

Negative Adsorption Phenomenon: Adsorbent, Adsorbates Reaction, and pH as Contributing Factors

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Abstract: The conditions that led to negative adsorption were investigated. Four different adsorbents were prepared and named raw *Danielliaoliveri* sawdust (RDS), sodium hydroxide treated sawdust (SHTS), zinc chloride activated carbon (ZCAC), and phosphoric acid activated carbon (PAAC). Batch adsorption experiments were conducted with solutions of ibuprofen (single solution) and pyrimethamine-paracetamol (binary solution). Un-carbonized RDS and SHTS contained contents that were extracted into the solution, which absorbed light at the same wavelength as ibuprofen and led to negative adsorption. The reaction between pyrimethamine and paracetamol in binary solution led to the disappearance of peaks at 274 and 242 nm (negative absorbances), which correspond to pyrimethamine and paracetamol, respectively, and the appearance of a new peak at 300 nm, which suggested the formation of a new product. At pH 9.6, the minor derivatives formed as a result of the chemical reaction between pyrimethamine and paracetamol reacted to form a major product and resulted in a final adsorbate concentration in the solution higher than the initial adsorbate concentration. The factors contributing to negative adsorption include adsorbent material, the reaction of adsorbates in a binary system, and changes in the pH of the solution.

Keywords: negative-adsorption; pH; adsorbates-reaction; extraction.

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1. Introduction

Adsorption is a surface phenomenon where a solid surface (adsorbent) is in contact with a liquid or gas. Mass transfer of solute (adsorbate) in the liquid or the gas occurs towards the solid. Adsorption is physisorption if weak interaction occurs between the adsorbent and the adsorbate. If there is a chemical interaction between the adsorbent and the adsorbate, it is chemisorptions. When the solute is transferred from the bulk solution onto the surface of the adsorbent, there is positive adsorption. There are areas of concern in the adsorption process [1-3]. Some of the factors that influence the adsorption process include adsorbent dose [4], pH [5], adsorbate concentration [6], temperature [7], nature of adsorbate [8], the surface area of adsorbent [9] and pressure in gaseous phase [10]. In a situation where the solvent of the solution is preferentially adsorbed onto the surface ahead of the solute, there is negative adsorption [11,12]. Negative adsorption reduces the amount of a component in the interfacial layer [13].

Sucrose was reported to be negatively adsorbed because of its higher surface tension in water [14]. A pressure increase also led to negative gas adsorption by a porous crystalline solid [15]. High pressure has been identified as a factor responsible for the negative adsorption of

methane [16]. The negative adsorption of chloride by kaolinite was attributed to the alkaline pH of the solution [17]. Electrostatic repulsion was cited as responsible for the negative adsorption of ions [18,19]. Williams [20] reported negative adsorption of electrolytes using charcoal and silica as adsorbents.

In the context of this article, negative adsorption is the phenomenon where the initial adsorbate concentration in solution is lower than the final adsorbate concentration in solution, which leads to a negative amount of adsorbate adsorbed per unit mass of adsorbent ($q_e = -x$ mg/g). The extraction brought about this condition from the adsorbent, reaction of adsorbates, and change in pH of the solution.

Many research students encountered this phenomenon of negative adsorption, and interpretation and discussion became a burden. It is, therefore, hopeful that this paper will help a lot in this regard.

2. Materials and Methods

2.1. Materials.

Daniellia oliveri sawdust was abundantly available and collected at the Pakiotan wood processing industry in Ogbomoso. ZnCl₂, H₃PO₄ 1 % formaldehyde, and NaOH were analytical grades purchased from chemical stores in Ibadan. Ibuprofen, paracetamol, and pyrimethamine were freely donated by Bond Chemical Industry Limited, Awe, Oyo State. Some of the equipment used was pH meter (Jenway 3520), oven (Carbolite), ultraviolet-visible (UV) (B-UV 1800PC) spectrophotometer, and furnace (self-generated atmosphere) (Carbolite AAF 1100). The molecular structures and properties of paracetamol and pyrimethamine were given respectively in Figures 1 and 2 and Table 1.

