Characterization of Powdered Pineapple (*Ananas comosus*) Crown Leaves as Adsorbent for Crystal Violet in Aqueous Solutions

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Abstract. This study investigated the potential of powdered pineapple crown leaves (PCL) as an effective adsorbent for the removal of crystal violet (CV) from aqueous solution using batch and column studies. The PCL was simply washed, dried, and powdered prior to adsorption. FTIR analysis of PCL surface before and after adsorption revealed that hydroxyl and carboxyl functional groups are among the groups responsible for surface bonding with CV. SEM photographs of the adsorbent before and after revealed clumping on the surface of PCL, possibly indicating the sites where CV had been adsorbed. Elemental analyses through XRF revealed that K⁺ ion is a major part of PCL, and this could explain the affinity of CV for PCL through cation-π interactions. Batch adsorption studies were carried out as a function of biosorbent dose and initial dye concentration. The %removal of PC increased as biosorbent dose was increased, but the biosorbent capacity decreased. This was attributed to scattering of CV to more active sites in PCL. Biosorbent capacity increased as the initial dye concentration was increased, while %removal decreased. This was due to the faster saturation of the substrate. For equilibrium studies, Langmuir and Freundlich isotherm models were applied. The equilibrium data fitted well to Langmuir isotherm with a maximum monolayer adsorption capacity of 6.4935 mg/g. The relatively high maximum biosorption capacity coupled with the absence of chemical treatment needed before adsorption makes PCL an effective and sustainable biosorbent for the removal of CV.

1. Introduction

Through the years, inexpensive and stable synthetic dyes were discovered, making natural dyes obsolete. The use of synthetic dyes has become broader that industries manufacturing these synthetic colorants have rapidly increased over the past decades. Substantial amount of residual dyes from industries using synthetic dyes such as textile, paint, pharmaceutical, cosmetics, plastic, food, etc., enter the water systems and the inappropriate discharge of such waste creates nuisance to the aquatic environment. About 17 to 20% of the total industrial water pollution comes from textile processes, where biggest quantities of dye effluents are being discharged [1]. Roughly 10 to 15% dyes during dyeing process are released into the environment, making the effluent strongly colored and aesthetically unpleasant [2]. One of the commonly used dyes is the crystal violet (CV), which can affect the aquatic fauna and flora by decreasing light penetration through the water surface and may be toxic to the aquatic biota due to the presence of aromatics. It is toxic, mutagenic, carcinogenic, and a recalcitrant, because without adequate treatment, it can persist in the environment for a long period of
time causing various health problems. Thus, different technologies arose such as the conventional biological treatment, chemical coagulation, ozonation, oxidation, and adsorption, especially when the removal of these dyes from aqueous effluents become of great importance. Among the said practices, adsorption has been recognized as the superior technique due to its simplicity, high efficiency, ease of operation, and lower cost for decolorization.

For several years, researchers are more interested in utilizing biosorbents due to their great potential in the adsorption process. Some of the commonly used biosorbents are agricultural wastes, because of their abundance in nature, non-toxicity, renewability, and lower cost. Various studies are being conducted to investigate the potential of different agricultural wastes such as fruit husks, seeds, and peels as biosorbents for CV. Coniferous pine bark powder (CPBP) was previously used as an adsorbent for CV, wherein it was found out that at a concentration range of 10 to 50 mg/L, the CV removal increases from 17.5 to 75% [3]. Furthermore, at 0.2 to 1.0 g of adsorbent, the percent dye removal increases with fixed concentration of dye. Avocado kernel seed powder (ASP) was also investigated for the removal of CV from two aqueous effluents. It was found that ASP could remove 92.9% of dye in effluent A and 84.4% in effluent B which shows that ASP could be used for dyes-rich waste water treatment [4]. Another study reported that 96.8 to 98.2% adsorption of CV onto NaOH-modified rice husks (NMRH) as the adsorbent dose increased from 0.5 to 1.0 g/L [5].

