

Eco-friendly adsorption of yellow hair dye from aqueous solutions onto spent green tea leaves

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ABSTRACT

Hair dying is a continuously growing industry of personal care. This growth increases the release of colored solutions into water, which needs remediation techniques that are appropriate and cost-effective. This study proposes the use of spent tea leaves for the elimination of the basic yellow 57 (BY57) hair dye. American (GT), Peruvian (PGT) and decaffeinated (DGT) spent tea leaves were used in batch experiments to eliminate BY57 at room temperature. Equilibrium parameters like pH, adsorbent mass, dye concentration, salinity, and effect of the presence of heavy metals and crowding agents were investigated to maximize dye removal. DGT shows the highest adsorption ($q_{\max} = 57 \text{ mg g}^{-1}$) at pH = 8 with only 100 mg of adsorbent. Adsorption was modeled by Langmuir and Freundlich theories and followed the trend: DGT>PGT>GT. Salinity and presence of a crowding agent decreased adsorption. Heavy metals had negligible effect on the adsorption onto DGT and GT. Desorption experiments indicate that diluted HCl is able to recover the adsorbent and recycle the adsorbents in repetitive cycles. Finally, point zero charge, surface area and porosity, and scanning electron microscopy indicate that the surface ionization and morphology are appropriate for the use of

these novel materials as a model hair dye in the removal of BY57 from aqueous solutions.

KEYWORDS: green tea leaves, basic yellow 57, isotherm, desorption, biosorption.

INTRODUCTION

Urban and industrial residual waters contain high amounts of contaminants that need to be eliminated prior to their discharge to the environment [1]. Colorants are species that confer color to other substances and can be classified as dyes and pigments [2]. Dyes are water-soluble, and commonly applied to textile fibers and cosmetics, whereas pigments are insoluble compounds that are added to products such as paints, ink or plastics [3, 4].

From the ecological point of view, the presence of dyes in water reduces its transparency and inhibits photosynthesis of plants, as dyes absorb sunlight in a more efficient manner [3, 5]. Likewise, some dyes are associated with the presence of heavy metals and sulfur that produce environmental problems due to their toxic nature [6-8]. From the toxicological point of view, the type of absorption and time of exposure are related to the hazardous risk of dyes on human health. Dyes have a low acute toxicity as a result of the short time of exposure. This is because dyes have a low solubility in corporal fluids and a high water

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solubility that favors their metabolism [9, 10]. Chronic toxicity due to continuous dye exposure is, in general, low. However, the carcinogenic potential of some azoic dye has been demonstrated and at least 3,000 azo dyes have been catalogued as carcinogenic. Their toxicity is associated with the release of aromatic amines by oxidation, hydrolysis, or reduction of the azo bond. Some aromatic amines that are used in the fabrication of dyes have also been recognized as carcinogenic [9, 11, 12].

The most widespread techniques for the elimination of dyes include oxidation, photocatalytic degradation, microbial degradation, filtration, ionic exchange, and adsorption by activated carbon [10]. For larger scales, activated sludge has demonstrated a great efficiency and applicability [4]. Although these techniques are able to remove dyes and keep their levels under the regulations, they still have some disadvantages. Most of them represent a high operational cost and require special training. Perhaps, adsorption by activated carbon is one of the most efficient amongst these techniques, but its low recyclability is still a drawback for its application at industrial levels [4, 7].

Biosorption, a growing area in bioremediation, develops new adsorbents for the removal of inorganic and organic pollutants from air, soil and waters [4, 13]. These adsorbents are non-living biological materials that have the property of concentrating pollutants using different mechanisms. This selectivity resides on the presence of important functional groups like carboxyl, amine, hydroxyl, phosphate and sulfides that have reported high affinity towards contaminants [4, 13]. Biosorption is attractive to the industry because of its fast adsorption kinetics, easy applicability, and extremely low cost when compared to the conventional methods [14-16]. Recent studies report the successful use of these biosorbents in the removal of heavy metals [17, 18], phenolic compounds [19, 20], and artificial dyes [21]. These studies also demonstrated that these materials have a high recyclability and pollutants desorbed with diluted acid solutions and re-used in repetitive cycles. This property is crucial for industrial applications where cost is one of the top priorities when deciding the most suitable decontamination technique.

The purpose of this work is the use of lignocellulosic materials derived from industrial waste in the removal of the hair dye basic yellow 57 (BY57). Green tea leaves are discarded in industrial amounts as by-products of tea-based industries such as Nestea[®] and Snapple[®]. Therefore, the need of a good waste disposal management will balance out with the decontamination of hair dyes and explore the adsorption capacity of these biomaterials. Decaffeinated, American and Peruvian spent green tea leaves were used in this study to compare their dye affinity and associate it with their processing and port of origin.

MATERIALS AND METHODS

Reagents and solutions

Stock solution containing 1000 mg L⁻¹ of BY57 was prepared by dissolving the dye in deionized water. Solutions of varying concentrations were prepared by dilution of the stock solution to reach the desired concentration. The initial pH of the solutions was measured with a pH-meter (Fisher Scientific, Accumet AB15) and adjusted to the required pH value prior to contact with the adsorbent.

Preparation of the adsorbents

Decaffeinated (DGT) and American (GT) green teabags were purchased from a local supermarket and used in sequential rinses of boiling distilled water to extract color, smell and flavor. Final rinses were done with boiling deionized water to remove any impurity. Then, the teabags were oven-dried at a temperature no higher than 50 °C to prevent any chemical or thermal decomposition. Peruvian green tea (PGT) was purchased in a local Peruvian market as whole leaves, and treated as the teabags. PGT was then crushed and sieved to a particle size between 425 and 850 µm. This particle size matched with the size observed in the teabags. Finally, all adsorbents were stored in plastic container until their usage.

