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Acid-Base Properties of the Adsorption of Synthetic Dyes from Solutions

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Abstract

The presence of synthetic dyes is often underestimated in environmental protection. However, it has been demonstrated the impact of colored compounds in ecology and human health. Green tea (GT) and peppermint (PM) tea bag wastes were used as potential adsorbents of dyes from aqueous solutions to evaluate the effect of pH on the adsorption. Basic yellow 57, basic blue 99 and crystal violet were chosen as model dyes due to their widespread use in the industry. Dye solutions at different pH values were placed in contact with the adsorbents in batch experiments at room temperature. Results indicate that crystal violet is totally removed from the solution by the adsorbents (100% removal), followed basic blue 99 and basic yellow. PM reports the highest dye removal. Our data was compared to recently published reports, indicating their potential applicability to real wastewaters, as it is optimum at neutral pH values. These results demonstrate that these materials are excellent and cost-effective candidates for the removal of dye pollutants from contaminated solutions.

Keywords: Tea leaves; Synthetic dyes; pH; Adsorption; Electrostatics

Introduction

Dyes are synthetic, water-soluble and dispersible organic compounds, which cause coloration of natural water bodies when released into the environment. They are widely used in industries such as dyestuff, textiles, rubber, leather, paper, plastics, cosmetics etc., to color their products and are invariably left in the industrial wastes. Synthetic dyes, suspended solids and dissolved organics are the main hazardous materials found in textile effluents. These materials can affect the physical and chemical properties of fresh water. In addition to the undesirable colors of textile effluents, some dyes may degrade to produce carcinogens and toxic products [1]. Furthermore, the colored effluents reduce light penetration and potentially prevent photosynthesis. Dyes even in very low concentrations affect the aquatic life and food chain [2]. Hence, the removal of dyes from process or waste effluents becomes environmentally important.

Because of the high degree of organics present in these molecules and the stability of modern dyes, conventional physicochemical and biological treatment methods are ineffective for their removal [3-5]. Adsorption has been shown to be one of the most promising and extensively used methods for the removal of both inorganic and organic pollutants from contaminated water. Activated carbon is the most widely used adsorbent for this purpose because it has a high capacity for adsorption of organic matter and it is proven to be effective in treating textile wastes [3]. However, in view of high cost and associated problems of regeneration, there is a constant search for alternate low-cost adsorbents. Such alternatives include walnut shell [4], dead macro fungi, bacteria, fruit barks, fruit peels, coconut wastes, pine sawdust, and other bio-materials [1-7]. More recent studies indicate that coconut shells [8] and pinang frond [9] can be used to prepare activated carbon for the removal of artificial dyes. Luk et al. [10] have also study the adsorption of dyes onto chemically modified chitosan beads. Chitosan is a polysaccharide, composed of units of glucosamine and obtained from chitin, which is found in seashells and the exoskeleton of insects. Moreover, the US Environmental Protection Agency (EPA) is currently focusing on the elimination of dyes using these eco-friendly adsorbents, due to their easy application and low-cost [11].

All these adsorbents share a common characteristic: they all derive from cellulose. They are plant-based materials and contain polysaccharides as their structural skeleton. The literature offers many alternatives but only a few have been dedicated to the study of powdered leaves as adsorbents of pollutants in general [12]. Green tea (GT) and Peppermint (PM) tea bag wastes are good candidates for this purpose. They are sold in their pure state (not as a mixture of other herbs) and come in small particles (avoiding grinding and sieving treatment). They both have a very important characteristic, after brewing; they are thrown to the garbage and are considered domestic waste.

The dyes that were studied in this research were selected based on their wide-spread use in the cosmetics market and research (Figure 1). Discharge of Crystal Violet (CV) into the hydrosphere can cause environmental degradation, because CV is readily absorbed into fish tissue from water exposure and is metabolically taken by fish. It has also been linked to increased risk of human bladder cancer. CV induces renal, hepatic and lung tumor in mice. CV is also a mutagen and mitotic poison [12]. On the other hand, Basic Yellow 57 (BY57) and Basic Blue dye 99 (BB99) are hair dyes that are ingredients for hair coloration and are present in hair dyes industries. We believe that the proposal of new alternatives for the treatment of their waste waters could be of their interest.