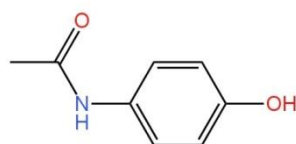


Figure 1. Molecular structure of paracetamol.

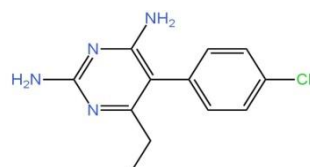


Figure 2. Molecular structure of pyrimethamine.

Table 1. Properties of Pyrimethamine and Paracetamol [21,22].

Common Names:	Acetaminophen, paracetamol	Pyrimethamine, Daraprim, Chloridine
IUPAC Name	N-(4-hydroxyphenyl)acetamide	5-(4-chlorophenyl)-6-ethylpyrimidine-2,4-diamine
Molecular formula	C ₈ H ₉ NO ₂	C ₁₂ H ₁₃ ClN ₄
Molecular weight	151.16 g/mol	248.71 g/mol
UNII	362O9ITL9D	2811
λ_{max}	242 nm	274 nm
Solubility	14,000 mg/L (25 °C)	10 mg/L (25 °C)
Toxicity	Liver failure, renal tubular necrosis	Gastrointestinal disturbance, convulsions
pKa	9.38	7.34
Log K _{ow}	0.46	
Description	Analgesic, antipyretic	
Interaction centres	-NH, OH, CO, π - π , n- π	-NH ₂ , \equiv N:, π - π , n- π , -Cl

2.2. Preparation of adsorbents.

Danielliaoliveri was washed with plenty of distilled water to remove surface impurities. The sample was then dried in an oven at 105°C overnight. The sample was ground, followed by sieving. The sample was re-washed several times with distilled water, oven dried at 80°C until completely dried, and then stored in an airtight container as Raw *Daniellia* Sawdust (RDS). Using the method of Raghuvanshi *et al.* [23], RDS was soaked in 0.5M NaOH for 12 hours. Excess NaOH was removed by washing with distilled water. It was then treated with 1% formaldehyde at 50 °C for 4 hours. It was then washed with distilled water, dried at 80°C for 24 hours, ground, sieved, and stored in an airtight container as SHTS. 3g of RDS was mixed with 3 mL of 1 M H₃PO₄ and 3 mL of 1 M ZnCl₂, each in separate crucibles. These were 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 warm water and then distilled water to pH 6 - 8 of the supernatants. The adsorbents were dried in an oven at 110 °C overnight and sieved to have a regular particle size, and stored in an airtight container as H₃PO₄ activated carbon (PAAC) and ZnCl₂ activated carbon (ZCAC), respectively [24].

2.3. Adsorption studies.

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

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

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 dye concentration at equilibrium (mg/L); the mass of the adsorbent (g) and the volume of the solution (L) respectively.

3. Results and Discussion

3.1. Contribution of adsorbent to negative adsorption.

As shown in Figure 3 below, the adsorption of ibuprofen by SHTC and RDS was negative because their q_e s (mg/g) were negative, while that of PAAC was positive. 20 ppm of ibuprofen solution read 0.771. After adsorption, the final solutions of ibuprofen which contained 0.1, 0.2, 0.3, 0.4, and 0.5 g of RDS, respectively, read 1.3, 1.417, 1.521, 1.618, and 1.724 while those of SHTC read 1.129, 1.287, 1.361, 1.436 and 1.543. The final solutions of ibuprofen with corresponding grams of PAAC read 0.511, 0.213, 0.215, 0.179, and 0.094, respectively. From the absorbances listed above, the values increased arithmetically from the least to the highest mass of adsorbents for RDS and SHTC systems and decreased for PAAC system. This showed that un-carbonized *Danielliaoliveri* sawdust contained contents that were extracted into the adsorption solutions during shaking, and these extracted contents absorbed light at a similar wavelength as ibuprofen. This led to higher absorbance of adsorbate after adsorption than that of the initial absorbance of the adsorbate. This eventually led to a negative

