Adsorptive Removal of 2, 4-D Using Activated Carbon Derived from Waste Biomass

Ektha V, Abdul Samad Kamdod, M. V. Pavan Kumar, S. Shika

Abstract— Degradation and decomposition of the pesticides by natural reagents after use can lead to producing various types of harmful intermediates. 2,4-Dichlorophenoxy acetic acid (2,4-D) is a toxic herbicide which kills most broadleaf weeds by causing an uncontrolled growth. In this work, thermally modified date pits treated with acid, a novel low cost biosorbent, was used for the removal of 2,4-D. Acid pretreatment is an essential method in the preparation of adsorbents. Acid treatment on biosorbrnt was observed to be providing more surface area and porosity. Batch experiments was carried out to evaluate the adsorption performance of 2,4-D. The salient parameters such as adsorbent particle size, stirring speed, contact time, biosorbent dosage, solution pH, initial 2,4-D concentrations and working temperature for 2,4-D biosorption were optimized in batch studies. The XRD pattern was identified and the structure of the biosorbent was depicted to be amorphous in nature. The FTIR test was also conducted, which revealed the functional groups such as C-H, C=O, O-H and C tripple bond C in the biosorbent. In this study, acid modified date pits with phosphoric acid gives a maximum adsoption capacity of 96.05%. At pH 4 of the herbicide solution, the maximum removal efficiency of 93.4% was obtained. Biosorbents showed a maximum of 94.3% removal efficiency at 0.1 g of dosage. The activated carbon prepared from the date pits is a promising adsorbent in removing 2,4-D herbicide in waste water.

Keywords—2,4-Dichlorophenoxy acetic acid, Date pits, Acid thermal modification, Biosorbent, Batch adsorption,

1 Introduction

Water is a basic need of life and is used in many ways to cater the needs of daily life. If drinking water contains unsafe levels of contaminants, it can cause health effects, such as gastrointestinal illnesses, nervous system or reproductive effects, and chronic diseases such as cancer. Pesticides are widely used in producing food to control pests such as insects, rodents, weeds, bacteria, mold and fungus [2]. In spite of the fact that the use of pesticides helps to improve crop productivity and yields, it is imperative to note when pesticides are used indiscriminately; they come with negative consequences – in the sense that they can cause environmental pollution. Water pollution is one form of pollution that is caused by the improper use of pesticides [6]. They are considered to be harmful to human health because of the potential mutagenicity and toxicity. Pesticides are chemical substances that are meant to kill pests. In general, a pesticide is a chemical or a biological agent such as a virus, bacterium, antimicrobial, or disinfectant that deters, incapacitates, kills pests. Because of their chemical stability, resistance to biodegradation, and sufficient water solubility, these compounds can either reach the groundwater or be washed away to the surface water bodies. 2,4-Dichlorophenoxy acetic acid (2,4-D) is a widely used herbicide on crops for killing broadleaf weeds [1].

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2,4-D residues can easily contaminate surface water bodies by surface runoff and seepage into the groundwater aquifers [7]. 2,4-D is a threat to the environment and human health. It also affects the immune and endocrine systems.

The various methods such as adsorption, electrocoagulation, an advanced oxidation process, anodic oxidation, bioremediation and photo-catalysts were adopted for the removal of herbicides from the water [3]. Of these, adsorption is considered to be probable method owing to its simplicity, ease of operation and efficiency in removal.

Carbon obtained from bio-waste has highly porous and large surface area; these carbon materials are an efficient and cost-effective method to remove organic pollutant from the water. Date pits are a low cost waste biomass which can be easily collected and available in sufficient quantity [4]. It is a promising biosorbent for the removal of contaminants, pesticides, heavy metals etc.,

2 Materials and Methods

2.1 Materials

2,4-Dichlorophenoxy acetic acid of molecular weight 221.04 g/mol of purity 97% and phosphoric acid were purchased. The selected biosorbent date pits were collected from juice shops and houses. The 2,4-D stock solution was prepared using Millipore water [7].

2.2 Preparation and characterization of activated carbon

The collected date pits were washed three times with normal water and three times with distilled water thoroughly for the removal of dirts. Then oven-dried for 24 hours at 50℃ for the removal of moisture content. Then ground and sieved for uniform particle size. For making activated carbon, the material was dried at 550℃ for two hours at a muffle furnace. For better adsorption capacity an acid treatment was provided. Acid treatment will help to open the pores and will increase the surface area. The selected acids were nitric acid, phosphoric acid, and sulfuric acid. In 1:1 ratio acid and date pits were mixed well for 10-15 minutes. The treated biomass was then kept for rest for 20 minutes. The date pits were then washed and filtered with distilled water until the pH of the filtrate becomes 7. It was then oven dried at 50℃ for 24 hours.

