Kinetic Study of Gelatin/Chitosan Based Nanocomposites for Acid Red 150 Dye Adsorption Using Ultrasonic Energy

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The effect of acid red 150 dye (AR150) adsorption parameters onto the prepared gelatin/chitosan/laponite based nanocomposites (NC I, II, III and IV) such as dye concentration, contact time, pH, and sorbent amount using ultrasonic energy had been studied. The standard adsorption affinity through the adsorbent suitability was also carried out. The results revealed that high concentrations of AR150 and chitosan content led to an increasing in the adsorption rate. A comparison between adsorption kinetics of the prepared nanocomposites with conventional and ultrasonic techniques was investigated. The time/dye-uptake isotherms were declared the improvement of dye adsorption in the second phase. Adsorption rate, reaction half-time and standard affinities were also studied. The dye adsorption uptake using ultrasound technique was higher than that in case of the conventional one in case of all the used nanocomposites. On the other hand, in case of using ultrasonic technique, the isotherms showed high dye uptake. In other words, the best dye adsorption rate could be obtained at different nanocomposite concentrations 0.3 and 0.8 g/L in case NCIII and IV, respectively.

Keywords: Chitosan, laponite, dye removal, ultrasonic, acid red150 dye, Kinetic isotherm.
The textile industry is one of the largest producers of industrial waste water which including several pollution sources such as the different colours and pigments. This is a serious environmental problem due to its high toxicity. Consequently, this issue is currently of great interest. Because of the difficulty of treating such water by conventional methods, the needing to use of the modern techniques is urgent issue. Ultrasonic Power could enhance a great variation of physical and chemical processes, essentially because of marvel known as cavitation inside the fluid environment which developed and exploded a breakdown of microscopical bubbles. Unexpected and burst breakdown of these bubbles could create centralize high pressure, high temperature, and stun waves [1,2]. The influence of ultrasonic application on the dye adsorption can emphases in terms of regular diffusion of the dye molecules in the fluid, accelerating of the dispersion rate of dye within the composite and enhancing the reaction between composite and dye[3-11]. Recently, some attempts have been made to prepared and investigate novel nanocomposites for adsorption of some toxic materials. Moreover, the polymeric hydrogels play an important role in the treatment of waste water[12]. Because of the ultrasonic power has a high impact in the different industrial applications, this work was to investigate the ultrasonic energy effects on the adsorption kinetics of AR150 dye onto gelatin/chitosan/laponite based nanocomposites.

Experimental

Materials

Acid dye red 150 (Table 1) was purchased from Ciba Co. and used without further purification.

All other chemicals and reagents were used as received.

<table>
<thead>
<tr>
<th>Name of the dye</th>
<th>Chemical structure</th>
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<tbody>
<tr>
<td>Acid Red 150 (AR 150)</td>
<td><img src="image" alt="Chemical structure" /></td>
</tr>
</tbody>
</table>

Apparatus

Ultrasonic bench top cleaner bath, model 575 D was used. The used experimental setup was composed of an electrical generator operated at a frequency of 38.5 kHz and power range 100-500 W. The output power levels are from 100 up to 500 W and supplied by three transducers at the bottom of the industrial grade tank. Precise digital control of time (0–90 min), thermostatically controlled heater (ambient to 80°C) and power level and degas functions. The conventional method device is Julabo SW 20 Seelbach/Germany, V/Hz 230/50/60.

