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Research Article

Factors Affecting the Biosorption of 2-Chlorophenol Using Spent Tea Leaf Wastes as Adsorbent

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Abstract

The presence of phenolic compounds is often underestimated in environmental protection. However, the combination of their prevalence in industrial runoffs and negative impact in human health and ecology is a top-priority concern. Chamomile (CM), green tea (GT) and peppermint (PM) spent tea leaves were used as potential adsorbents of 2-chlorophenol (2-CP) from aqueous solutions in batch conditions at room temperature. Equilibrium parameters such as pH and adsorbent dose were studied to maximize the uptake of 2-CP. Moreover, the effect of interfering inorganic and organic substances on the adsorption was studied. Results indicate that the adsorption of 2-CP is strongly affected by the pH, showing its lowest and highest values at pH 6 (21%) and pH 9 (90%) for CM. Adsorption of 2-CP followed the trend: CM (80%) > PM (58%) > GT (47%) and was slightly affected by the presence of Cu (II) and Pb(II) metal ions and polyethyleneglycol as ionic and covalent interfering substances, respectively. According to the results, solid wastes such as spent tea leaves have not only proven to be potential 2-CP adsorbents, but also inexpensive and biodegradable materials.

Keywords: 2-Chlorophenol; Adsorption; Bioremediation; Tea Leaf Wastes

Introduction

Over the past few decades, water bodies have been exposed to synthetic chemicals, such as plasticizers, insecticides, herbicides, and fungicides. The discharge of these substances into the environment (through industrial, agricultural, medical and domestic activities) has produced significant eco-toxicological problems with serious consequences for all living organisms. One group of these toxic molecules is chlorophenols, which have been classified as major pollutants by the US Environmental Protection Agency (EPA) [1].

Chlorophenols (CPs) pose serious environmental hazard due to their prevalence in industrial activities (i.e. bactericides, insecticides, herbicides and fungicides). They are found in wastewater, industrial runoffs, and underground water. Other sources of contamination by chlorophenols are hazardous waste disposal sites, storage tanks, and public landfills. Pharmaceuticals also use chlorophenols as potent antiseptic, contributing to the pollution of water resources. Moreover, previous studies have demonstrated that chlorophenolic compounds are also formed during the combustion of organic matters [2,3].

Chlorophenols is the name of a big family of compounds, including mono-, di-, tri-, tetra-, and penta-chlorinated phenols. The 2-chlorophenol (2-CP), 2,4-dichlorophenol (2,4-DCP) and 2,4,6-trichlorophenol (2,4,6-TCP) are commonly present as ingredients for standard procedures for manufacturing companies. A larger industry involves the application of CPs for the production of more potent pesticides. For example, chlorobenzenes and chlorinated cyclohexenes are synthetized from CPs [2,3].

From the toxicological point of view, it has been proven that different classes of CPs can cause liver, kidney and DNA damage in the long term [4-6]. Likewise, the relationship between cancer and exposure to CPs and related chlorophenoxy acid herbicides has been examined in a number of epidemiologic studies [5]. One of them is the Hodgkin's lymphoma disease, where the body produces abnormal type of white blood cells [7]. In addition to this disease, clinical studies indicate that exposure to CPs is also associated with tumors, sarcoma and lung cancer [7]. Hence, CPs have been identified as hazardous substances.

Considering CPs are commonly present in pesticides, scientists have realized that our ecosystem has to be protected from these chemicals that contaminate potable [4,8,9]. Unfortunately, soil is not acting as a protective filter. Thus pesticides can reach water- bearing aquifers below the ground to crop fields, seepage of contaminated surface, accidental spills, leaks, and improper disposal. It takes decades for chemical effects to become apparent in the ground water, which makes it important to include a time lag between the application of pesticides and fertilizers. The land and shallow ground water will improve before the deep ground water does. This problem is also observed in the water recycling systems in industries that use CPs and any toxic organic compound [3,10-12].

Wastewater treatment techniques of CPs from industrial sources include processes such as biological degradation, oxidation, adsorption on activated carbon, membrane filtration, electro-dialysis and reverse osmosis, among others [13-15]. Although these methods are widely used and can be applied for large volumes CPs in contaminated water, nevertheless they decrease their removal efficiency at low pollutant concentrations in solution and they demand high cost of operation, energy and workforce [14].

Moreover, many countries agree with the fact that water recycling is a top-priority research. Our natural water resources are depleting, partially due to the constant growth of world population [13,14]. As a result, water recycling processes need more innovative techniques, which should be cost-effective and easily applicable.

