

# Adsorptive Removal of Acetylsalicylic Acid in Wastewater Onto Crosslinked-Chitosan

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## ABSTRACT

The detection of pharmaceutical such as acetylsalicylic acid (ASA) in water bodies has gained a great concern due to causing adverse effects on the environment. This study aims to explore the potential of magnetic crosslinked-chitosan (MACsorb) adsorbent in the removal of ASA. In the adsorbent synthesis study, the optimal volume of glutaraldehyde (GTA) used for crosslinking is 1 ml. The MACsorb demonstrated high removal percentage (96 %) towards ASA (0.1 g/L) at 120 min reaction time, 27 °C temperature and pH3. The excellent adsorption performance combined with its unique magnetic separation property makes MACsorb a promising candidate for treating pharmaceutical waste of ASA in wastewater.

**Keywords:** Adsorption, pharmaceutical, acetylsalicylic acid, chitosan, magnetic

## 1. INTRODUCTION

Pharmaceutical pollutants have attained substantial concern in recent years due to their potential in causing negative impacts on the ecosystem. The presence of pharmaceuticals in water bodies has increased tremendously over the past few years due to the improper dumping of waste from hospitals, pharmaceutical industries and natural excretion (by humans and animals). This situation has raised a great concern from both the scientists and society, due to the unfavorable properties of pharmaceuticals, that is highly resistant to biological degradation, subsequently lead to bio-accumulation.

Acetylsalicylic acid (ASA) as representative of pharmaceutical has been reported in the World Health Organization (WHO) as an essential medicine with significant consumption for anti-inflammation applications. According to Teo, et al. [1], it is estimated that around 35,000 metric tons of ASA tablets are produced worldwide annually. The environmental problem arises when the disposal of such medicine into water bodies become unavoidable, including from natural excretion by consumers. Such risks increase as the pollutants cannot be obliterated using conventional technologies because it does not explicitly be designed to remove pharmaceuticals pollutants. Consequently, some of them will remain in the aqueous media and affect the balance of ecological environment [2]. Therefore, it is of paramount importance to develop effective techniques for treating pharmaceuticals pollutants.

Among the potential techniques for removal of ASA in wastewater, adsorption using activated carbon (AC) is considered as the most convenient one due to its excellent performance in removing pollutants without sludge formation. In view of the hazards brought by ASA in wastewater, a few studies have been conducted on the removal of ASA using AC. Moacă, et al. [3] had successfully synthesized magnetic AC via combustion with the adsorption capacity on ASA, 142.01 mg/g. Hoppen, et al. [4] also explored the potential of AC from babassu coconut mesocarp as an adsorbent for ASA. Nonetheless, the utilization of AC is often restricted by its complex synthesis processes (carbonization, activation, washing, etc.) and fine-size (hardly be separated from the solution after used) [5]. In these regards, there is a need to develop a superior adsorbent from cheaper sources with simple process design and operation.

Recently, adsorption by biopolymer-based adsorbent, chitosan, has gained popularity, as another potential strategy due to its advantages of green and sustainable chemistry [6, 7]. Particularly, chitosan possesses plenty of adsorption sites including amine (NH<sub>2</sub>) and hydroxyl (OH) groups in its structure that can interact with pollutants through  $\pi$ - $\pi$  interaction, electrostatic interaction [8] and hydrogen bonds [9]. Despite the advantages mentioned, unmodified chitosan has drawbacks of poor mechanical strength, weak chemical stability, and unsatisfactory adsorption capacity. Additionally, used chitosan is challenging to be separated from aqueous solution due to its fine-size powder. In these regards, cross-linking modification of chitosan with glutaraldehyde (GTA) is an excellent way to improve the chemical stability of chitosan in acid solution and enhance its

adsorption efficiency. Recently, magnetic-driven separation of adsorbents containing magnetic nanoparticles (MNP) has attained a great deal of attention because of the ease and simplicity in recovering adsorbent from the solution using an external magnetic field. The addition of MNP into chitosan matrix not only performs rapid separation, but also minimizes the adsorbent loss in the solution. Following the raising attention on the green technology advancement, it is worth developing simple and economical solid-liquid separation technique for adsorption process. To date, there is no study have been reported in using this structurally simple adsorbent for removing ASA from wastewater.

