsorption (Ho and McKay, 1999b; Kelleher et al., 2001). The pseudo second-order equation has the following advantages: it does not have the problem of assigning an effective sorption capacity; the sorption capacity, rate constant of pseudo second-order, and the initial sorption rate can all be determined from the equation without knowing any parameter beforehand. Recently, Ho (2006a,b) and Ho and Ofomaja (2006c) analyzed the sorption of cadmium ions onto tree fern and the sorption of copper ions onto palm kernel fibre using the four linear forms of the pseudo second-order equation and reported that the Type-1 gave the best fit of to the experimental data. The equilibrium capacities obtained from the pseudo second-order expression has also been used to evaluate equilibrium concentrations and pseudo-isotherms were obtained by changing initial concentration,  $C_0$ , (Ho, 2004; Ho and Wang, 2004) or sorbent dose,  $m_s$ , (Ho and Ofomaja, 2006b) and equilibrium capacity obtained based on the pseudo-second-order constants. These pseudo-isotherms have been found to represent the measured adsorption data well.

The rate controlling step of an adsorption process may not be described by kinetic models alone, especially with porous materi-

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als. Using kinetic models alone to describe such reactions may be incorrect since adsorption on active sites takes place mostly in the micropores and pollutants must diffuse through these micropores to be adsorbed at these sites. Therefore, it is also important to have information relating to the rate of pollutant removal from the liquid phase to the various mass and diffusion coefficients of the system.

Several authors have shown that the kinetics of large organic compounds onto untreated sawdust may be limited by diffusion through micro and mesopores. Hameed and El-Khaiary (2008) showed that the intraparticle diffusion plots of the biosorption of malachite green onto rattan sawdust showed multiple lines indicating diffusion into pores. Ahmada et al. (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 mesopore diffusion. Both authors however noted that pore diffusion was not the sole limiting step but was important in the biosorption kinetic process.

In this investigation, the effect of diffusion processes in the biosorption of 4-nitrophenol onto mansonina sawdust at different doses was examined. The effect of film and pore diffusion on intraparticle diffusion was investigated and compared with external diffusion of 4-nitrophenol biosorption onto mansonina sawdust when sawdust dose was varied. Four forms of the Ho's pseudo-second order kinetic model were used to model the effect of initial 4-nitrophenol concentration on the biosorption process. Batch biosorption pseudo-isotherm were also developed by applying biosorption capacity which is obtained from Ho's pseudo second order Type-1 kinetic rate law and was used to predict the monolayer adsorption capacities and adsorption constants. A comparison of the linear regression ( $r^2$ ) and chi-square ( $\chi^2$ ) analysis of the four forms of the pseudo-second order expression and the four pseudo-isotherms: Langmuir-1, Langmuir-2, Freundlich and Dubinin–Radushkevich isotherms have been applied to the experimental adsorption data of 4-nitrophenol onto mansonina sawdust.

## 2. Experimental procedure

### 2.1. Materials

The mansonina 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  $\mu\text{m}$ . The sieved sawdust was then stored in an airtight container.

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

### 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. Moving solution pH to a high pH value of 11–12 will efficiently develop the color (Al-Asheh et al., 2004). The procedure for 4-nitrophenol analysis involves adding equal volumes of the 4-nitrophenol sample and a 0.5 M sodium carbonate solution. The absorption of the resulting mixture was read at 400 nm wavelength using sawdust sample and distilled water without 4-nitrophenol as blank. Blank samples were found to show slight absorbance (0.001–0.003 depending on solution pH) due to

extraction of components of sawdust. This absorbance was subtracted from the sample readings. Absorption was found to vary linearly with concentration up to 20  $\text{mg dm}^{-3}$ ; therefore, dilutions were undertaken when 20  $\text{mg dm}^{-3}$  were exceeded (Al-Asheh et al., 2004).

#### 2.2.2. Proximate analysis and surface functional group analysis

The proximate composition of mansonina sawdust was determined using methods of the Association of Official Analytical Chemists (1990). The IR spectra of the mansonina sawdust sample was recorded using KBr disk in conjunction with a Perkin–Elmer infrared spectrophotometer.

#### 2.2.3. Iodine number

The iodine number determination was carried out by back titration of excess iodine solution with sodium thiosulphate as described by Daifullah et al. (2003).

#### 2.2.4. pH at point zero charge ( $\text{pH}_{\text{PZC}}$ ) determination

The pH at point zero charge ( $\text{pH}_{\text{PZC}}$ ) of the pine cone powder was determined by the solid addition method (Mall et al., 2006). To a series of 100 ml conical flasks, 45 ml of 0.01  $\text{mol dm}^{-3}$  of  $\text{KNO}_3$  solution was transferred. The initial solution pH values ( $\text{pH}_i$ ) were roughly adjusted from pH 2 to 12 by adding either 0.10  $\text{mol dm}^{-3}$  HCl or NaOH using a pH meter (Crison Basic 20+). The total volume of the solution in each flask was then made up to 50 ml by adding  $\text{KNO}_3$  solution of the same strength. The  $\text{pH}_i$  of the solution was accurately noted, and 0.10 g of sawdust was added to each of the flask, which was then securely capped immediately. The suspensions were then manually shaken and allowed to equilibrate for 48 h with intermittent manual shaking. The final pH values ( $\text{pH}_f$ ) of the supernatant liquids were then noted. The difference between the initial and final pH values ( $\Delta\text{pH} = \text{pH}_i - \text{pH}_f$ ) was plotted against the  $\text{pH}_i$ . The point of intersection of the resulting curve at which  $\Delta\text{pH} = 0$  gives the  $\text{pH}_{\text{PZC}}$ .

#### 2.2.5. Determination of active sites

Acidic and basic sites on the sawdust surface were determined by the acid–base titration method proposed by Boehm (1994). The total acid sites matching the carboxylic, phenolic and lactonic sites (Boehm, 1994) were neutralized using a 0.10  $\text{mol dm}^{-3}$  of NaOH solution while the basic sites were neutralized with a 0.10  $\text{mol dm}^{-3}$  HCl solution. The carboxylic and lactonic sites were titrated with a 0.05  $\text{mol dm}^{-3}$   $\text{Na}_2\text{CO}_3$  solution and the carboxylic sites were determined with a 0.10  $\text{mol dm}^{-3}$   $\text{NaHCO}_3$  solution, while the phenolic sites were estimated by difference (Boehm, 1994).

The acidic and basic sites were determined by adding 50 ml of 0.1  $\text{mol dm}^{-3}$  of the titrating solution and 1.00 g of sawdust to a 50 ml volumetric flask. The flasks were partially immersed in a constant temperature water bath set at 20 °C and it was left for 5 days. The flasks were agitated manually twice a day. Afterward, a sample of 10 ml was titrated with 0.10  $\text{mol dm}^{-3}$  HCl or NaOH solution. The titration was carried out in triplicates.

#### 2.2.6. Effect of solution pH on 4-nitrophenol biosorption

An accurately weighed amount (0.15 g) of mansonina sawdust ( $d_p = 275 \mu\text{m}$ ) was added to nine 250 ml beakers containing 100 ml of 120  $\text{mg dm}^{-3}$  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 200 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.

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