For characterization, Fourier transform infrared analysis (FTIR) and X-Ray diffraction were carried out. FTIR is a test for identifying the functional groups, unknown materials, quality and consistency of a sample, amount of compounds in a mixture etc. and XRD is a test for analyzing whether the adsorbent is amorphous or crystalline in nature.

2.3 2,4-D Adsorption Experiments

The concentration of 2,4-dichlorophenoxyacetic acid in the aqueous phase was measured by a UV–vis spectrophotometer at a wavelength of 284 nm [9]. The first parameter analyzed in the adsorptive assay of 2,4-D on date pits was the pH. For this, five Erlenmeyer flasks containing 25mL of herbicide solution and 25mL of distilled water, making it upto 50mgL^{-1}. 0.1g of adsorbent was previously adjusted with NaOH and HCl at different pH values such as 2, 4, 6, 8, 10 and posteriorly stirred for 100 rpm at 32℃. For the determination of the ideal adsorbent dosage, seven Erlenmeyer flasks were taken and filled with 25mL of herbicide solution (50mgL^{-1}) containing 0.02, 0.04, 0.06, 0.08, 0.1, 0.12 and 0.14g of date pits sample. Each flask was adjusted to the pre-determined ideal pH (pH =4) at a 2,4-D concentration of 50 mgL^{-1}. The initial concentration study was carried out for the concentrations of 20, 30, 40, 50, 60, 70, 80, 90 and 100 mgL^{-1}. All the tests were carried at 100 rpm for 120 minutes by fixing the dosage at 0.1 g at pH 4.

3 Results and Discussions

3.1 Biosorbents Modifications

The preteatment of adsorbent was carried out by acid treatment.

The three different acids are namely sulphuric acid, phosphoric acid and nitric acid. Acid treatment is a promising treatment for improving the adsorption capacity and helps to open the pores, thus increasing the surface area of adsorbent. Hence, this treatment helps to increase the 2, 4-D removal efficiency.

The removal efficiency of 2, 4-D was oberserved to be maximum (96.05 %) when the biosorbent was treated with the phosphoric acid. And 82.9% of 2,4-D removal from nitric acid and 81.6% removal of 2,4-D using sulphuric acid (Fig. 1).

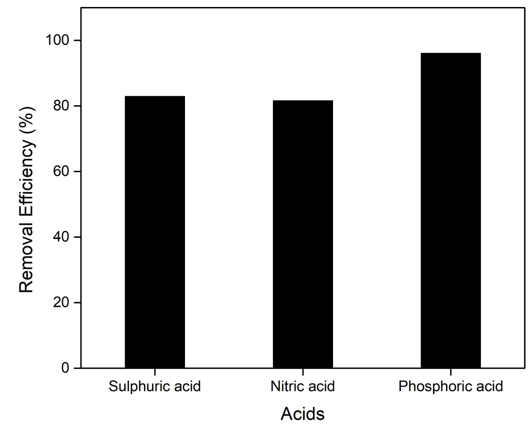

Fig. 1 Removal effieciency of biosorbent treated with different acids

Thus for further analysis date pits treated with phosphoric acid was used.

3.2 XRD Diffraction

The XRD analysis of acid modified date pits are shown in Figure 2.

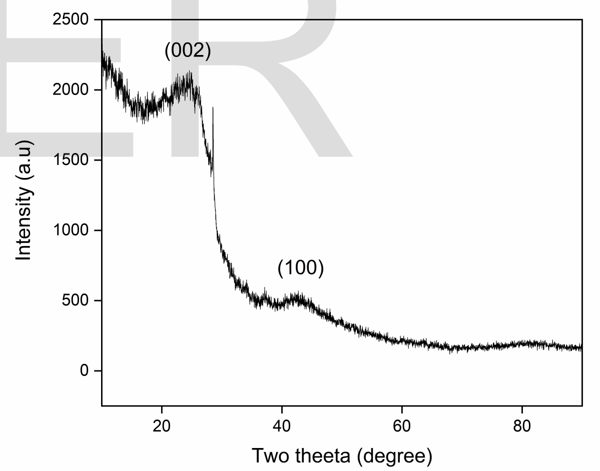

Fig. 2 X-Ray diffraction of date pits

Data showed a broad diffraction peak at 2θ = 24.062° and 2θ = 42.33° for the biosorbents, indicating carbonaceous and amorphous nature of the biosorbents.