Bioremediation, as a field of biotechnology, proposes alternative and eco-friendly solutions for the decontamination of toxic inorganic and organic pollutants from wastewaters. Different materials, such as marine algae, fruit peels, and polymeric hydrogels have been utilized for the elimination of heavy metals [16,17], dyes [18,19] and antibiotics [20] with positive results. The use of these biological materials is supported by the high affinity between natural polysaccharides and the pollutants by physical adsorption. Functional groups such as hydroxyl, carboxyl, amino and carbonyl contain lone pairs of electrons that serve as active sites for the formation of dipole, hydrogen bonding, ion-dipole and electrostatic interaction with these toxic substances [16,17,20]. On the other hand, cellulose is the most abundant natural polysaccharide in the planet and cannot be used for human consumption due to its structure and because humans lack of an enzyme that is needed for its catabolism [8]. Spent tea leaves are mainly composed of cellulose and have been studied as adsorbents for the removal of metals and organic compounds [21,22]. As indicated in these studies, spent tea leaves are solid industrial wastes of tea-based factories such as Snapple, Nestea, and Arizona that produce large amounts of these wastes that need to be disposed of. Most likely, these tea leaves end up as landfill without any beneficial use [22].

In this research, spent tea leaves of chamomile (CM), green tea (GT) and peppermint (PM) were used as a low-cost adsorbent for the removal of 2-CP from aqueous solutions. The potential of these biomaterials for the elimination of 2-CP was tested with different experimental conditions to determine the best adsorption parameters that maximize the uptake of 2-CP. A broader impact of this study also includes the establishment of a new ecological mindset that envisions the use of solid industrial wastes for the remediation of contaminated waters and a better understanding about the negative impact of CPs in the environment.

Materials and methods

Reagents and solutions

A stock solution of 1000 mg/L of 2-CP (ACS Grade, ACROS Organics) was prepared with deionized water. Solution was kept in a glass container and covered with aluminum foil to prevent photodegradation. For the adsorption experiments, 2-CP solutions were made by dilution of this stock solution with deionized water to reach the desired concentration. The stock solution was always maintained under refrigeration and its concentration was periodically determined to assure no degradation of the pollutant.

Preparation of the adsorbents

Spent tea leaves of chamomile (CM), green tea (GT) and peppermint (PM) were prepared by a methodology that has previously used [21,22]. In brief, tea bags were purchased from a local market and treated in sequential rinses of boiling distilled water to remove color, taste and smell. Final rinses were conducted with deionized water to eliminate any salt and water soluble impurities. Then, the spent tea bags were oven-dried overnight at a temperature not higher than 60 ºC to prevent any chemical or thermal decomposition. Finally, the dry tea bags were opened and stocked in plastic containers. No organic decomposition was observed in any of the adsorbents over the time. These adsorbents were stored at room temperature and use for the batch experiments.

Adsorption experiments

The uptake of 2-CP on spent tea leaves was studied in discontinuous experiments in triplicates using amber glass vials to prevent photo-degradation of the phenolic compound. Experiments were carried at room temperature under orbital agitation of 250 rpm (revolutions per minute) in an incubator shaker (New Brunswick Scientific, Model C24). Preliminary experiments indicated that less than 24 needed to reach the equilibrium. For the discontinuous experiments, a given mass ranging from 25 to 250 mg of adsorbent, were placed in contact with 30 mL of solutions of variable concentrations 2-CP (between 50 and 100 mg/L). Different equilibrium parameters were considered including initial pH (ranging from 2 to 10), mass of adsorbent (ranging from 25 to 250 mg), and the presence of heavy metal ions and surfactants as ionic and covalent competitors. Lead (II) and copper (II) ions were used as heavy metals ions in concentrations between 0 and 100 mg/L) and polyethylene glycol (PEG) as a surfactant in a concentration range between 0 and 10% m/v. Vials were sealed with parafilm to avoid leaks. Upon equilibrium, the adsorption of 2-CP on CM, GT and PM was determined by comparison of the initial and final 2-CP concentrations. These concentrations were determined by UV-vis spectrophotometry at wavelengths of 510 nm, following the methods of Gales and Booth [23]. This method involves the reaction of 4-aminoantipyrine with potassium ferricyanide and phenolic compounds in a buffer at pH 8. These analyses were carried out using an automatized microplate reader (Synergy4, Biotek).

Data analysis

The amount of adsorbed 2-CP onto spent tea leaf samples was expressed as adsorption percentage and calculated as shown in Equation (1):

$$\%ADS = \frac{(C_i - C_{eq}) * 100}{Ci} \qquad (1)$$

where C_i and C_{eq} are the initial and final concentrations of 2-CP in mg/L, respectively. Data analysis and plotting was conducted using the statistical software Origin v8.0. All the experimental results shown in the graphs have errors ≤ 3.5%.