On the basis of the above ideas, the objective of this work is to synthesize magnetic crosslinked-chitosan adsorbent (termed as MACsorb) for the removal of ASA in wastewater. The effects of different parameters including glutaraldehyde volume, contact time, initial ASA concentration, temperature and solution pH, on the percentage removal of ASA are investigated systematically.

## 2. EXPERIMENTAL

### 2.1 Material

The materials used, such as raw chitosan (powder) and ethanol (C<sub>2</sub>H<sub>6</sub>O, 95% v/v) were purchased from QReC. The glutaraldehyde (25 wt%), acetylsalicylic acid (ASA), sodium hydroxide (NaOH), and hydrochloric acid (HCl) were purchased from Sigma Aldrich. All chemicals were utilized as received without further purification.

### 2.2 Preparation of magnetic crosslinked-chitosan adsorbent

The MACsorb was synthesized through covalently cross-linking chitosan on the MNP surface, using GTA as a crosslinker. First, 1 g of chitosan powder was utterly dissolved into 50 ml of 0.1 mol/L acetic acid solution. Following that, an amount of GTA was added into the solution and stirred vigorously for 1 hour. The effect of GTA volume on the percentage removal of ASA was investigated by varying the amount from 0.5 ml to 4 ml. After that, the optimal GTA volume was selected according to the highest percentage removal of ASA. Next, 2 g of MNP was added and mixed with the chitosan-containing solution and stirred for 1 hour. Finally, the sample was rinsed with distilled water, followed by filtering and drying in the oven until a constant weight was obtained.

### 2.3 Surface area and pore volume analysis

The specific surface area and pore volume of the adsorbents were analyzed using multipoint Brunauer-Emmett-Teller equation (BET) based on nitrogen adsorption-desorption isotherm model.

### 2.4 Preparation of acetylsalicylic acid solution

The ASA stock solution was prepared by the dissolution of ASA powder in distilled water. Then, the stock solution was analyzed using UV-Vis spectrophotometer, which revealed the characteristic peak of ASA at 226 nm. The peak at 226 nm was related to the  $\pi$ - $\pi^*$  transition in ASA, and the absorbance value at this peak has been often used to determine the concentration of aqueous ASA solutions in adsorption studies.

### 2.5 Adsorption study

The batch adsorption was conducted by investigating several effects of certain parameters such as contact time (5-180 min), initial ASA concentration (0.025-0.3 g/L), temperature (27-70 °C) and solution pH (3-11) towards the removal of ASA. The adopted experimental method was taken from the study done by Su, et al. [10] and it was conducted under the following conditions: 50 mL of ASA solution, 0.2 g adsorbent dosage and 200 rpm of rotary shaker speed. Then, the adsorption was run at a certain temperature and time interval. The solution pH range was controlled using 0.1 M sodium hydroxide and 0.1 M hydrochloric acid solutions when necessary. After the completion of adsorption, the MACsorb was separated off the solution, and the absorbance of the filtrate was measured using UV-Vis spectrophotometer at the absorption wavelength of 226 nm. Finally, the values of ASA concentrations, before and after adsorption were determined using standard calibration curves of the solutions. The determined values were used to calculate the percentage removal of ASA, according to Eq. (1).

$$\text{Percentage removal (\%)} = \frac{C_o - C_f}{C_o} \times 100 \quad (1)$$

where  $C_o$  and  $C_f$  (mg/L) are the initial and final concentrations of ASA, respectively.