3.3 Fourier Transform Infrared (FTIR) analysis

The biosorbents were tested for their surface functional groups and morphology by FTIR spectrometry in the range of 4000–500cm^{-1}.

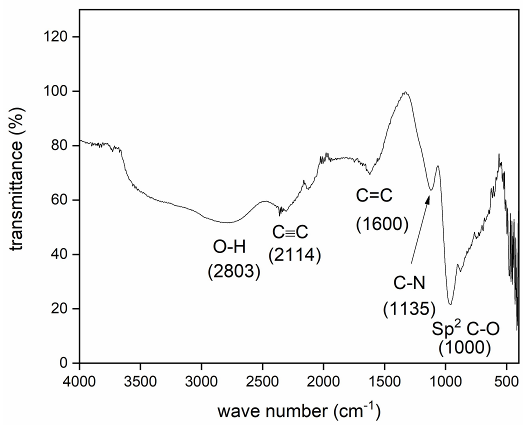

Fig. 3 FTIR analysis after 2,4-D adsorption

It was observed that the activated carbon obtained from the date pits sample (pretreated), presents a wide variety of functional groups compared to date pits.

The characteristic peaks of date pits were observed at 2803cm^{-1} (O–H carboxylic acid strong), 2114cm^{-1} (C≡C stretching of alkyne medium bond), The sign of 1636cm^{-1} corresponded to C=O bonds and remained present in the two materials but lost its intensity after thermal treatment and 1000cm^{-1} (C–O ester groups) (Fig. 3).

3.4 Influece of pH

The effect of initial solution pH on 2,4-D biosorption by date pits was studied in the range of 2–10 as shown in Figure 4.

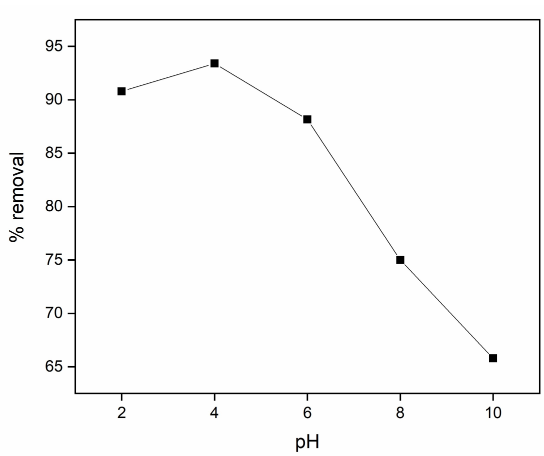

Fig. 4 Effect of initial solution pH

An increase in removal efficiency from 90% to 93.4% was observed for pH 2 to 4. Beyond pH 4, the removal efficiency consistently decreased up to 65%.

Hence, the optimum pH was taken as 4, since at pH 4 the removal efficiency of 2,4-D was maximum. Also the pH of the 2,4-D stock solution was 3.78, which shows that the sample can be directly treated without any pH adjustment.

3.5 Influece of Adsorbent Dosage

The influence of adsorbent dosage on the efficiency of 2,4-D removal has shown in Figure 5.

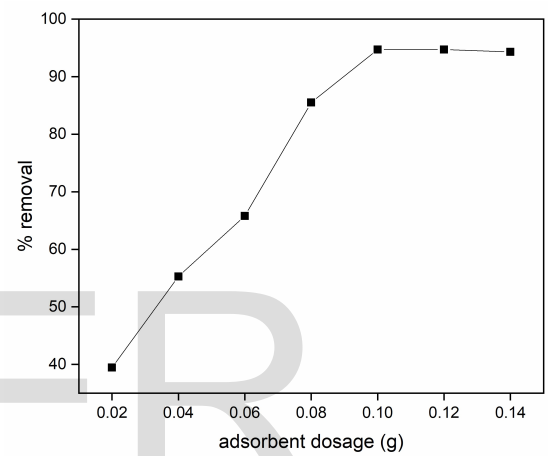

Fig. 5 Effect of adsorbents dosage on 2,4-D adsorption.