Batch adsorption experiments using ultrasonic energy

Table 2 shows the chemical composition of the prepared nanocomposites (hydrolyzed polyethylene terephthalate, gelatin and chitosan were blended in equimolar ratios in presence of different concentrations of laponite, as described previously in details [13]. The dye AR150 solution was prepared without pH adjustment (the initial dye concentration 277 mg L\(^{-1}\)). 0.3 g of the prepared NCs (I, II, III, and IV) and 50 mL of the standard solutions were stirred for a certain period of time (40 min). After filtration, the concentration of AR150 in the supernatant was analyzed by ultraviolet visible spectrophotometer (Schimadzu, Japan) with 2 nm resolution using calibration curve at \(\lambda_{530}\) nm. The adsorption of AR150 was studied in pH range 3–9, through adjusting pH using either HCl or NaOH. The prepared NCs were equilibrated at a particular pH value for different time and temperature intervals (20, 40, 60, and 80) min, (40, 50, 60, and 70°C), and power level (100, 200, 300, 400 and 500 w) respectively. Adsorption equilibrium tests were conducted at optimum conditions. The adsorption capacity was calculated according to Lambert-Beer law and the adsorption kinetics Langmuir isotherm equations. The concentration of dye solutions was determined after reference to the respective calibration curve of acid dye.

**TABLE 2. Chemical composition of the prepared Nanocomposites.**

<table>
<thead>
<tr>
<th>Nanocomposites</th>
<th>Chemical compositions (wt %)</th>
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<tbody>
<tr>
<td></td>
<td>Gelatin</td>
</tr>
<tr>
<td>I</td>
<td>1</td>
</tr>
<tr>
<td>II</td>
<td>1</td>
</tr>
<tr>
<td>III</td>
<td>1</td>
</tr>
<tr>
<td>IV</td>
<td>1</td>
</tr>
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</table>

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Results and Discussion

Effect of pH value on AR150 adsorption ratio (%) using ultrasonic technique

Figure 1 demonstrates the influence of pH on adsorption ratio (%) of AR150 in various NCs. The pH influences essentially the adsorption limits of AR150 onto the various NCs. Generally, high uptake always happened in acidic medium rather than neutral or alkaline ones. As expected, at low pH, a lot of protons had been accessible to give protonated amino groups for chitosan and/or gelatin particles for forming –(NH3), that way augmenting electrostatic attraction of positive charge of adsorption positions and negative charge of dye anions which led to creating a higher adsorption of dye [14,15]. This clarification concurs with our information on pH affect. As described previously, the pH of hydrous solution assumes a critical part in acid dye adsorption on adsorbents [16-27]. (Fig 1).

![Fig.1. Effect of pH values on dyestuff sorption of prepared NCs using ultrasonic method.](image)

Effect of time on AR150 adsorption ratio (%) using ultrasonic technique

Figure 2 illustrates the impact of time on adsorption ratio (%) of acid dye onto several NCs. The impact of time on dyestuff sorption of prepared NCs was investigated for different time periods (20–80 min). With all NCs (I, II, III and IV), the sorption ratio of dye progressively augmented within 20 to 80 min and the percentage adsorption of acid dye were stabilized at 60 min.

Effect of temperature on AR150 adsorption ratio (%) using ultrasonic technique

Figure 3 demonstrates the influence of temperature on adsorption of acid dye onto various NCs at pH 3 for 60 min using 500 mg L-1 dye concentration utilizing ultrasonic technique with power level 400 Watts. The effect of temperature (40-700C) exhibited an augmenting of dye uptake. After equilibrium, the augmentation of dye uptake showed endothermic type of adsorption [28,29].

Effect of nanocomposites dose using ultrasonic technique

Figure 4 demonstrates the adsorption ratio (%) of AR150 dye onto various prepared NCs using pH 3 at 60°C for 60 min utilizing ultrasonic technique with power level 400 Watt. The ratio augmented essentially with rising of adsorbent dose from 0.1 till 0.8g. Increasing of the adsorbent dose using constant concentration of AR150 gave more accessible adsorption positions to acid dye and along these lines augmented the range of acid dye uptake. NCs III afforded better results at 0.3 g\L, while IV afforded better results at 0.8 g\L adsorbent concentration.