### 3. RESULTS AND DISCUSSION

#### 3.1 Surface area and pore volume analysis

The result of surface area and pore volume of the adsorbents is tabulated in Table 1. It can be observed that the surface area of MACsorb has slightly decreased from 43.20 m<sup>2</sup>/g (raw chitosan) to 39.15 m<sup>2</sup>/g after modification. The result may be due to the loading of MNP onto the surface of chitosan, subsequently increase the size of MACsorb and reduce its surface area. Also, the low surface area of the adsorbents was expected as there was no activation process involved during the adsorbents synthesis process as in preparation of activated carbon (AC). Commonly, AC possesses high surface area, ranges between 500 to 2000 m<sup>2</sup>/g after activation process, at high temperature. The low pore volume of the MACsorb, 0.01 cm<sup>3</sup>/g, also indicated that the porosity of the adsorbent was not the main factor involved in adsorption mechanism.

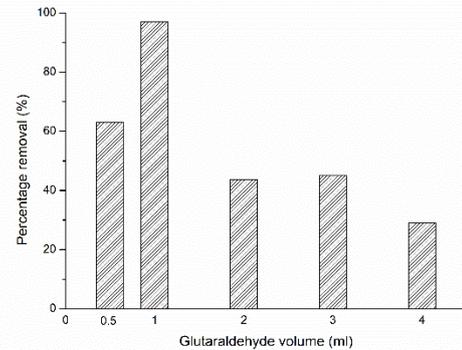
**Table 1** Surface area, pore volume and pore size of raw chitosan and MACsorb

Adsorbent	Surface area (m <sup>2</sup> /g)	Pore volume (cm <sup>3</sup> /g)
Raw chitosan	43.20	0.01
MACsorb	39.15	0.01

#### 3.2 Effect of glutaraldehyde volume

The effect of GTA volume on the percentage removal of ASA by MACsorb is shown in Figure 1. The results revealed that the percentage removal of ASA increased from 63% to 96% with the increase of GTA volume from 0.5 ml to 1 ml. This is due to the fact that GTA helps chitosan to form the quaternary structure on the surface of MNP and increase the number of protonated amino groups (-NH<sub>3</sub><sup>+</sup>) which have a high affinity towards negatively charged ASA [11]. The finding is in agreement with the results found by Crini and Badot [12] in the investigation on the adsorption of negatively charged pollutants by chitosan in wastewater treatment. However, as the GTA volume was further increased to 2 ml and 4 ml, the percentage removal of ASA decreased to 43% and 28%, respectively. This is because increasing volume of GTA more than desired leads to the loss of amino binding sites for adsorption, due to extensive crosslinking reaction between amino groups from chitosan and aldehyde group from GTA. Consequently, these amino functionals remain no longer available for adsorption and result in low percentage removal of ASA [13]. From the results, it can

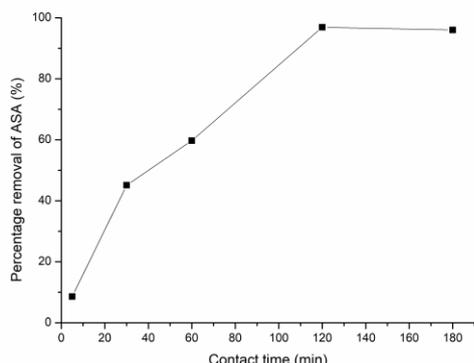
be observed that an appropriate addition of GTA can improve the characteristics of the biopolymer-based adsorbent for adsorption, without carbonization and activation as in the preparation of AC.