amount of ibuprofen adsorbed at equilibrium per unit mass of each RDS and SHTS ($q_e = -x$ mg/g). Unlike RDS and SHTS systems, PAAC system was positive as absorbances of ibuprofen solutions after adsorption was smaller than that of the initial ibuprofen solution. This system gave a positive amount of ibuprofen adsorbed at equilibrium per unit mass of PAAC ($q_e = +x$ mg/g) (Fig. 3). The carbonization and/or activation processes might have eliminated those contents that led to negative adsorptions in RDS and SHTS systems. This phenomenon might suggest that, unless specially treated, un-carbonized sawdust materials might not be suitable as adsorbents for ibuprofen removal from aqueous solutions.

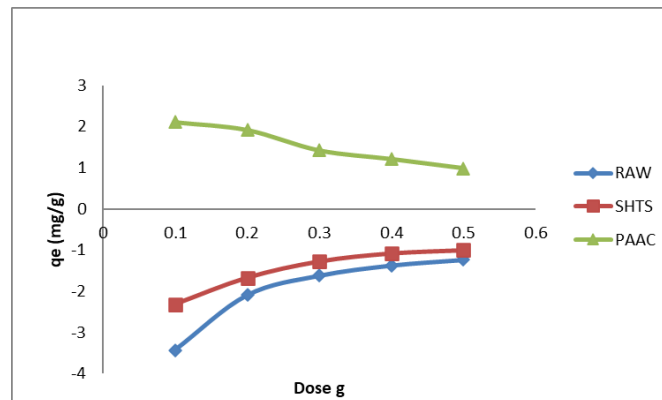


Figure 3. Effect of adsorbent dose on adsorption of IBU.

3.2. Effect of pyrimethamine-paracetamol reaction in the binary system on adsorption.

The lambda maximum (λ_{max}) of pyrimethamine and paracetamol in a single solution were determined to be 274 and 242 nm, respectively, in UV spectrum. However, scanning, between 400 and 200 nm (UV region), of binary solution which contained equal concentrations (in ppm) of pyrimethamine and paracetamol revealed the disappearance of peaks at 274 and 242 nm; and the emergence of the peak at 300 nm. This suggested a chemical reaction between pyrimethamine and paracetamol in the solution and the formation of new product (s). The effect of doses of PAAC and ZCAC each on the adsorption in binary solution at 242, 274, and 300 nm revealed negative absorbances at 242 and 274 nm except at 300 nm (Fig. 4). Also, the effect of contact time showed negative absorbances at 242 and 274 nm except at 300 nm (Fig. 5). Implication of this is that study adsorption of either of pyrimethamine or paracetamol in binary solution by setting UV spectrometer at 274 or 242 nm respectively will give negative results. In a multi-component solution adsorption study using UV equipment, it is, therefore, ideal for scanning through the UV region to determine the reactions among the components.

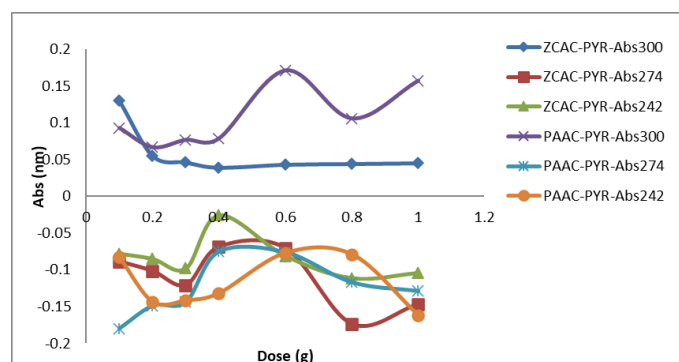


Figure 4. Effect of PYR and PARA chemical reaction on the adsorption: dose factor.