Effect of AR150 concentration on the dye adsorption using ultrasonic technique

Figure 5b demonstrates the influence of the different AR150 concentrations on the adsorption rate of various NCs at pH 3, 60 °C for one hour, and power level 400 Watt. With NC II and III, the increasing of AR150 concentration caused an augmentation in the adsorption quantity of acid dye on the NC. Contrary, using NC I and IV, the adsorption rate exhibited an increasing in the dye concentration and NC IV gave better result at 0.2 g/L. From Fig. 5a and 5b, it was observed that the dye adsorption rate of various NCs using ultrasonic technique was higher than that in case of using the conventional one, except NC III and NC IV at 0.5 g/L dye concentration. This indicates that both of the dye concentration and the composition of NC assumed a significant aspect in the adsorption quantity of acid dye onto various NCs. Moreover, the dye particles might transfer from outer surface to internal lamellar area and bringing about the disaggregation of the whole load. With high capacity rate of acid dye, agglomeration is predictable to be predominating, but monomers in addition to dimmers are basically missing within acid dye–NC complexes [30-37]. From Table 3, it can be concluded that in case of the nanocomposites I and II, the dye adsorption rate (%) was increased by increasing the dye concentration and the best dye adsorption rate can be obtained at 0.5 g/L dye conc. But for the nanocomposites III and IV, the dye adsorption rate (%) was decreased by increasing the dye concentration and the best dye adsorption rate can be obtained at 0.2 dye concentration.

Fig. 5a. Effect of conventional dye concentration, b: Effect of ultrasonic dye concentration.

TABLE 3. Effect of the dye exhaustion rate (%) using ultrasonic method.

<table>
<thead>
<tr>
<th>Dye conc. g/L</th>
<th>Exhaustion rate (%)</th>
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<tbody>
<tr>
<td></td>
<td>E %=(Abs. before -Abs. after /Abs. before)X 100</td>
</tr>
<tr>
<td></td>
<td>NC I</td>
</tr>
<tr>
<td>0.2</td>
<td>61.7</td>
</tr>
<tr>
<td>0.3</td>
<td>73.8</td>
</tr>
<tr>
<td>0.4</td>
<td>81.7</td>
</tr>
<tr>
<td>0.5</td>
<td>96.7</td>
</tr>
</tbody>
</table>

Effect of ultrasonic power on the dye adsorption

Figure 6 demonstrated the influence of power of ultrasound on the adsorption of the acid dye on the NCs surface conducted at various power levels (100–500 watt). The acid dye adsorption on the various NCs was directly increased proportionally with an increasing of the power level supplied. Besides, the highest values of acid dye adsorption of the various NCs can be obtained at power level of 500 watt. This may be attributed to the effect of cavitation phenomena.

Adsorption kinetics

It is realized that the rate of any procedure implies an alteration in any of the starting substrates which happens in the procedure or the item that gained for each time unit. Stratifying this clarification in the adsorption procedure could be seen as an adjustment in dye uptake for each duration unit [37, 38]. Duration of dye uptake isotherms for the composites adsorbed by acid red150 using conventional and ultrasonic heating methods are presented in Figs 7 a, b, c and d. These figures explains that dye uptake percentages for the adsorbed nanocomposites using ultrasound technique. It was observed that in the most part the adsorption rate was lower than those got from the conventional technique. Furthermore, the isotherms for the two techniques were separated against each another and showed lower dye uptake in case of the ultrasonic technique relative to the conventional one(39). Data in Fig. 7 a, b, c and d could be evaluated via available common type of the primary order rate for the adsorption of NCs I, II, III and IV to the acid dye red150.
Fig. 7a. Ultrasonic and conv. adsorption rate of composite I, b: ultrasonic and conv. adsorption rate of composite II, c: ultrasonic and conv. adsorption rate of composite III, d: ultrasonic and conv. adsorption rate of composite IV