Adsorption experiments

Batch experiments were carried out in triplicate at room temperature by combining variable masses of the adsorbents with 50 mL of dye solutions under orbital agitation at 250 rpm for 24 h. Preliminary studies indicated that less than 24 h

are needed to reach equilibrium. Upon equilibrium, the suspensions were separated by gravity and the remaining dye concentration was determined by spectrophotometry, using a microplate reader (Biotek, Synergy4) at a wavelength of 380 nm. Equilibrium parameters were sequentially optimized, including pH, mass of adsorbent, initial dye concentration, salinity and presence of crowding agents and heavy metals.

Desorption experiments

A larger scale adsorption assay was carried out with all the optimized equilibrium parameters to obtain dye-loaded adsorbents. Then, a given mass of the adsorbents was mixed with 20 mL of different co-solvents. These co-solvents were chosen based on their chemical properties such as acid-base, ionic strength, and polarity. Samples were sealed and shaken overnight at room temperature. Finally, the desorbed materials were separated by gravity and the dye concentration was quantified by spectrophotometry.

Analysis of the data

The amount of adsorbed BY57 onto the adsorbents was expressed as adsorption capacity (q , mg g⁻¹) as shown in equation (1)

$$q = \frac{(C_i - C_{eq}) \times V}{m} \quad (1)$$

where m is the mass of the adsorbent in grams,

V is the volume of the solution in L, and C_i and C_{eq} are the initial and at equilibrium concentrations of BY57 in mg L⁻¹.

A different way to express the adsorptive properties of a given adsorbent is adsorption percentage (%ADS), where the initial and final adsorbent concentrations are compared and expressed as percentage as shown in equation (2). Desorption percentage (%DES) can also be calculated with a similar expression.

$$\%ADS = \frac{(C_i - C_{eq}) \times 100}{C_i} \quad (2)$$

Characterization of the adsorbents

Surface texture and morphological properties of all the tea leaves were explored by scanning electron microscopy, (SEM) using a Tabletop microscope (TM3000, HITACHI). Samples were directly observed without gold coating. Acid-base properties and degree of ionization of the adsorbents were studied by the determination of their Point Zero charge (pH_{pzc}) by a method described elsewhere [22]. Specific surface area (SSA) and porosity were determined for all the adsorbents following the report of Nunes and Guerreiro [23] for activated carbon. In summary, methylene blue (MBN) and iodine (IN) numbers were determined and replaced in equations (3), (4), and (5) for SSA, micropore volume (MPV) and total pore volume (TPV), respectively.

$$SSA \left(\frac{m^2}{g} \right) = 2.28 \times 10^2 - 1.01 \times 10^{-1} MBN + 3.00 \times 10^{-1} IN + 1.05 \times 10^{-4} MBN^2 + 2.00 \times 10^{-4} IN^2 + 9.38 \times 10^{-4} MBN IN \quad (3)$$

$$MPV \left(\frac{cm^3}{g} \right) = 5.06 \times 10^{-2} - 1.00 \times 10^{-3} MBN + 1.55 \times 10^{-4} IN + 7.00 \times 10^{-6} MBN^2 + 1.00 \times 10^{-7} IN^2 - 1.18 \times 10^{-7} MBN IN \quad (4)$$

$$TPV \left(\frac{cm^3}{g} \right) = 1.37 \times 10^{-2} + 1.90 \times 10^{-3} MBN + 1.00 \times 10^{-4} IN \quad (5)$$

Determination of these parameters was done in wet conditions. MBN was determined by the adsorption of methylene blue on the adsorbents and modeled by the Langmuir isotherm model to

determine the maximum adsorption capacity. Iodine number was determined according to the ASTM-D4607-94 method and based upon a three-point isotherm in triplicate experiments [23].

RESULTS AND DISCUSSION

Effect of pH on the adsorption and ionization

Intermolecular and ionic forces such as electrostatic interactions, hydrogen bonding, dipole-dipole and dispersion forces drive physical adsorption [15]. Amongst them, electrostatic forces and hydrogen bonds are known to be the strongest and pH-dependent. The relevance of pH on the adsorption of pollutants resides on the formation of these interactions and therefore the presence of charged atoms on the adsorbent and the pollutants enhances the adsorption. As seen in Figure 1, BY57 is an organic molecule that contains a permanent positive charge (quaternary amine) and highly polar functional groups. This dye is water-soluble, even in the presence of other solutes like inorganic salts.