Results and discussion

pH effect

Industrial wastewaters are typically acidic; therefore finding the most appropriate adsorbents has always been a challenge. As shown in Figure 1, pH plays an important role in the adsorption of heavy metals [16,17,21] and organic pollutants [17,18,22]. According to the results, pH has a very strong effect on adsorption, as it is high at low pH, then decreases at mildly acidic media and displays its highest value at high pH values. The role of pH resides on the ionization of functional groups that are present on the surface of adsorbents and on the deprotonation of 2-CP. The pKa value for 2-CP is 8.56 [24], meaning that at solution pH values of 8.56 and higher, 2-CP becomes negatively charged as a phenoxide ion. On the other hand, acidic functional groups on the adsorbents (mainly carboxylic acids) have a pKa around 4 [8], involving that the surface of the adsorbent becomes negatively charged at pH higher than 4. These pKa values agree with the results observed in Figure 1 for the effect of pH on the adsorption of 2-CP. As expected, at low pH values, both adsorbent and 2-CP are in their neutral form and therefore interaction forces like hydrogen bonding, dipole and dispersion are formed and a positive adsorption is observed, reaching values as high as 63% with GT. As the solution pH increases, it approaches the pKa of the adsorbent and the adsorption decreases to its lowest value. At this pH medium, the adsorbent is negatively charged whereas 2-CP remains neutral.

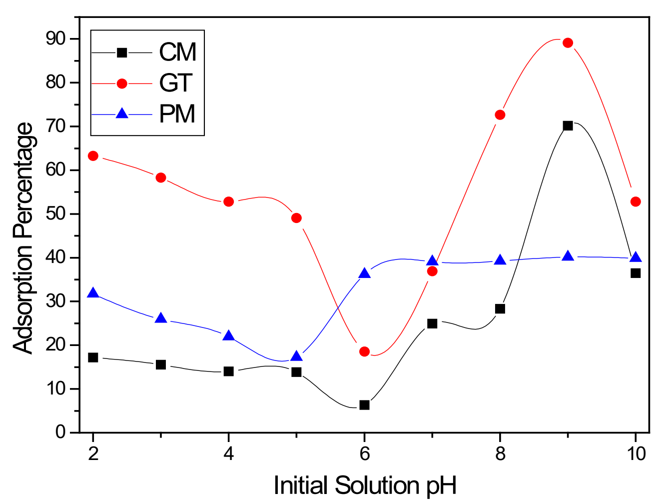

Figure1: Effect of the solution initial pH on the adsorption of 2-CP onto tea leaf samples.

Apparently, this adsorbent/adsorbate combination does not produce a favorable adsorption. As the pH increases towards the pKa value of 2-CP, the adsorption percentage spikes up to 90% with GT at pH 9, and finally slightly decreases at a pH value of 10. This behavior could be explained by the fact that

2-CP becomes negatively charged and is able to form more stable hydrogen bonds with the hydroxyl groups of the surface of the adsorbents. Then, adsorption slightly decreases at pH 10 for all the adsorbents. A plausible explanation for this decrease could be the increase of hydroxide ions in solutions that compete with phenoxide ions for active sites on the adsorbent. Higher pH values were not studied because wastewaters, in general, are not very basic. Finally, the pH effect experiment in indicates that the adsorption percentage follows the trend: GT>CM>PM, with values of 90%, 75% and 43%, respectively.

Effect of the adsorbent mass

An optimum and sustainable bioremediation process involves the use of minimum biomass to achieve the highest elimination of 2-CP. This will not only reduce transportation and operational costs, but also contribute to prepare scaled-up processes in continuous-flow experiments (i.e. column adsorption). As shown in Figure 2, nearly 80% of 2- CP was adsorbed with a mass of 150 mg of CM. Conversely, GT and PM display a decrease in the adsorption at increasing adsorbent doses. This behavior has already been observed in previous adsorption studies [16-22]. According to these reports, the decrease in adsorption is associated with the formation of adsorbent aggregates in solution that reduce the specific surface area and the number of available active sites. From the results, CM does not aggregate in solution, and therefore higher adsorbent masses provide more active sites for the adsorption of 2-CP. This conclusion was experimentally corroborated during the adsorption test, where CM was well-dispersed in the glass vials. This adsorbent aggregation could be produced by the decrease in polarity of the solution with 2-CP. CM has a lower density, when compared with GT and PM, and therefore is able to disperse in the solution even at higher adsorbent doses.