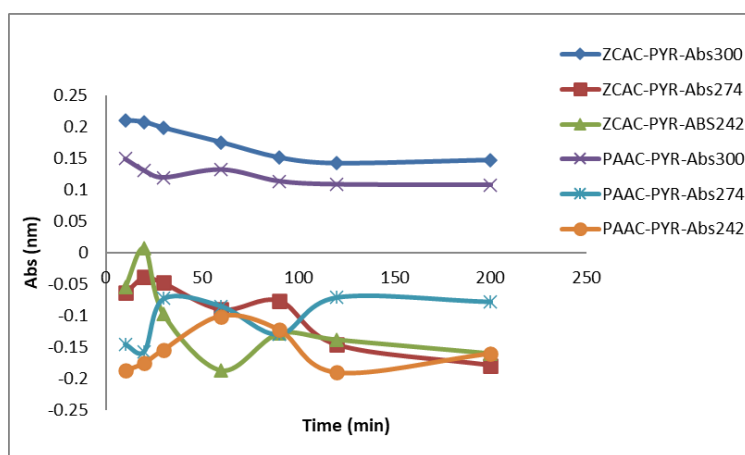


Figure 5. Effect of PYR and PARA chemical reaction on the adsorption: the time factor.

3.3. Effect of pH of the solution.

The effect of pH was studied in the adsorption of pyrimethamine and paracetamol from binary solution by PAAC and ZCAC. Scanning of the initial binary solution in the UV region showed a prominent peak at 300 nm and a few small peaks at other wavelengths. These small peaks were considered responsible for minor derivatives of the major product (which was absorbed in 300 nm). After adsorption, the adsorbate concentrations in solutions between pH 2.8 and 7.6 were lesser than the initial adsorbate concentration. These gave positive q_e ($q_e = +x$ mg/g). At these pH, the surfaces of the adsorbents (pH_{pzc} ZCAC = 7.6; PAAC = 6.6) were positively charged while the adsorbate(s) was neutral. Electrostatic attraction occurred, and the adsorbate adsorbed onto the adsorbents. At pH 9.8, both the adsorbents and the adsorbates were negatively charged, and there was repulsion. Also, minor derivatives that formed from the reaction of pyrimethamine and paracetamol reformed to form the major product. This led to negative adsorption in which the final adsorbate concentration was higher than the initial adsorbate concentration. This gave negative q_e ($q_e = -x$ mg/g) (Figure 6).

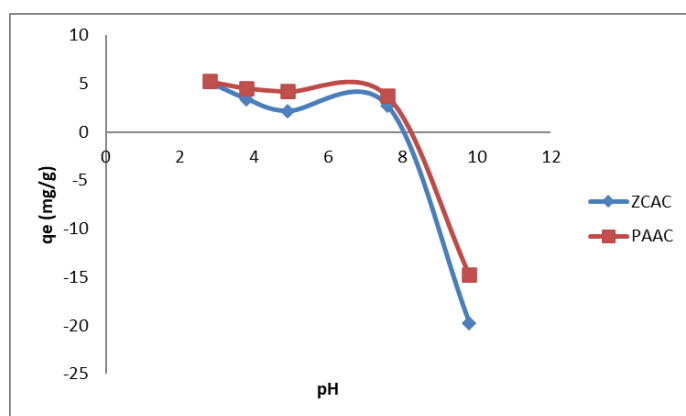


Figure 6. Effect of pH on adsorption (from positive to negative) of PYR from binary aqueous solution.

4. Conclusions

Negative adsorption is a phenomenon where the final adsorbate concentration in the solution is higher than the initial adsorbate concentration. This condition arose when adsorbent was introduced by extraction in the solution of the content that absorbed light at the same wavelength as the adsorbate in the UV region. Also, the reaction of adsorbates in a multi-component system might lead to negative adsorption. A change in the pH of the solution could

also lead to a reaction of minor derivatives formed during a chemical reaction to form a major product and result in a final adsorbate concentration in the solution higher than the initial adsorbate concentration. It is ideal in adsorption studies to scan multi-component solutions through UV region. Un-carbonized sawdust adsorbent, unless specially prepared, may not be used for the adsorptive removal of pharmaceuticals from aqueous solutions.

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Conflicts of Interest

The authors declare no conflict of interest.

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