Recent studies reported that lignocellulosic materials contain hydroxyl, carbonyl and carboxyl groups. These functional groups are responsible for the adsorption of heavy metals [17]. Other biomaterials like chitosan and alginates show similar chemical composition, and have been reported to have a great affinity towards heavy metals and organic compounds [19, 21]. Therefore, potential ion-dipole, hydrogen bonds and dipole-dipole interactions could be expected between the green tea leaves and BY57. Figure 2 shows the pH dependence of the adsorption of BY57. As observed, all the adsorbents maximize the dye removal at different pH values of 4, 6 and 8 for PGT, GT and DGT, respectively. Structurally speaking PGT and GT have different origins, and therefore different industrial treatment and harvesting conditions. However, their dye uptake needs slightly acidic media. Conversely, DGT shows a high adsorption at basic conditions. This might be associated with the chemical treatment green tea undergoes during decaffeination. This process involves the extraction of caffeine with ethyl acetate as a solvent with low polarity. This treatment also carries some important metabolites such as polyphenols. The extraction with ethyl acetate could also cause changes in the structure of the cellulose by dehydration of the leaves and produce internal structure rearrangements that expose more alkaline functional groups to the surface and improve the adsorption at higher

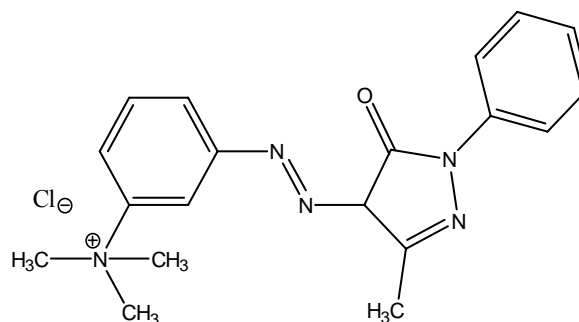


Figure 1. Chemical structure of basic yellow 57 (BY57).

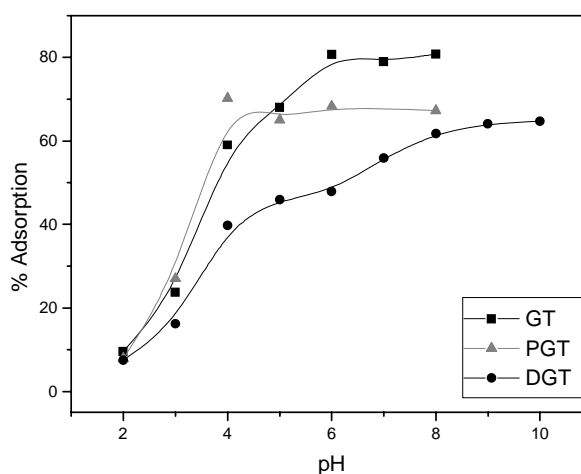


Figure 2. Effect of pH on the adsorption of BY57 onto tea leaves.

pH values. Figure 2 also indicates that all adsorbents have a poor adsorption at low pH (close to 10% removal). This could be explained as a competition of the dye with hydronium ions for the same active sites. As the pH decreases, the concentration of H_3O^+ ions increases and their smaller size favors their adsorption. The small adsorption that is observed at pH 2 and 3 could be explained by the formation of dipoles and hydrogen bonds that could still exist at low pH due to the presence of polar functional groups in BY57 and the hydroxyl groups on the leaves. At higher pH, carboxyl and other ionizable groups get deprotonated and more BY57 could be potentially adsorbed by electrostatic or ion dipole interactions. This last statement is supported by the adsorption plateau that is observed at high pH values.

Adsorbent dose and surface saturation

Scaled up processes take into account the amount of adsorbent that is needed [18]. Industries are in constant search of cost-effective methods that minimize the production of sludge [4, 14, 24]. As observed in Figure 3, GT, PGT and DGT reach their maximum value at 100 mg. No substantial changes are seen at higher doses. A plausible reason for this phenomenon could be the aggregation of leaf particles [16, 21]. Higher doses create a crowded suspension where all leaf particles are so close to each other and form aggregates. These aggregates decrease the total surface area. Under the experimental conditions, 100 mg of adsorbent is appropriate to remove up to 90% of the dye from the solutions.

Initial dye concentration and adsorption isotherms

Figure 4 shows the dye concentration dependence on the adsorption. A given mass of adsorbent has a finite number of adsorption sites that are totally saturated at a particular pollutant concentration. These equilibrium parameters determine the maximum adsorption capacity and the adsorption efficiency for each adsorbent. A variety of isotherm models have been developed, some of which have a theoretical basis and some of empirical nature [4, 24]. The adsorption of BY57 onto tea leaves was analyzed by the conventional models of Langmuir and Freundlich [4, 13]. Equilibrium data was fitted to these theories and important parameters were obtained. Linear regression was used to fit all the data points. Correlation coefficient and p-values were determined to confirm the statistical significance of the results.

Langmuir theory assumes uniform adsorption energy on the surface of the adsorbent, where the migration of the pollutant among neighboring active sites is restricted [4, 13]. The form of the Langmuir isotherm is calculated as follows (Equation 6):

$$q = \frac{q_{max} \times b \times C_{eq}}{1 + b \times C_{eq}} \quad (6)$$

where q_{max} (mg g^{-1}) and b (L mg^{-1}) are the Langmuir constants related to the maximum adsorption capacity and to the adsorption energy,

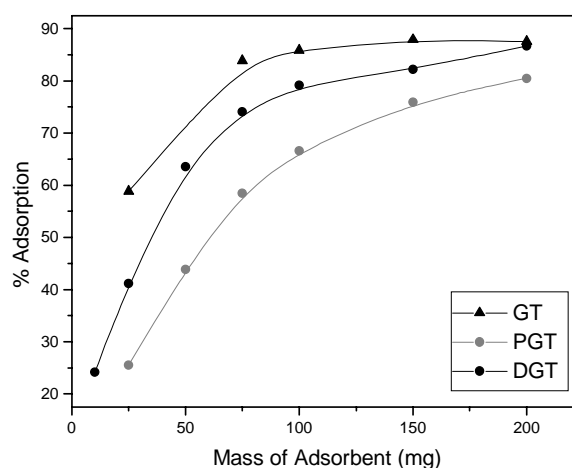


Figure 3. Effect of adsorbent dose on the adsorption of BY57 onto tea leaves.