The affinity between adsorbents and pollutants could be driven by acid-base properties, as predicted by the presence of pH-dependent ionizable functional groups on the adsorbent and the target adsorbates. This can be understood as the attraction of a positive and negative charge between the adsorbent and the dye. These charges are conditions by the acidity of the solution in which the dye and the adsorbents are in contact. The aim of the present study is to evaluate the effect of pH on the adsorption of BY57, BB99 and CV dyes onto peppermint

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and green tea bags wastes. These results will be compared with other adsorbents that have been studied recently with other dyes. Based on this comparison, a conclusion about the acid-base properties of these natural adsorbents will be elaborated.

Materials and Methods

Reagents and solutions

Stock solution containing 1 g/L of the dyes were prepared by dissolving Basic Yellow 57 (Vanshi Chemicals), Basic Blue 99 (Vanshi Chemicals) and Crystal Violet (Sigma-Aldrich) in distilled water. Solutions were prepared by dilution of the stock solution to reach the desired concentration (0.1, 0.012, 0.035 g/L for each of the dyes). Stock solutions were refrigerated in a volumetric flask and only taken for each experiment to prevent spoilage of the solution. The initial pH of the solutions were measured with a pH-meter (Fisher Scientific Accumet Model AB15) and adjusted to the required pH value by adding small volumes of HCl and NaOH prior to contact with the adsorbent.

Preparation of the adsorbents

Peppermint tea (PM) and Green tea (GT) bags were purchased from a local supermarket and spent in sequential rinses of boiling distilled water to extract color, taste and flavor. Final rinses were done with the mixtures of boiling distilled water. The spent tea bags were oven-dried overnight at a temperature not higher than 50°C to prevent any chemical or thermal decomposition. Finally, the adsorbents were opened and stocked in plastic containers. Figure 2 shows different preparation stages of the adsorbents.

Adsorption experiments

Batch experiments were carried out in duplicate at room temperature by combining 50 mg of the adsorbents PM and GT with 50 mL of dye solutions. These suspensions were placed under orbital agitation at 250 rpm for 48 hours. The adsorption time was determined by preliminary experiments, confirming that less than 2
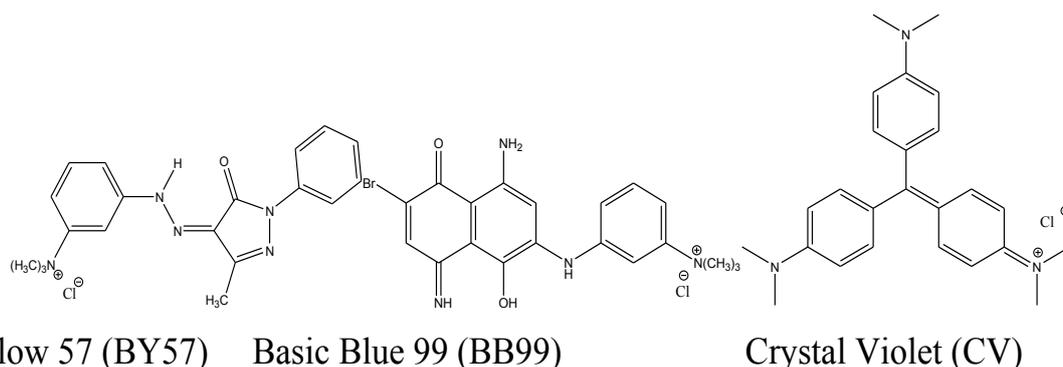

Figure 1: Chemical structure of the synthetic dyes.

Figure 2: Preparation and adsorption experiments of the tea bag waste on the adsorption of dyes. (Left) Continuous boiling of tea bags; (Center) Tea bags of GT after boiling and drying; (Right) Adsorption of BY57 in batch experiments, showing control solution and with GT in the middle.

days is needed to reach equilibrium. Upon reaching the equilibrium, the suspensions were decanted and the remaining concentrations of the dyes were determined by UV-vis spectrophotometry (Synergy 4, BioTek) which has an automatic plate reader. Dyes were measured at different wavelengths: BY57 at 380 nm, BB99 at 574 nm and CV at 590 nm. These wavelengths are associated with the color that is absorbed by a given colored solution and is used as a quantification method.