Pineapple (Ananas comosus) is a customary and well-known fruit cultivated in the Philippines. According to the Philippine Department of Agriculture, pineapple ranked fourth on the Top Philippine Agricultural Exports based on Freight on Board (FOB) value. Approximately 270 tons per day of solid pineapple fruit wastes are produced by Del Monte. A previous characterization has reported that pineapple leaf has 70 to 82% holocellulose, 5 to 12% lignin and 1.1% ash, which makes it a good adsorbent for cationic dyes like CV because in aqueous solutions, cellulose and lignin release hydrogen ions forming negatively charged surface area [6]. With this amount of generated wastes including pineapple peels, stems and leaves, utilization of these would be highly recommended. This study aims to investigate the potential of pineapple crown leaves as a biosorbent for CV from aqueous solutions using batch studies. The surface and chemical characteristics of the adsorbent were determined to analyze its efficacy in adsorbing CV. The effects of biosorbent dose and initial dye concentration employing batch adsorption were evaluated. Moreover, biosorption behavior using Langmuir and Freundlich models were examined to understand the biosorption mechanism of CV onto pineapple crown leaves.

2. Methodology

2.1. Materials and equipment

The crystal violet (CV) in pure powdered form was of commercial quality (C.I. 42555, MF: C_{25}H_{30}ClN_{3}, MW: 408) and was not further purified. A stock solution (1000 mg/L) was initially prepared with distilled water, and different concentrations of the solutions (20 mg/L, 70 mg/L, and 120 mg/L) were prepared by dilution. The pH of solution was adjusted to a pH of 8 by adding appropriate amounts of 0.1 M HCl and 0.1 M NaOH solutions. Pineapple crown leaves were collected from Nasugbu Public Market, Philippines. The crown leaves were washed several times with tap water to remove any dirt, dust, and unnecessary substances. The washed crown leaves were oven dried at a temperature of 90 ± 1°C until constant weight, ground to a powder and sieved using electronic sieve shaker to a constant particle size of 100 mesh screen to serve as the biosorbent. The FTIR spectra (Nicolet 6700 FTIR) of powdered PCL before and after adsorption were recorded to determine the main functional groups present in the powdered PCL that may be the possible sites for binding. Scanning electron microscopy (JSM-5310 SEM) analysis was done before and after biosorption to obtain information which includes the surface morphology of the PCL. Also, elemental analysis was performed using Panalytical Epsilon 5 X-ray Fluorescence (XRF) System, which provides the elemental composition of the PCL.
2.2. Batch biosorption studies

Batch studies were conducted in a set of 250 mL Erlenmeyer flasks containing 100 mL aliquot of CV standard solutions. The flasks were agitated in a water bath shaker at 150 rpm and at a temperature of 30°C. After a contact time of 180 minutes (3 hours), the solution was filtered and the filter cake was dried for further analysis while the filtrate of each solutions were examined using UV-VIS spectrophotometer to determine residual dye concentration. 

The effect of initial dye concentration on the uptake of CV on powdered PCL was examined under sorbent dosage of 2.0 g. On the other hand, the effect of biosorbent dose was analyzed under an initial dye concentration of 50 mg/L.

Using the initial dye concentrations and the determined equilibrium dye concentrations, the amount of dye absorbed per gram of biosorbent was calculated using Equation (1).

\[ q_e = \frac{(C_i - C_e)V}{m} \]  
\[ \% \text{removal} = \frac{(C_i - C_e)}{C_i} \times 100\% \]  

where \( C_i \) is the initial dye concentration (mg/L), \( C_e \) is the equilibrium dye concentration in solution (mg/L), \( V \) is the volume of the solution (L), and \( m \) is the mass of the biosorbent (g). Moreover, the percent removal of the dye from the solution was calculated using Equation (2).

2.3. Biosorption isotherms

The equilibrium data were fitted to Langmuir and Freundlich isotherm models, which are expressed as Equations (3) and (4), respectively:

\[ \frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_Lq_m} \]  
\[ \log q_e = \log K_F + \frac{1}{n} \log C_e \]

where \( q_e \) and \( C_e \) are solid and liquid phase concentration of adsorbate at equilibrium (mg/L), respectively, \( q_m \) is the maximum adsorption capacity (mg/g), \( K_L \) is the Langmuir adsorption equilibrium constant (L/mg), \( K_F \) is the Freundlich constant related to sorption capacity (mg/g)(L/g)^\(1/n\) and \( n \) is the heterogeneity factor which gives the measure of biosorption favorability.