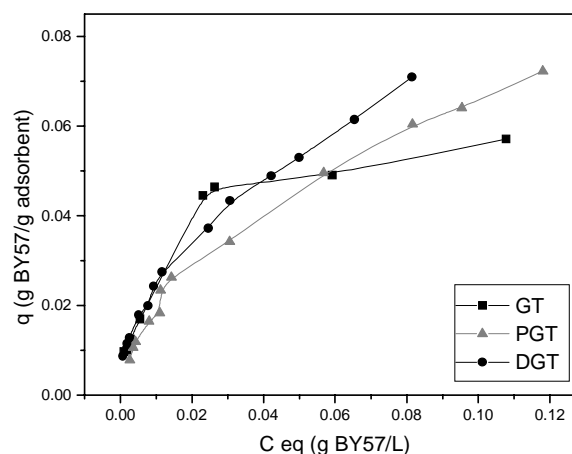


Figure 4. Effect of initial dye concentration on the adsorption of BY57 onto tea leaves.

respectively. The q_{max} constant represents the total number of available adsorption sites for one adsorbent and is commonly used to compare adsorbents based on their ability to remove pollutants. The b constant is also important because it allows us to compare the adsorption efficiency between two different adsorbents under the same experimental conditions. A higher b constant means a higher adsorbent/pollutant affinity. The data was also analyzed by the model of Freundlich that is derived assuming a logarithmic decrease in the enthalpy of adsorption with the increase in the fraction of occupied sites and

based on sorption on heterogeneous surfaces [13, 14, 24]. Freundlich's expression is given by equation (7):

$$q = k \times C_{eq}^{1/n} \quad (7)$$

where k and n are the Freundlich constant, related to the adsorption capacity and the adsorption intensity, respectively. If $n = 1$, then the partition between the two phases are independent of the concentration. If $n > 1$, it indicates a normal adsorption, whereas $n < 1$ suggests cooperative adsorption [15, 25].

Table 1 summarizes the adsorption isotherms for the three adsorbents. According to the results, the maximum adsorption capacities follow the trend: DGT>PGT>GT. However, there are no substantial differences amongst them. On the other hand, the b Langmuir constant indicates a higher adsorbent/dye affinity for GT with almost two-fold the value reported for PGT. Previous studies with other biological adsorbents with cationic dyes report lower or similar adsorption capacities (q_{max}). For example, rice husk only adsorbed 45 mg of crystal violet per gram of adsorbent [26]. Hameed *et al.* [27] studied the adsorption of malachite green onto sawdust, obtaining a q_{max} of 62 mg g⁻¹. Recently, our research group has investigated the adsorption of malachite green onto GT and DGT and found smaller adsorption capacities: 27 and 35 mg g⁻¹, respectively (unpublished work). The n Freundlich constant also indicates that the adsorption of BY57 is favorable for the three adsorbents, but in higher intensity with GT. Finally, statistical significance indicates that Langmuir and Freundlich models fit the adsorption of BY57 onto all the studied adsorbents, suggesting a combined adsorption mechanism.

The importance of this study falls on the use of real industrial wastes like spent tea leaves that are produced in large amounts for the decontamination of dye-containing waters.

Effect of the salinity on the adsorption

Wastewaters are complex solutions where others substances such as common ions are dissolved. Moreover, spills of pollutants in high-salt solutions like seawater are an environmental challenge due to the competition for the adsorption sites [17]. As observed in Figure 5, the adsorbents are negatively affected by the salts. Different salts were used in this study to elucidate the adsorption mechanism of BY57 onto the adsorbents. From the results, Na⁺ ions caused a decrease of 40% on the adsorption. Apparently, the anions did not affect the adsorption, as indicated by Figure 5 (A and B). Conversely, Ca⁺² ions not only caused a 60% decrease in the adsorption, but also reported a faster rate, with concentrations as low as 10 mM of salts. This difference suggests a strong electrostatic competition for active sites as the charge of the interfering cation increases. The adsorbents have a higher affinity towards calcium ions, which displaces BY57 dye. Sodium ions also compete for active sites, but not in the same intensity as calcium ions.

It is also important to highlight that even though the adsorption is decreased to 40% in the presence of salts; a significant adsorption is still observed. Therefore, these adsorbents can be potentially used for the removal of BY57, even in the presence of high salt concentrations.

Resembling real wastewaters with crowding agents

Contaminated wastewaters also contain other nonionic substances like oils, hydrocarbons,

Table 1. Langmuir and Freundlich isotherm constants for the adsorption of BY57 onto green tea leaves.