*Standard affinity (\(-\Delta \mu\))*

The information of dyeing equilibrium are usually announced as the standard affinity of adsorption [40], therefore, the standard affinity can be mentioned in the experimental part. Fig. 8a demonstrates a plot for \(\ln|Q_t - Q_f|\) as a parameter for duration of adsorption of NCI utilizing both conventional and ultrasonic techniques. Figure 8b demonstrates a plot for \(\ln |Q_t - Q_f|\) as a parameter for duration of adsorption of NCII using both conventional and ultrasonic techniques. Figure 8c demonstrates a plot for \(\ln|Q_t - Q_f|\) as a factor for duration of adsorption of NCIII using both conventional and ultrasonic techniques. Fig. 8d demonstrates a plot for \(\ln|Q_t - Q_f|\) as a factor for duration of adsorption of NCIV using both conventional and ultrasonic techniques. As expected, the linear suitability holds without a doubt and the amounts of the adsorption constants can be calculated and recorded in Table 4.
Fig. 8a. Relation between Ln (Qt-Qf) and time using conventional and ultrasonic conditions for composite I, b: Relation between Ln (Qt-Qf) and time using conventional and ultrasonic conditions for composite II, c: Relation between Ln (Qt-Qf) and time using conventional and ultrasonic conditions for composite III, d: Relation between Ln (Qt-Qf) and time using conventional and ultrasonic conditions for composite IV.

TABLE 4. Adsorption percentage (%) of constant K, time for half reaction t₁/₂, standard affinity -Δμ and quantity for final dyestuff uptake using NC I, II, III and IV.

<table>
<thead>
<tr>
<th>NCs</th>
<th>K x 100 (min⁻¹)</th>
<th>-Δμ (kJ/mol)</th>
<th>t₁/₂ (min)</th>
<th>Qf (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NC I</td>
<td>7</td>
<td>10</td>
<td>18</td>
<td>19.1</td>
</tr>
<tr>
<td>NC II</td>
<td>10</td>
<td>11.6</td>
<td>16.9</td>
<td>18.7</td>
</tr>
<tr>
<td>NC III</td>
<td>10</td>
<td>13.2</td>
<td>16.7</td>
<td>17.1</td>
</tr>
<tr>
<td>NC IV</td>
<td>8.6</td>
<td>9</td>
<td>16</td>
<td>17.7</td>
</tr>
</tbody>
</table>

Conclusion

The data confirmed that the adsorption rate of acid red 150 dye onto the prepared gelatin/chitosan/laponite based nanocomposites was improved using ultrasonic technique relative to the conventional one. On the other hand, in case of high content of laponite (2 wt%), the maximum adsorption rate could be obtained at low dose of the nanocomposite. In other words, both chitosan and laponite concentrations played an important role for enhancing the adsorption capacity.

References


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دراسة حركية متراكبات متناٌية الصغر مبىيً علي الجيلاتيه مع الكيتوزان لإمتساز الصبغٌ الحمضي الحمراء 150 بإستخدام طاقه الموجات فوق الصوتية

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ينظف هذا البحث إلى دراسة تأثير مختلف عناد إمتصاز الصبغاء الحمضي الحمراء 150 علي متراكبات متناٌية الصغر مبىيً علي الجيلاتيه مع الكيتوزان في وارد طاقه موجات فوق الصوتية لإمتصاز الصبغاء، زمن الإمتصاز: درجة الهيدروجيني، تركيز الموجات المستخدمه.

بالإضافة إلى المقارن بين إستخدام طاقه الموجات فوق الصوتية وطاقه الحرارية التقليديه في توضيح مدى التأثير في قابلية إمتصاز المتراكبات المحضره للصبغاء الحمراء. علاوة على دراسة ديناميكية المواد المحضره لإمتصاز.

ألختينت النتائج أنه كلاً زادت نسبة الصبغه وكذلك نسبة الكيتوزان زاد معدل الإمتصاز. كذلك كلاً زادت قوة طاقه الموجات فوق الصوتية زاد معدل الإمتصاز لكل المتراكبات المستخدمة. ومن ناحية أخرى كان أفضل معدل إمتصاز عند استخدام تركيز للصبغه 277 ملليجرام/لتر وتركيزات للمتراكبات تتراوح من 0.3 إلى 0.8 جرام حسب التركيب الكيميائي للموجب المحضر.

يمكننا القول بأن كل من طاقه الموجات فوق الصوتية ولكلي الكيتوزان يلعبان دوراً مهماً في زيادة معدل الإمتصاز عند استخدام طاقة الموجات فوق الصوتية.