Data analysis

One way to express the adsorptive properties of a given adsorbent is Adsorption Percentage (%ADS) where initial and final dye concentrations are compared and expressed as percentage as shown in Equation (1).

$$\% ADS = \frac{(C_i - C_f)}{C_i} \times 100 \qquad (1)$$

Where C_i and C_f are the initial and final concentrations. Processing of the data was conducted using Microsoft Excel and graphs were prepared using the statistical software, Origin V 8.0.

Adsorbent characterization

Spent tea leaves of GT and PM were characterized to study the presence of potential adsorption sites and to explore the morphology and surface properties of these adsorbents. Scanning electron micrographs (SEM) were taken of both adsorbents using a Table Top 3000 m Hitachi. Gold coating was not used to observe these samples. Then, the presence of functional groups was analyzed by Fourier-Transformed Infrared (FTIR) spectroscopy using a spectrometer Frontier, equipped with an universal ATR device, Perkin Elmer.

Results and Discussion

The pH value of the adsorption medium is the most critical parameter that affects the adsorption capacity of pollutants by adsorbents. pH influences the charge of the adsorbent's surface and also the charge of the dye. To avoid this dual effect, dyes that are always positively charged (Figure 1) were used in this study. This would leave us with the pH effect only on the chemistry of the adsorbent. In other words, the adsorption will reside only on the positive or negative charge of the tea bags wastes. This is conditioned by the acidity or alkalinity of the solution. Figure 3 shows the results obtained on the experimental data with GT and PM with the dyes. As observed by the results, both adsorbents increase their dye adsorption as the pH increases (close to neutrality for most of them). A clear predominance is present in PM, which reaches adsorption percentages close to 100% for all the dyes. The increase of dyes adsorption with the pH could be explained by the electrostatic interactions between negatively charged groups on the adsorbents and the cationic dyes. As the pH increases, acidic groups on the adsorbents are deprotonated, producing a negative surface on the tea wastes. Several acidic functional groups have been identified in lignocellulosic materials like tea leaf wastes [13]. The presence of these active adsorption sites were confirmed by FTIR analysis. For example, marine algae, are composed a polysaccharide called polyalginic acid, which at high pH ionizes producing polyalginate anions [14,15]. Polyalginate anions are widely known for their high affinity towards heavy metals [14-16]. For these adsorbents, it could he hypothesized that the adsorption mechanism is mostly driven by electrostatic interactions, since % ADS dramatically decreases with pH for all the adsorbents. All dyes were highly soluble in water in the entire pH range of this study; therefore a decrease in solubility at changing pH was discarded. At increasing pH values, weak acidic groups like carboxyl become negatively charged, and are able to interact more efficiently with the cationic dyes.

Residual and surface waters are normally in the pH range of 5 to 7 [13,14]. The adsorbents show their highest adsorption within this range, showing their applicability in real conditions. These results were compared against recently published data and summarized in Table 1.