Adsorbent	Langmuir				Freundlich			
	q_{max} (mg/g)	b (L/mg)	R^2	p	k_F	n	R^2	p
GT	52.08	0.123	0.966	< 0.0001	8.675	2.419	0.989	< 0.0001
PGT	55.79	0.063	0.979	< 0.0001	5.277	1.829	0.984	< 0.0001
DGT	57.14	0.102	0.929	< 0.0001	8.927	2.177	0.989	< 0.0001

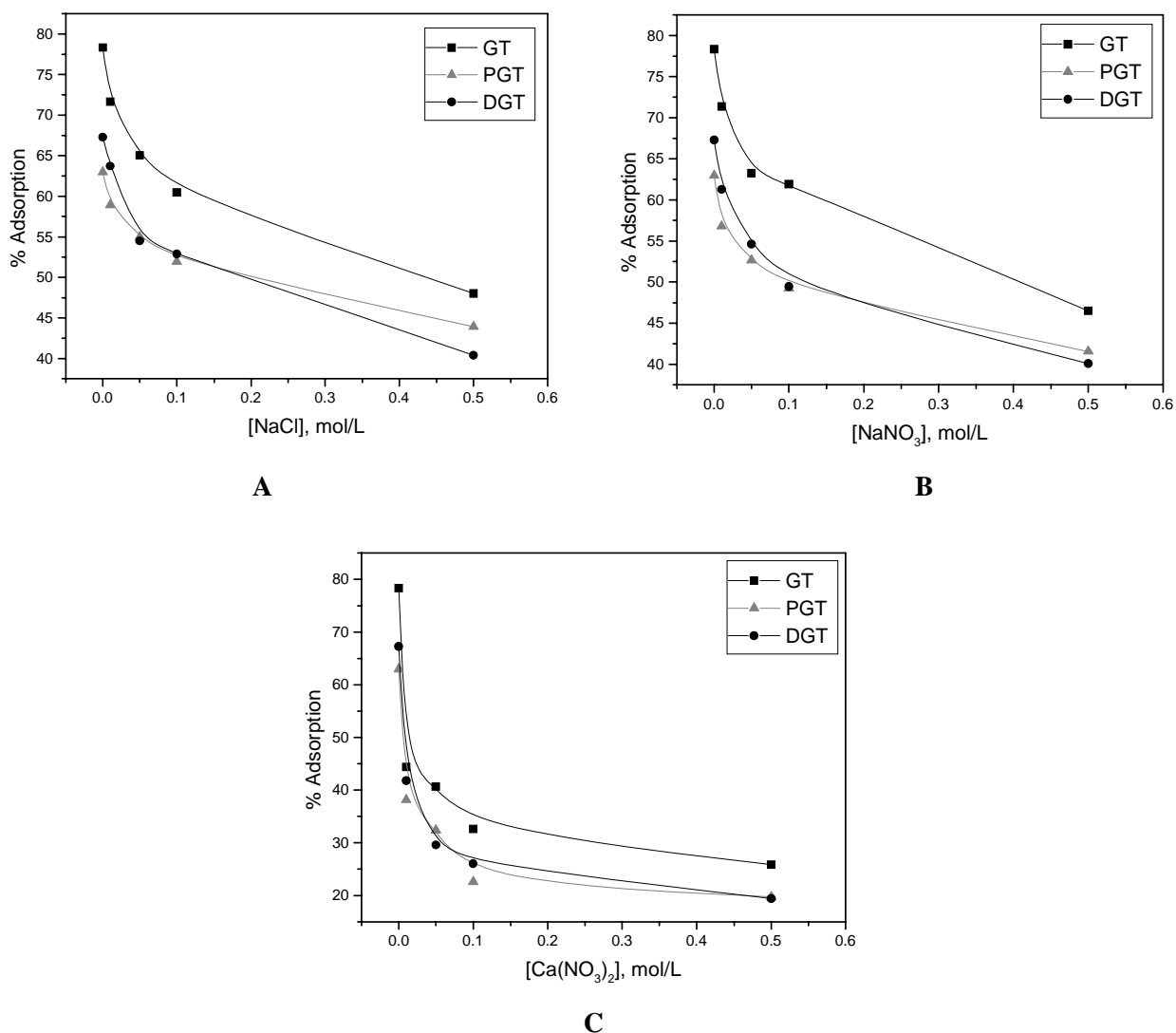


Figure 5. Salinity effect on the adsorption of BY57. NaCl (A), Sodium nitrate (B), and Calcium nitrate (C).

proteins and carbohydrates. Even though, these substances do not compete for the adsorption sites due to changes in the electrostatic environment of the solution, they prevent the correct approach to their respective active centers. Polyethyleneglycol (PEG) is a polyether substance that is highly soluble and increases the density of a solution. Preliminary experiments reported no adsorption capacity for PEG; therefore, all the BY57 adsorption is associated with the green tea as adsorbent. Figure 6 shows a negative effect of crowding agent PEG on the adsorption of BY57. As observed, DGT tolerates better the presence of PEG, followed by PGT and GT. This could be

explained by the distribution of the active sites on the adsorbents. More exposed active sites will not be greatly affected by crowding agents as it is easily accessible. In the case of GT, a more secluded active site is hindered by the presence of PEG.

Presence of heavy metals and competition with larger cations

The salinity effect involved the competition for active sites by relatively small ions like sodium and calcium. However, environmental pollution is normally associated with the presence of heavy metals as prevalent elements due to their

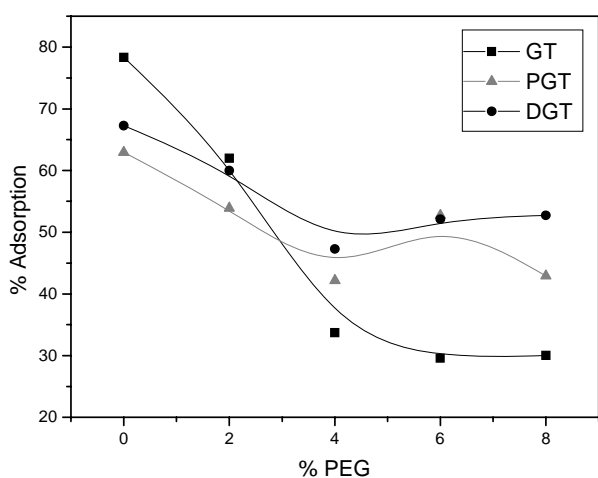


Figure 6. Effect of crowding agent (PEG) on the adsorption of BY57.