3. Results and discussion

3.1. Biosorbent characterization

Pineapple crown leaves mainly contain holocellulose, lignin and ash [6]. The FTIR spectra of powdered PCL prior and after adsorption were obtained to identify the involved functional groups for biosorption. Figure 1 shows the spectrum of powdered PCL before and after adsorption. After adsorption, shifting of peaks were observed. Through this analysis, the different functional groups that may be involved in the biosorption process of CV onto powdered PCL were determined. Table 1 shows the comparison of band positions of the functional groups in powdered PCL before and after CV adsorption.

In Table 1, the band positions that shifted significantly were the O-H band at 3405.62 cm\(^{-1}\) (shifted to 3415.67 cm\(^{-1}\)), C = O stretching of carboxylic acid at 1631.41 cm\(^{-1}\) (shifted to 1641.90 cm\(^{-1}\)), -CH\(_2\) and -CH\(_3\) twisting at 1400.56 cm\(^{-1}\) (shifted to 1397.40 cm\(^{-1}\)), C-O stretching of carboxylic acid at 1316.27 cm\(^{-1}\) (shifted to 1320.96 cm\(^{-1}\)), and C-N stretching at 1152.54 cm\(^{-1}\) (shifted to 1160.37 cm\(^{-1}\)). With these observations, it can be said that O-H, -CH\(_2\) and -CH\(_3\), C-N, and -COOH groups can be the major bonding sites on powdered PCL. Other groups also shifted after adsorption minimally (C-H, and C-O), which indicated their participation in the binding process [7].
Figure 1. FTIR spectra of powdered PCL before (●) and after adsorption (●).

Table 1. Comparison of Band Positions of Powdered PCL Functional Groups Before and After CV Adsorption

| Assignment                          | Wavelength Number (cm$^{-1}$) | Before Adsorption | After Adsorption |
|-------------------------------------|-------------------------------|-------------------|------------------|
| O-H stretching                      | 3405.62                       | 3415.67           |
| C-H stretching                      | 2923.15                       | 2922.02           |
| C-O stretching                      | 1733.82                       | 1734.42           |
| C = O stretching                    | 1631.41                       | 1641.90           |
| C = C                               | 1514.56                       | 1514.16           |
| -CH$_2$ and -CH$_3$ twisting        | 1400.56                       | 1397.40           |
| C-O stretching                      | 1316.27                       | 1320.96           |
| -NO$_2$ aromatic nitro compound    | 1251.18                       | 1251.19           |
| C-N stretching                      | 1152.54                       | 1160.37           |
| C-O stretching                      | 1058.08                       | 1059.62           |

The surface morphology of the adsorbent was examined by SEM analysis and are presented in Figure 2. Before biosorption, the biosorbent was characterized by an irregular surface. In addition, the surface of the pineapple leaves appeared to be covered with foreign embodiment with minimal visible porous structures. Nevertheless, after dye uptake, porous structures in the surface were covered with uniform layer as can be seen from Figure 4, which indicated the binding of CV.

To identify the elemental content on powdered PCL, elemental analysis was performed. Table 2 shows the results of analysis by X-ray Fluorescence (XRF) Spectrometry. The major, minor, and sub-minor components of powdered PCL are listed on the table.
Figure 2. SEM micrograph of powdered PCL (a) before and (b) after adsorption with CV

Table 2. Elemental Analysis of Powdered PCL

| Components            | Composition                              |
|-----------------------|------------------------------------------|
| Major (>10 %)         | K⁺, Mg²⁺, Al³⁺, Si⁴⁺, P³⁻, S²⁻, Cl⁻, Ca²⁺, Mn²⁺, Fe⁵⁺, Rb⁺ |
| Minor (0.1 to 10 %)   | Ti⁺, Ni²⁺, Cu²⁺, Zn²⁺, Sr²⁺, Zr⁺, Br⁻    |
| Sub-minor (<0.1 % or ppm range) |                                                  |