**Figure 1** Effect of glutaraldehyde volume on the percentage removal of acetylsalicylic acid (Conditions: initial ASA concentration, 0.1 g/L; adsorbent dosage, 0.2 g; sample volume, 50 ml; solution pH, 3; temperature, 27 °C)

#### 3.3 Effect of contact time

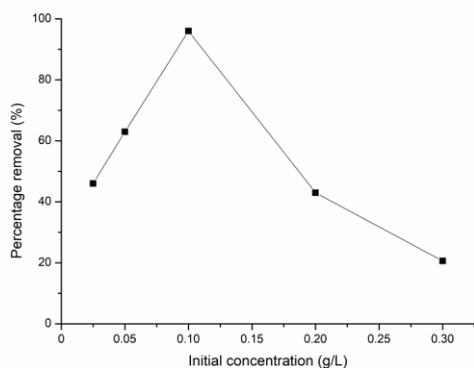
The effect of contact time (5-180 min) on the percentage removal of ASA is displayed in Figure 2. It can be observed that the amount of ASA adsorbed increased with reaction time until the equilibrium was reached. Initially, the rate of adsorption increased rapidly from 8.6% to 96%, before showing a constant line at a reaction time of 120 min. The rapid increase of adsorption was due to strong driving force from high concentration gradient generated between ASA molecules in aqueous solution and the number of vacant active sites available on the adsorbent surface during the initial stage of adsorption. Then, there was no significant change in percentage removal as the adsorption process continued over 120 min. At this stage, the adsorption had reached an equilibrium with the percentage removal of ASA is maintained at around 96%. A parallel trend was obtained in the previous study done by Wong, et al. [14] in the investigation on the removal of ASA using activated carbon from spent tea leaves. Therefore, the sufficient time for the occurrence of adsorption equilibrium between MACsorb and ASA to occur was around 120 min, and this time period was used in the subsequent investigation.



**Figure 2** Effect of contact time on percentage removal of acetylsalicylic acid (Conditions: initial ASA concentration, 0.1 g/L; adsorbent dosage, 0.2 g; GTA volume, 1 ml; solution pH, 3; temperature, 27 °C)

### 3.4 Effect of initial concentration of ASA

The initial concentration provides an important driving force to overcome all mass transfer resistance of ASA between the aqueous and solid phase. Figure 3 represents the results of initial concentrations effect on ASA adsorption within range of 0.025–0.3 g/L. A rapid increase in the adsorption of ASA onto MACsorb was spotted at the initial concentration of ASA solution from 0.025 g/L to 0.1 g/L with the percentage removal of 46% to 96%, respectively. Then adsorption efficiency decreased to 26% as the initial ASA concentration increased to 0.3 g/L. This trend is in agreement with the previous study done by Luo, et al. [15] on the removal of patulin by magnetic chitosan.

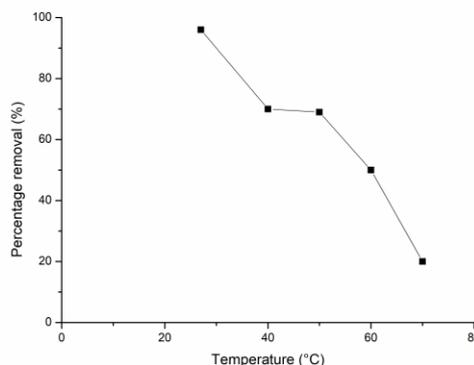


**Figure 3** Effect of initial acetylsalicylic acid concentration on percentage removal of acetylsalicylic acid (Conditions: contact time, 120 min; adsorbent dosage, 0.2 g; GTA volume, 1 ml; solution pH, 3; temperature, 27 °C)

The high percentage removal of ASA at low concentrations is because of the vacant active sites on the MACsorb surface to accommodate the ASA are sufficient. On the contrary, at the high adsorbate concentration, the available adsorption sites are fewer than the number of the ASA molecules present. Thus, inadequate vacant active sites to accommodate more ASA molecules were present in the solution. The results revealed that the vacant active sites on MACsorb surface are the limiting factor for ASA adsorption. The optimum concentration used in the subsequent investigation was 0.1 g/L, due to the highest removal efficiency obtained.