non-degradability [4, 13]. Conventional heavy metals include copper, iron, lead and zinc. For this experiment, copper and lead ions were explored due to their prevalence in industrial applications and toxicity. Heavy metals are known for their large ionic radii and their charge density correlated to the mass/charge ratio [16, 17]. As shown in Figure 7, not all the adsorbents respond in the same way to the presence of heavy metals. The presence of copper ions reduces the adsorption percentage of BY57 of PGT to almost 10%, whereas GT and DGT retain the same adsorption under the same experimental conditions. On the other hand, lead and zinc divalent ions have stronger effects on the adsorption of BY57. Lead (II) ion was not used with DGT, because lead nitrate precipitates at the optimum adsorption pH of DGT (pH 8). Zinc (II) ion was used as an alternative heavy metal, and as expected, similar results were obtained when compared to copper (II) ions.

Lead (II) ions show a more negative effect on GT, where the adsorption gets reduced from 78% to 43%. This reduction could be explained by the higher charge density of Pb (II) ions. This heavy metal experiment confirms the predominance of electrostatic interactions in the adsorption of BY57 onto green tea leaves. Same divalent charges of heavy metals show different adsorptions as a consequence of the ionic radii.

Desorption of BY57 by mild co-solvents

This study proposes the use of cost-effective materials such as spent green tea leaves that are daily discarded by industries. An eco-friendly alternative should also be sustainable and do not create side products. One of the most important drawbacks of the commonly used techniques is the generation of sludge or by products that later need to be taken care of and even require an extra expense or have a higher toxicity than the original pollutants [14, 24]. The recyclability of adsorbents is an important factor to consider when choosing the most appropriate material. For this purpose, different low-concentration solutions were used to remove BY57 and recover the adsorbent for consecutive adsorption cycles. These co-solvents were chosen based on their chemical properties including polarity, ionic strength, acidic and alkalinity. Figure 8 shows desorption of BY57 with these co-solvents. The results indicate that a 0.1 M HCl and 30% v/v ethanol are the most effective solutions to recover BY57. Desorption percentages of 75% demonstrate that green tea leaves can be re-used in repetitive cycles. However, HCl seems to be more effective for all the adsorbents. A 0.1 M NaOH solution is also able to recover PGT and DGT. It could be hypothesized that the high optimum pH of DGT could be associated with this response, whereas a different active site in PGT responds to NaOH. The most valuable result from this experiment is the almost negligible desorption with distilled water. This indicates that these green tea wastes can be used in the preparation of filters for large scale purification because clean water cannot get contaminated by the discharge of the adsorbed dye. Decent desorption is also observed with 0.1 M NaCl and $\text{Ca}(\text{NO}_3)_2$, most likely due to adsorbate competition, as demonstrated by the salinity experiments.

Characterization of the Adsorbents

Point zero charge (PZC) is defined as the pH value at which the pH_{final} curve versus $\text{pH}_{\text{initial}}$ intersects the straight line corresponding to $\text{pH}_{\text{initial}} = \text{pH}_{\text{final}}$. This physical parameter is important in biosorption, as it indicates the pH value where the surface charge of a given material is reversed [22]. As observed in Figure 1, the yellow dye BY57 holds a permanent positive charge and

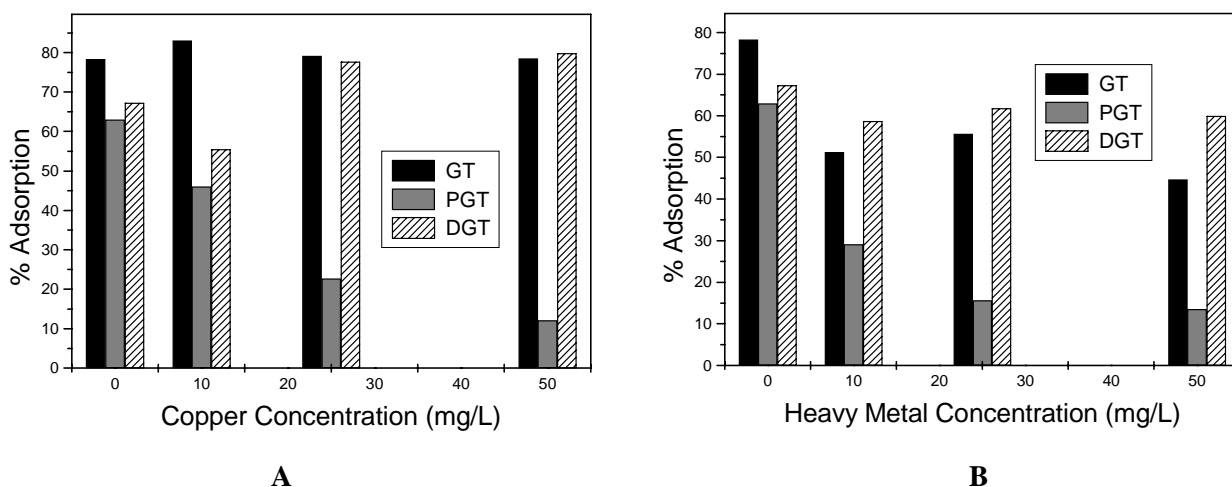


Figure 7. Effect of heavy metals on the adsorption of BY57. Copper (II) effect (A). Lead (II) for GT and PGT and Zinc (II) for DGT (B).