Adsorbents like walnut shell show a high adsorption, but it occurs at pH 9. It is very unlikely to observe wastewaters with this alkalinity. Conversely, Cellulosic adsorbents, fruit residues and dead bacteria,
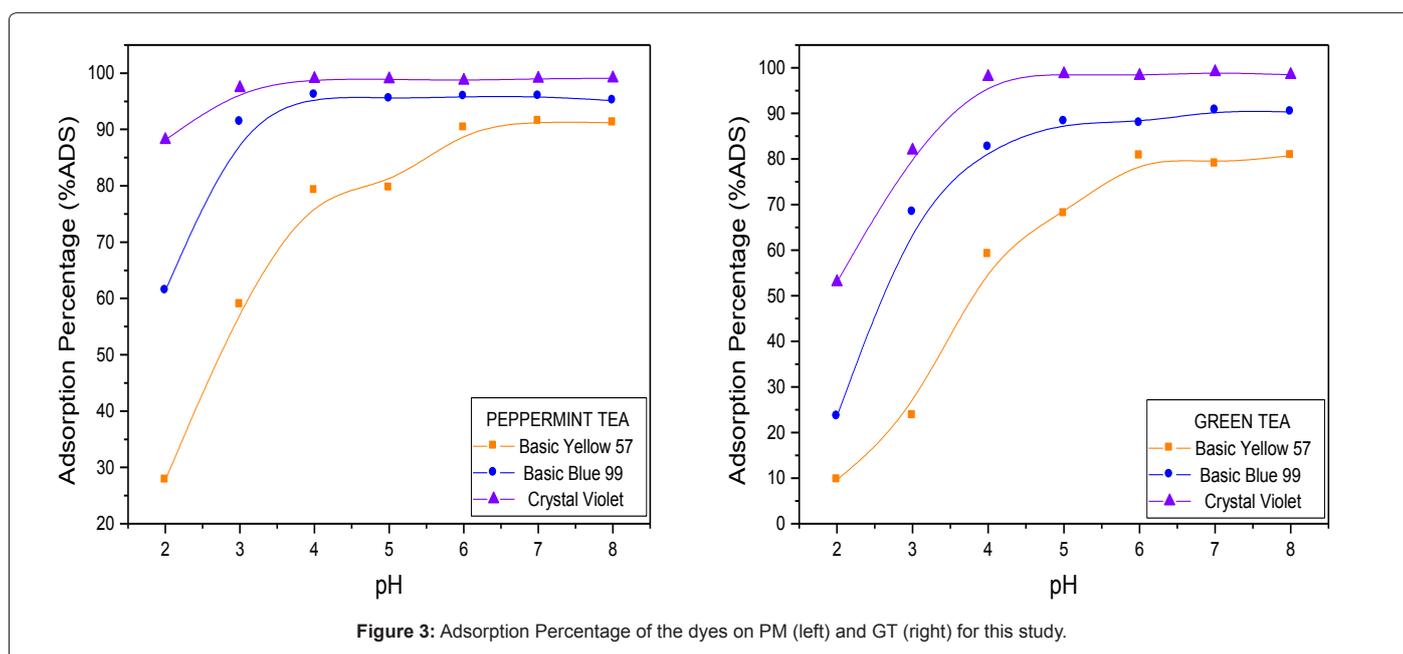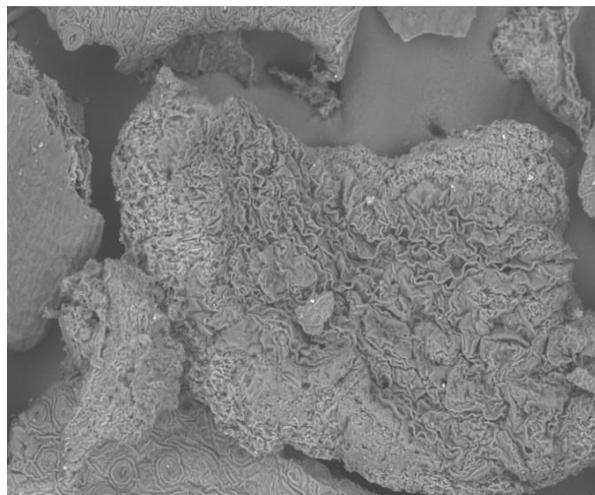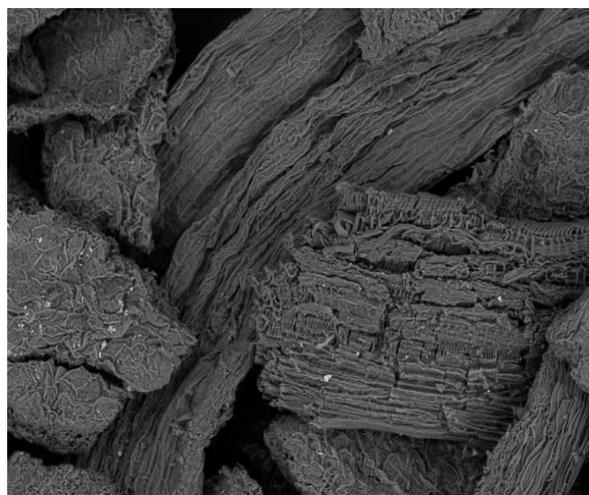

Figure 3: Adsorption Percentage of the dyes on PM (left) and GT (right) for this study.

Figure 4: Scanning electron micrographs of GT (left) and PM (right) showing the heterogeneity of their surfaces.

Synthetic dye	Adsorbent	Adsorption Percentage	Reference
Brilliant green	Cellulosic adsorbents	97%	[14]
Malachite green	Fruit residues	90%	[1]
Navy blue dye	Dead bacteria	82%	[2]
Red 131 dye	Leather waste	100%	[13]
Rhodamine B	Walnut shell	100%	[4]

Table 1: Summary of recent studies on the adsorption of synthetic dyes.