Based on the structure of CV, a cationic dye, it carries a net positive charge and can undergo a sorption mechanism by means of ion exchange. However, the positive charge of CV can be delocalized and can be found on the outer nitrogen or on the central carbon. Aside from the ion exchange mechanism, which can be hindered because of the bulky structure of CV, other possible mechanisms are cation-π interactions between the cation present in the adsorbent like K⁺ and the electron rich surface of CV, and n-π interactions between the deprotonated carboxyl groups of the sorbent and the aromatic ring of the CV. In addition to these are aromatic-aromatic and C-H-π interactions which are also possible because of the structure of CV and the powdered PCL. Since the results in the FTIR analysis showed that the band positions were shifted minimally, most likely, ion exchange did not occur and cation-π interaction may be the possible mechanism because of the high percentage of K⁺ in powdered PCL and the characteristic of CV having electron rich surface.

3.2. Batch biosorption studies

3.2.1. Effect of initial dye concentration

Figure 3 shows the dependence of the adsorptive uptake on the initial dye concentration. The results show that the adsorption capacity increased from an average of 0.98 mg/g to 5.27 mg/g with the increase in initial dye concentration from 20 to 120 mg/L. The behavior depicted from the plot is the result of the increase in driving force provided by the increase in concentration gradient. With this, all mass transfer resistances between the dye molecules are minimized leading to an increased equilibrium uptake capacity [5]. In addition, the increase in concentration driving force accelerates probable collision between metal ions and sorbents, thus resulting in higher uptake of CV. The results showed that the higher the concentration of CV in the solution, the more efficient the bioprocess is because the active sites of the biosorbent are surrounded by much more CV ions. However, Figure 3b shows a decreasing trend for the % dye removal. This behavior is due to the fact that at lower CV concentration, the percentage uptake was higher due to larger surface area of adsorbent being available for adsorption. When the concentration of CV is increased, the percentage removal decreased since the available sites for adsorption became less due to saturation of adsorption sites. Hence, the decrease in biosorption efficiency with the increase in dye concentration [8].
3.2.2. Effect of biosorbent dosage

The impact of biosorbent dosage on %dye removal and adsorption capacity at an initial dye concentration of 50 mg/L and the dependence of biosorption capacity on the biosorbent dose can be observed in Figure 4.

Figure 4. Effect of biosorbent dose on (a) %dye removal and (b) biosorbent capacity (mg/g) of CV on powdered PCL

The percent dye removal increases with the increase of dosage. The increase in the %dye removal is contributed by the substantial build-up in the biosorbent area resulting to the availability of more binding sites [5]. Maximum percentage of dye removal is observed at a sorbent dosage of 2.0 g. It can be deduced from Figure 4a that a dosage more than 2.0 g does not significantly change the biosorption yield. This insignificant change is because of electrostatic interactions and interference of binding site which have an influence to reduce adsorbent densities. Hence, a sorption dosage of 2.0 g established an equilibrium relationship between the dye molecules on the biosorbent and in the solution. Same observations were also reported by previous studies [5][9].

Figure 4b, on the other hand, shows exactly the opposite trend, whereas, as the sorbent dosage is increased, its capacity decreases. Apparently, the adsorbent capacity of the biosorbent was not fully utilized at a higher sorbent dosage [10]. Therefore, the adsorption capacity decreases as the dosage is increased.

3.2.3. Equilibrium sorption studies

Langmuir isotherm is based on three assumptions which include maximum adsorption corresponds to a saturated monolayer of adsorbate molecules on the surface of the adsorbent, constant energy of adsorption, and there is no transmigration of adsorbent in the surface’s plane. Langmuir model can be expressed in equation 3 in its linearized form. A $C_e/q_e$ against $C_e$ plot was constructed for which the slope is equal to $1/q_m$ and intercept equal to $(q_mK_L)^{-1}$. Figure 5a shows the Langmuir plot of adsorption of CV onto powdered PCL.
Figure 5. Linearized (a) Langmuir and (b) Freundlich adsorption isotherms for CV onto powdered PCL. Points represent experimental data while lines represent fitted line.