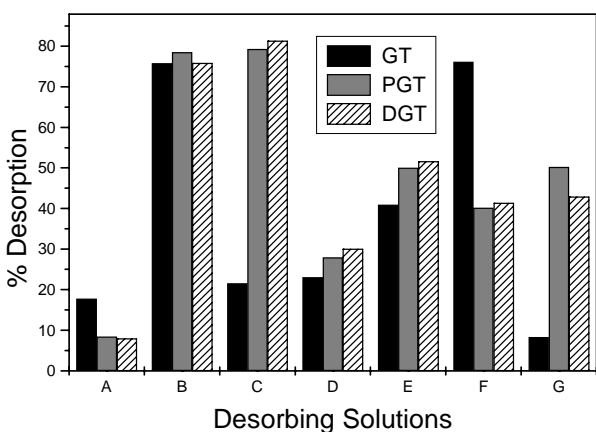


Figure 8. Desorption of BY57 from the adsorbents using: A) Distilled water, B) 0.1M HCl, C) 0.1 M NaOH, D) 0.1 M NaCl, E) 0.1 M Ca(NO₃)₂, F) 30% v/v ethanol, and G) 30% v/v acetone.

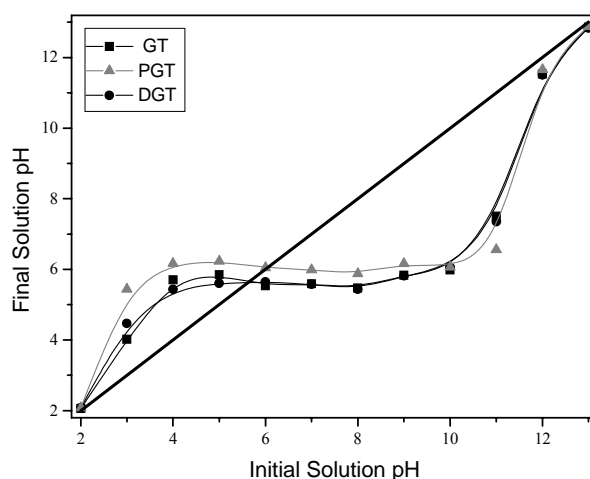


Figure 9. Point zero charge (PZC) determination for the green tea adsorbents.

therefore will have a stronger affinity towards negatively charged surfaces. According to the results observed in Figure 9, all the green tea adsorbents report a PZC around pH 5.5. Therefore all these adsorbents are positively charged at pH values below 5.5.

These observed PZC values agree with the adsorption percentages obtained in the experiments evaluating the effect of pH (Figure 2), where maximum adsorptions are observed at pH 6 and 8 for GT and DGT, respectively. These two

adsorbents optimize their adsorptions when their surfaces are negatively charged and suggest an adsorption mechanism with BY57 that is mainly driven by electrostatic interactions. Apparently, PGT utilizes a different adsorption mechanism as it reports a maximum adsorption at pH as low as 4. At this pH, PGT has a surface predominantly positive, demonstrating an adsorption mostly directed by polar forces. These differences could be explained by the pre-treatment techniques that are utilized in Peru (for PGT) and the US (for GT).

DGT is a separate adsorbent, as it undergoes an organic extraction with ethyl acetate to remove the caffeine. However, it can be concluded that the organic composition of these green tea adsorbents is similar as they all share the same PZC values. The charge reversal can be understood as the ionization of acidic functional groups that produce changes on the surfaces of the adsorbents.

Figure 10 shows the scanning electron micrographs of the three adsorbents and their textural and morphological profiles. As expected,

the three adsorbents show very heterogeneous surfaces with hills and valleys where pollutants can potentially be housed and trapped [15, 16, 21]. These active sites are appropriate as they trap BY57 and maximize the adsorptive forces. As displayed in the micrographs, GT and PGT have similar surfaces. However, DGT shows a more homogeneous and smoother surface. This image is supported by the chemical treatment that DGT undergoes for its decaffeination. We believe that organic extraction eliminates not only caffeine, but also removes lipid and nonpolar protein