### 3.5 Effect of temperature

Figure 4 shows the effect of temperature from 27°C to 70°C, on the percentage removal of ASA. It can be seen that the percentage removal of ASA decreased with the increase in temperature. The decrement in adsorption efficiency indicates an exothermic process, and the adsorption was presumably dominated by weak interaction forces at high temperature [16]. The same result was reported in a study investigated by Kilic, et al. [17]. The optimum solution temperature was selected as 27 °C for subsequent investigation.



**Figure 4** Effect of temperature on percentage removal of acetylsalicylic acid (Conditions: contact time, 120 min; initial ASA concentration, 0.1 g/L; adsorbent dosage, 0.2 g; GTA volume, 1 ml; solution pH, 3)

### 3.6 Effect of pH

Solution pH is a significant parameter which affects the adsorption process as it alters the degree of surface charge of the adsorbent and ionization of adsorbate molecule. The effect of pH on the ASA removal can be illustrated based on the point of zero charge (PZC) on the MACsorb surface. Based on the results shown in Figure 5, the  $pH_{PZC}$

of MACsorb is 4.2. As a rule, the MACsorb is protonated and increase its positively charged intensity at pH of the solution below  $pH_{PZC}$ . Hence, in acidic medium of pH 3, the percentage removal of ASA is the highest (Figure 6) due to strong electrostatic attraction between protonated MACsorb and negatively charged ASA. Contrarily, at solution pH above PZC, the surface of the adsorbent is deprotonated and its negatively charged intensity increased which are unfavorable for adsorption of negatively charged pollutant. Also, at high solution pH, the excess  $OH^-$  ions in the solution compete with ASA molecules for adsorption sites on the MACsorb surface and result in less adsorption. Hence, it can be observed that the percentage removal of ASA is low as the solution pH increased. A similar observation was recorded in the study of adsorption of ASA onto carbon black-based adsorbent derived from tire waste [18].

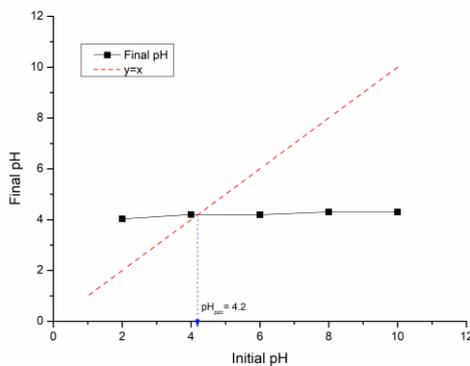


Figure 5 Point of zero charge of MACsorb adsorbent

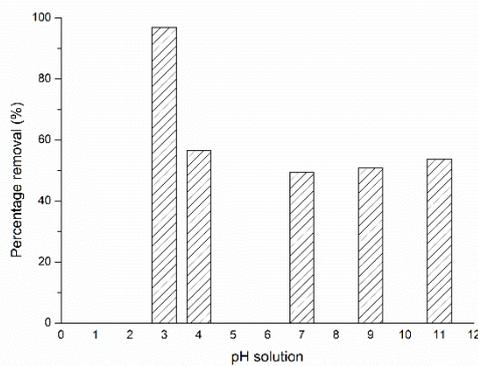


Figure 6 Effect of solution pH on percentage removal of acetylsalicylic acid (Conditions: contact time, 120 min; initial ASA concentration, 0.1 g/L; adsorbent dosage, 0.2 g; GTA volume, 1 ml; temperature, 27 °C)

#### 4. CONCLUSION

In this research work, the adsorption of ASA from aqueous solution onto MACsorb was investigated. The MACsorb was synthesized via crosslinking method with the optimal volume of glutaraldehyde, i.e. 1 ml. The highest removal efficiency of ASA observed was 96% under the following adsorption conditions: 120 minutes of reaction time, 0.1 g/L ASA concentration, 0.2 g of MACsorb, acidic ASA solution (pH3) and at a temperature of 27 °C. This study gives valuable insight where ASA can efficiently be removed by biopolymer adsorbent, chitosan without carbonization and activation as in AC preparation process.

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