Adsorbent	O-H Stretching (alcohol)	C-H Stretching (alkane)	C=O Stretching (ketone)	O-H Stretching (carboxylic acid)	C=O Stretching (carboxylic acid)
t	3250	2800-2960	1665	3050	1715
PM	3245	2850-2920	1680	3000	1710

Table 2: FTIR assignments for the adsorbents in cm^{-1}.

show good adsorption at very acidic pH values. This diminishes their applicability [15,16]. An adsorbent that compares to the results in this work is leather wastes, which reports adsorption at neutral conditions (pH=7), indicating 100% removal.

Acidic conditions can be understood as the overpopulation of H$^+$ ions in solution. These ions react with the surface of the adsorbents, making it positively charged. On the other hand, an alkaline condition is the overpopulation of OH$^-$ ions in solution. As mentioned, in acidic conditions, the OH$^-$ ions will also react with the adsorbent surface and turn it negatively charged. Since the dyes are all positively charged (Figure 1), the more negative the adsorbent surface, the more adsorption will be observed. This is driven by the attraction of negative and positive charges (electrostatic forces).

Chemically speaking, and according to the observed results, both adsorbents (PM and GT) tend to adsorb more dye at neutral conditions. These conditions mean that no positive or negative charge predominate the surface of the adsorbents. This adsorption is maintained from pH 6 to 8, showing that a slightly positive and slightly negative surface of the adsorbent is still tolerated for the adsorption. Very low pH, like 2, greatly decreases the adsorption for all the dyes and both adsorbents. We expect to observe the same effect with very high pH. These experiments were not conducted at high pH due to the low applicability in waste waters.

SEM and FTIR experiments were conducted to confirm the adsorptive properties of GT and PM. As shown in Figure 4, the scanning electron micrographs indicate a heterogeneous surface for both adsorbents. The presence of these hills, pores, caves and pockets have proven to house and trap pollutants [13,14]. Fibrous lignocellulosic materials contain adsorption sites that are target for the pollutants.

This dye/pollutant affinity is enhanced by the prolonged contact between the dye and the surface of the adsorbent. The randomness of GT and PM's surfaces maximized this contact. Finally, FTIR results are summarized in Table 2. As expected, these lignocellulosic materials are highly composed of carbohydrates (mainly cellulose) as demonstrated by the peaks at 3245-3250 cm^{-1} and 1665-1680 cm^{-1}, representing hydroxyl and carbonyl groups, respectively. The typical absorbance at 2960-2800 cm^{-1} was also observed, indicating the presence of saturated methylene, methyl and methine groups. On the other hand, a shoulder at 3000-3050 cm^{-1} and a peak at 1710-1715 cm^{-1} were observed for both samples, suggesting the presence of hydroxyl (carboxylic) and carbonyl (carboxylic), respectively [17]. These results elucidate not only the presence of active adsorption sites like hydroxyl and carbonyl that have a high electron density, but also the presence of carboxyl groups that are pH responsive. The pH-dependence of the adsorption could be justified by the presence of these ionizable carboxyl groups, and explain the higher dye adsorption at higher pH values.

Conclusion

Acid-base properties of spent GT and PM tea bags wastes were studied for the adsorption of Basic Yellow 57, Basic Blue 99 and Crystal Violet dyes. The results show that 90-100% of the dyes were removed at pH values close to 7 (neutral conditions). PM showed a higher adsorption when compared to GT. Dye adsorption was strongly conditioned by the pH, showing an interesting positive-negative interaction between the adsorbents' surface and dye molecules. SEM images show the presence of pockets and protrusions that could potentially behave as adsorption sites for pollutants. Moreover, FTIR analysis confirmed the presence of hydroxyl, carbonyl and ionizable carboxyl groups that are known active centers for the adsorption of

pollutants are also responsible for the pH dependence of the process. These results were compared to previous studies with other dyes and adsorbents. GT and PM adsorbents showed a better applicability to real conditions and are potential alternatives for the currently available techniques. Among the consulted literature, leather waste also represents a good adsorbent due to the convenient pH at which a very decent adsorption is observed.

Acknowledgement

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