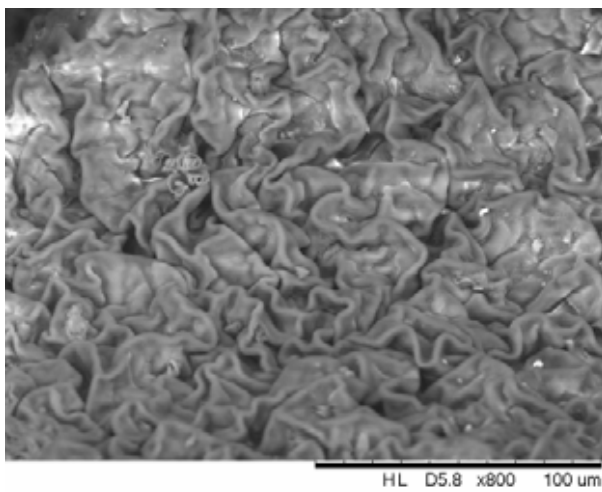
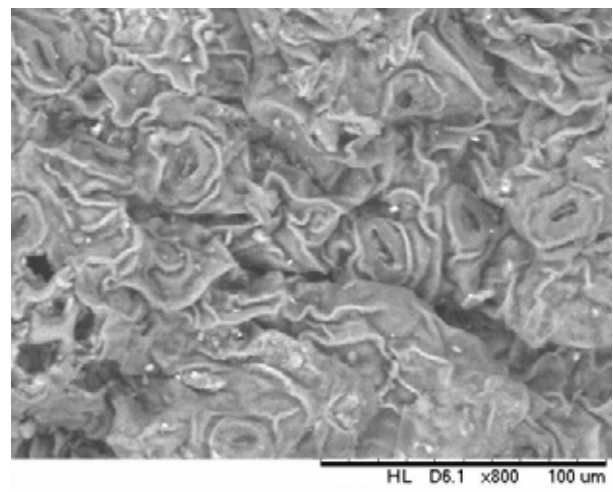
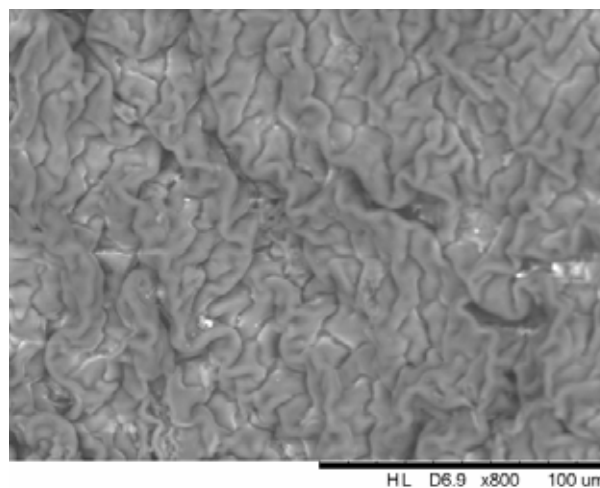
**GT****PGT****DGT**

Figure 10. Scanning electron micrographs of the green tea adsorbents.

Table 2. Specific surface area and porosity analysis for the green tea adsorbents.

Adsorbent	SSA (m ² /g)	MPV (cm ³ /g)	TPV (cm ³ /g)
GT	2,736	0.69	1.11
PGT	221	0.06	0.41
DGT	274	0.22	0.59

structures that increase surface heterogeneity. The elimination of these nonpolar species might also be responsible for the superior adsorption capacity of DGT when compared to GT and PGT, as demonstrated by the Langmuir modeling. As indicated in Table 1, DGT has a q_{\max} of 57 mg g⁻¹ that could be associated with a polar surface of DGT that shows lower repulsion towards the polar BY57.

Finally, Table 2 shows the SSA, MPV and TPV for the adsorbents. Nitrogen adsorption is a well-known technique, carried out in dry conditions, for the determination of specific surface area and porosity [13, 28]. Green teas are mainly formed by fiber and polysaccharides that swell in aqueous solutions; therefore changes in their surface area and porosity are definitely expected. The MBN and IN tests in solution are more reliable area and porosity parameters since they are conducted under the same conditions in which the adsorption occurs [23]. From the results, GT reports the largest SSA, followed by DGT and PGT. These values can be compared to activated carbons [23] that range between 200 and 2,000 m² g⁻¹. DGT and PGT show a smaller area perhaps due to their treatment with organic solvents (by removing part of the natural structure of the leaf or due to the grinding process that was done manually in our lab. Porosity data also shows higher values for GT, followed by DGT and PGT. When comparing area and porosity results to adsorption capacities (Table 1), we can conclude that the adsorption of BY57 is not driven by area and pore availabilities, but mostly by intermolecular forces, that are stronger in DGT, due to its increased polarity by the removal of lipids and waxes. It is hypothesized that adsorption of BY57 onto DGT could be enhanced if part of the structure could be maintained after the solvent extraction.

CONCLUSIONS

Different spent green tea leaves were compared based on the adsorption of BY57 hair dye from aqueous solutions. American (GT), Peruvian (PGT) and Decaffeinated (DGT) green tea wastes were studied under the same experimental conditions to maximize the removal of the dye from aqueous solutions. Equilibrium parameters like initial pH, adsorbent dose, initial dye concentration, salinity, presence of crowing agents and heavy metals were explored in batch experiments at room temperature. Results indicate that adsorption is optimized at pH values of 4, 6 and 8 for PGT, GT and DGT, respectively, with a minimum mass of 100 mg. Isotherm experiments were fitted according to Langmuir and Freundlich theories, indicating an adsorption trend of DGT>PGT>GT with a maximum adsorption capacity of 57 mg g⁻¹. Salinity and presence of crowding agents had a strong negative effect on the adsorption of BY57 onto all the adsorbents. However, adsorption onto DGT and GT resisted the effect of heavy metals as a secondary pollutant. Finally, a diluted solution of HCl was able to desorb almost 80% of the dye from the adsorbents, demonstrating the recyclability of these materials for their use in consecutive cycles. Characterization of the adsorbents included the determination of their point zero charge, PZC, which shows a surface charge reversal at pH 5.5 for all the adsorbents. Scanning electron microscopy elucidated the heterogeneity of the surfaces and confirmed the chemical treatment DGT undergone for its decaffeination. Finally, surface area and porosity indicate that adsorption of BY57 is not driven by area availability, but by intermolecular forces. This study clearly demonstrates the use of these cost-effective and recyclable spent green tea leaves for their application on the removal of hair dyes from solutions. We expect

this study will start a new trend in the development of new eco-friendly alternatives for the decontamination of pollutants from wastewaters.

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CONFLICT OF INTEREST STATEMENT

The authors declare that they have no conflict of interest.

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