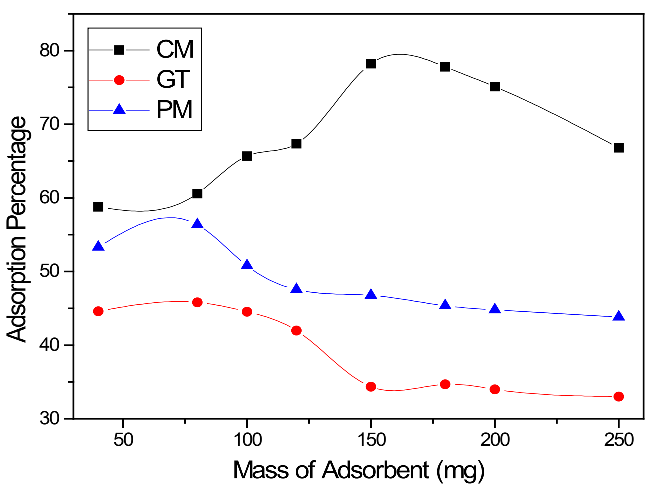

Figure 2: Effect of the mass of the adsorbent on the adsorption of 2-CP.

Effect of the presence of surfactant

One of the most important challenges in wastewater bioremediation is the complexity of solutions, which are not only composed of the pollutants, but also of other substances that prevent an efficient adsorption. For example, soluble salts and detergents are innocuous or have low impact in ecology; however they are able to bind to the adsorbents, occupying active sites that are meant to be used in the elimination of pollutants. In this experiment, 2-CP solution were also mixed with PEG at different concentrations. PEG is a water-soluble polymer that consists of long chains of poly-ethers. Preliminary tests have demonstrated that PEG does not interact with 2-CP, and does not get adsorbed onto the tea leaf samples. The purpose of PEG in solution is to mimic soluble covalent substances in solution to prevent the adsorption of 2-CP. According to the results in Figure 3, the adsorption percentage increases at low PEG concentrations for all the adsorbents. However, at higher PEG concentrations, 2-CP is severely affected. This phenomena could be explained by the increase in solubility of 2-CP in PEG. This surfactant creates a more hydrophobic environment that promotes the total dissolution of 2-CP (perhaps by stabilizing the phenoxide ions that has a non-polar aromatic ring). Conversely, higher PEG concentrations cause the opposite effect. PEG does increase the dissolution of 2-CP in solution, but at these PEG doses, the surfactant blocks the access of 2-CP to the active sites and decreases the adsorption of the pollutants. This blocking effect is not observed at low PEG levels, due to the predominance of 2-CP in solution.

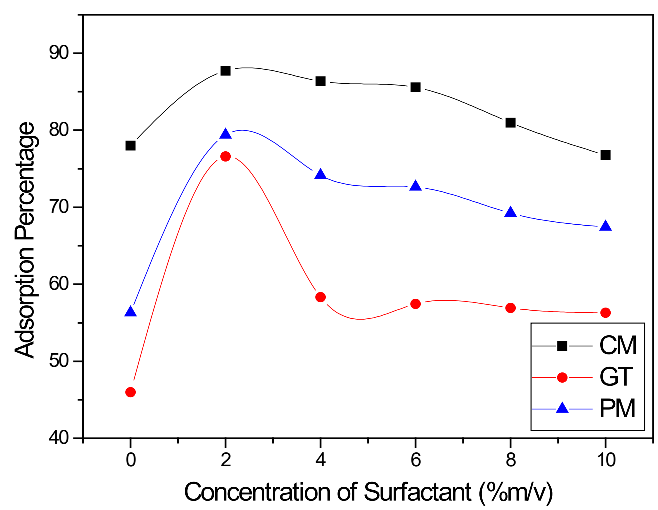

Figure 3: Effect of the presence of PEG on the adsorption of 2-CP onto spent tea leaf samples.

Effect of the presence of heavy metal ions

Heavy metal ions of Cu(II) and Pb(II) were used as inorganic interfering substances for the adsorption of 2-CP. These metals are species that are commonly found in wastewaters and pose high toxicity to humans and ecology. Previous reports have demonstrated that biological materials have a high affinity towards heavy metal ions [16,17,21], therefore it is important to consider the presence of these ions on the adsorption of 2-CP. Experimental data is shown in Figures 4 and 5 for copper and lead divalent ions, respectively. From the results, a higher adsorption is observed at low Cu(II) ion concentrations, whereas higher levels of copper ions seem to decrease the adsorption. However, up to 100 mg/L of Cu(II) in solution does not affect the adsorption of 2-CP. These results agree with the conclusions that 2-CP and Cu(II) ions do not compete for the same adsorption sites.