The selected adsorbent dosages for the removal of 2,4-D was 0.02, 0.04, 0.06, 0.08, 0.1, 0.12 and 0.14g. It was found that with the increase in the dosage of acid modified date pits, the removal efficiency of 2,4-D increases from 39.46% to 94.7%. After a dosage of 0.1g, no further change in the removal efficiency was observed. Hence, the maximum removal efficiency of 94.7% was at 0.1 g of date pits was taken as optimum.

3.6 Influece of initial 2,4-D concentration

The biosorption studies were carried out using the optimal values of biosorbent dosage of 0.1g and pH as 4 for different initial concentrations of pesticide 20–100 mgL^{-1} (Fig 6).

In the range of 20–100 mgL^{-1}, with the increase in initial pesticide concentration a decrease in the removal percentage was observed. A maximum removal percentage of 96.7% was observed for an initial 2, 4-D concentration of 20 mgL^{-1}.

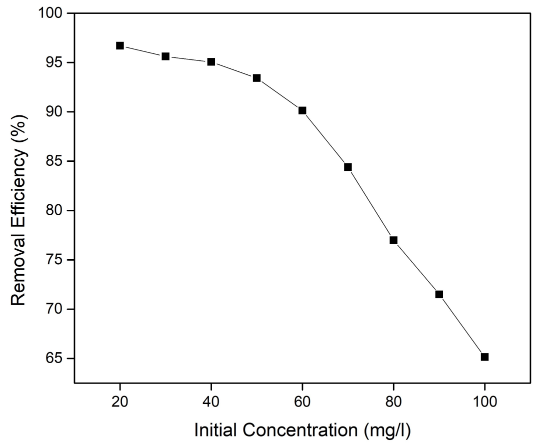

Fig. 6 Effect of initial solution concentration on 2, 4-D adsorption.

The available active sites present on the biosorbents surface relatively decreases upon increasing the initial concentration beyond the optimum value of initial concentration (100 mgL^{-1}) which can be seen as lowered percentage removal of pesticide. The usually observed range of 2,4-D in the effluents come around 50 mgL^{-1} and in our experiment a removal effiency of 94% was obtained for that range. Hence, the optimum dosage of 0.1g of the acid modified biosorbent can be effectively used.

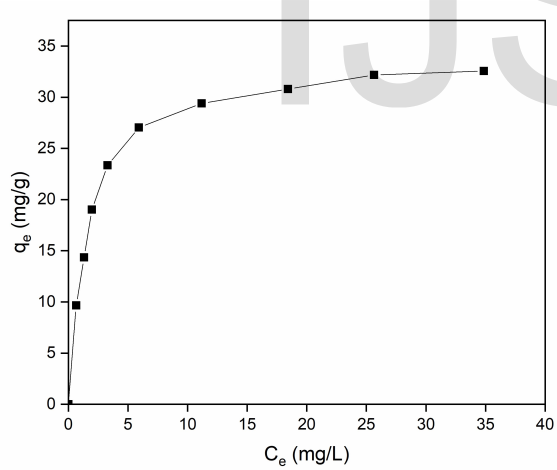

Fig. 7 2, 4-D Adsorption capacity of date pits with final concentration in abscissa and adsorption capacity in ordinate.

With the acid modification pore will open and surface area of date pits increases. Figure 7 shows that with the increase in time, the adsorption capacity of the date pits increases futher adsorbtion does not takes place as the pores are completely filled with the contaminants. Here the maximum absorbent capacity of the adsorbent was upto a concentration of 25mgL^{-1}. Beyond this concentration the adsorbent should be either replaced or regenerated.

4 CONCLUSION

In the current investigation, date pits in modified forms were analysed for the 2,4-D removal from water. Acid modifiations using sulfuric acid, nitric acid and phosphoric acid of the date pits were analyzed and the exhibited maximum affinity for the pesticide biosorption of 96.05% was obtained for date pits treated with phosphoric acid. The acid modification of the biosorbent resulted in enhanced porosity and surface area with the incorporation of surface functional groups suitable for maximum 2,4-D removal. The initial pH of the stock solution was 3.78 and the best adsorption capacity of 93.4% was obtained at pH 4. The optimum biosorbent dosage of 0.1g was obtained for a maximum removal efficiency of 94.7% and initial solution concentration were found to be 50 mg L-1 for a 2,4-D adsorption capacity of 94%. In this work, acid treated date pits powder biomass is shown to be an efficient biosorbent for the removal of 2,4-D from its aqueous solution.

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