From the equation of the line, the maximum biosorption capacity was found to be 6.4935 mg/g. Moreover, the Langmuir isotherm constant was also computed from the intercept. This constant, $K_L$, is related to free energy of adsorption and was found to be 0.3277 L/mg.

An assumption of Freundlich isotherm is that the type of biosorption is multilayer and the surface is heterogeneous. Aside from that, the distribution of heat of biosorption over the surface is not uniform. Equation 4 is the linearized form of the Freundlich model. A plot of $\log q_e$ versus $\log C_e$ was constructed where the slope of the line is equal to $1/n$, where $n$ is the heterogeneity factor, giving the measure of biosorption favorability, and the intercept represents $K_F$, which has a relation to sorption capacity.

Figure 5b shows the Freundlich isotherm plot. A line was also formed, and using this equation, the parameters $K_F$ and $n$ were calculated and found out to be 1.6255 (mg/g)(L/g)$^{1/n}$ and 1.9920, respectively.

Values of $n$ ranging from 1 to 10 indicates favorable sorption process [11]. Moreover, smaller values of $1/n$ indicates greater heterogeneity. This suggested that the sorption process of CV onto powdered PCL was favorable because of the obtained value of $n$. To summarize, parameters and correlation coefficients acquired from the plots of Langmuir, and Freundlich isotherm models are listed in Table 3.

| Parameter | Value | Parameter | Value |
|-----------|-------|-----------|-------|
| $q_m$ (mg/g) | 6.4935 | $K_F$(mg/g)(L/g)$^{1/n}$ | 1.6255 |
| $K_L$(L/mg) | 0.3277 | $n$ | 1.9920 |
| $R^2$ | 0.9901 | $R^2$ | 0.9870 |

By looking at the correlation coefficient of each isotherm model, the Langmuir isotherm ($R^2 = 0.9901$) gave a better fit for the sorption process than the Freundlich isotherm ($R^2 = 0.9870$). With this observation, it can be said that CV was adsorbed onto powdered PCL’s surface by means of monolayer pattern. This can be also observed on the SEM micrographs of powdered PCL after adsorption, in which its surface was uniformly covered. However, the $R^2$ obtained in the Freundlich model was also high suggesting that not only monolayer adsorption occurred, but also multilayer adsorption. This conformed to the small value of $1/n$ of 0.502. This model also indicates that the surface of the adsorbent is heterogeneous. This can be supported by the FTIR analysis, in which it was found out that there were several functional groups present in the powdered PCL.

A literature survey was conducted to compare the performance of powdered PCL as biosorbent for CV with other reported adsorbents (Table 4). Powdered PCL registered the highest biosorption capacity compared to other cellulosic adsorbent materials. Together with its abundance and lack of end-usefulness, PCL has a big potential to be used as a simple, low-cost, yet effective adsorbent for CV contamination.
Table 4. Literature values of $q_m$ for CV on different sorbents

| Sorbent                   | Maximum Biosorption Capacity (mg/g) | Reference |
|---------------------------|-------------------------------------|-----------|
| Coir pith                 | 2.56                                 | [12]      |
| Sugarcane dust            | 3.80                                 | [13]      |
| Calotropis procera leaf   | 4.14                                 | [14]      |
| Sagaru sawdust            | 4.25                                 | [15]      |
| Pineapple crown leaves    | 6.49                                 | This study|

4. Conclusion
The potential of powdered pineapple crown leaves as a biosorbent for crystal violet in aqueous solution was investigated. Based on the batch studies, the higher the concentration of CV in the solution, the more efficient the bioprocess, because the active sites of the biosorbent are surrounded by much more CV ions. However, the increase in the CV concentration resulted to a decrease in % dye removal since the available sites for adsorption became less due to saturation of adsorption sites. On the other hand, an increase in the sorbent dose resulted to an increase in % dye removal but the biosorption capacity decreases since it is not fully utilized at high sorbent dosages. Biosorption behavior was also examined, and was found that the type of adsorption occurred was monolayer on a homogeneous surface. This was concluded because the experimental equilibrium data fitted well to the Langmuir isotherm model. The estimated maximum adsorption capacity was 6.4935 mg/g. However, based also on the $R^2$ obtained using the Freundlich model, which was high, multilayer adsorption was also present.

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