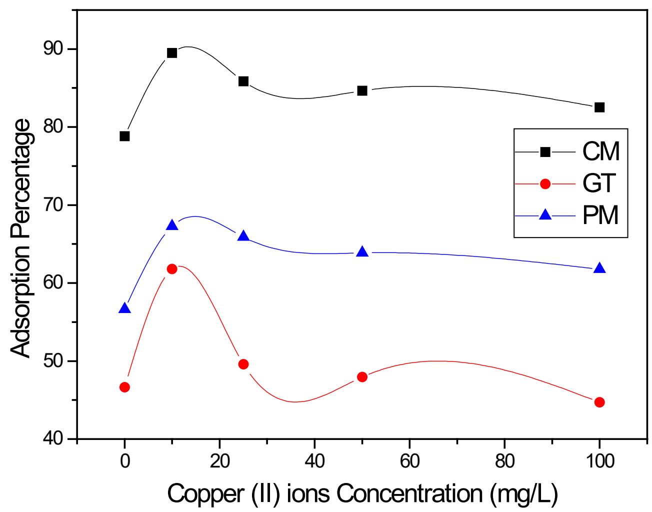

Figure 4: Effect of the presence of Cu(II) ions on the adsorption of 2-CP.

A similar study was conducted with Pb(II) ions. From the results, as observed in Figure 5, Pb(II) ions have a positive effect on the adsorption of 2-CP. For this metal ion, the graph indicates that Pb(II) metal ions and 2-CP do not compete for the same adsorption sites. A plausible explanation for the small increases on the adsorption with both metal ions could be the binding of the metal ions on the adsorbent that can potentially form complexes with 2-CP (mostly with the negatively charged phenoxides). More studies are needed to demonstrate the enhancement of the adsorption in the presence of these heavy metals. However, it is important to highlight that the results indicate that 2-CP can be efficiently adsorbent onto the spent tea leaf samples, even in the presence of Cu(II) and Pb(II) metal ions in solutions.

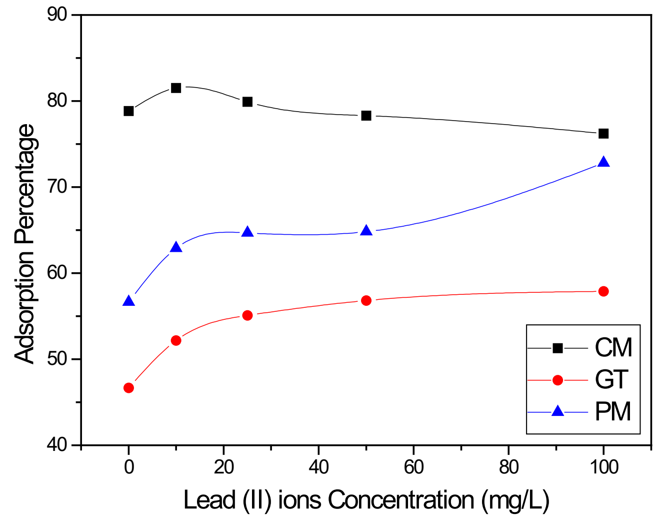

Figure 5: Effect of the presence of Pb(II) ions on the adsorption of 2-CP.

Conclusions

Chlorophenolic compounds are prevalent pollutants in pesticides and adhesives industries. Therefore, the development of eco-friendly and sustainable adsorbents is can be potentially applied for water remediation. This study proposes the use of spent tea leaves of chamomile (CM), green tea (GT) and peppermint (PM) as adsorbents for the elimination of 2-chlorophenol (2-CP) from aqueous solutions. Experimental data indicate that these solid wastes can be potentially used to adsorb 2-CP. Adsorption tests demonstrated a strong pH effect on the adsorption, reporting adsorption capacities of 80%, 58% and 47% for CM, PM and GT, respectively. The presence of interfering inorganic and organic substances was also studied. Results indicate that Cu(II) and Pb(II) metal ions do not compete for the same active sites with 2-CP. On the other hand, a covalent surfactant PEG, does prevent an efficient adsorption, but improves the dissolution of 2-CP in solution. The pH-dependence and pKa analyses indicate that the adsorption is mainly driven by hydrogen bonding between the phenoxide ions of 2-CP and the hydroxyl groups of the spent tea leaves. This research proposes tea leaf wastes as potential, low-cost and eco-friendly alternative for the remediation of 2-CP. These biomaterials are not only able to remove 2-CP from contaminated waters, but also represent a better use of solid industrial wastes.

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