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PRELIMINARY STUDY OF THE EFFECT OF USING BIOSORBENTS ON THE POLLUTION OF THE TREATED WATER

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ABSTRACT

Several adsorbents have been tried out by researchers to remove different pollutants from wastewater. However, the adverse effect of these biosorbents on the treated water and the possibility of leaching new pollutants to the treated water have not been investigated. A batch technique was employed to study this phenomenon. Three agricultural wastes namely sawdust, dates stones and palm fibers were investigated. The possible leaching of total dissolved solids (TDS) and organic compounds in the form of chemical oxygen demand (COD) from these substances to water were investigated. The effect of water pH and particle size of these biosorbents on the extent of the leaching process was studied. The results indicate high release of both TDS and COD for the three biosorbents. A COD value as high as 230 mg l^{-1} was obtained, while the highest TDS leached was 29 mg l^{-1}. DS was found to have the highest leaching ability, followed by SD and PF. The highest leaching was obtained at high pH and small particle size of the adsorbent.

Keywords: Adsorption, Date Stones, leaching, Palm fibers, Saw dust, COD, TDS

1. Introduction

Water is one of the most vital natural resources on the earth. However, rapid industrialization and urbanization have resulted in the production of huge amount of wastewater containing all types of pollutants. Increasing of environmental awareness has led to more stringent regulations on the quality of water and wastewater. This has led to search for appropriate techniques to cope with these limits. Various techniques have been developed by researchers for treatment of such wastewater. The real challenge is to select the efficient, economic technique that has the least adverse effect on the environment. The treatment method may be physical, chemical or biological in nature. Examples of the treatment methods include; foam filtration, filtration, ion exchange, sedimentation, solvent extraction, adsorption, chemical oxidation, membrane processes (Bhatnagar and Minocha, 2006), stepwise coagulation, GAC/O3 oxidation (Qian *et al.,* 2013), Fenton process (Zhang *et al,.* 2012), lime softening (Varga *et al.,* 2013), coagulation, electrochemical processes (Ahmad *et al.,* 2012), electrocoagulation (Muthukumaran and Beulah, 2010), chemical precipitation (Rathinam *et al.,* 2010).

These methods have some drawbacks; including low efficiency for removal of trace concentration of pollutants in case of chemical/biological oxidation, electrolysis, ion exchange and solvent extraction (Bhatnagar and Minocha, 2006; Zhang *et al.,* 2012). Coagulation and precipitation processes produce large amount of sludge and require pH control. Furthermore, ozonation will remove color from wastewater without decreasing the COD (Bhatnagar and Minocha, 2006; Ahmad *et al.,* 2012). Membrane processes suffer from the problem of fouling of the membrane used (Dang *et al.,* 2009). Many of these processes lack in cost effectiveness, energy intensive processing and the low removal efficiency for some pollutants (Rathinam *et al.,* 2010).

On the other hand, adsorption has many advantages on the other processes. This process has the characteristics of convenience, easy operation and simplicity in design (Bhatnagar and Minocha, 2006). It has a wide application for removal of different pollutants (Bhatnagar and Minocha, 2006; Ansari and Mosayebzadeh, 2010). Other important advantages of this process include: low operation cost, high flexibility, simple design and operation, easy automation, lack of sensitivity to toxic pollutants and the capability of operation at very low concentration, environmentally friendly, less investment in terms of initial cost (Ansari and Mosayebzadeh, 2010; Auta and Hameed, 2013; Galán *et al.,* 2013; Ismail *et al.,* 2013).

The most important criteria in adsorption processes is to find a low cost adsorbent that is widely available, having high adsorption capacity, possess rapid rate of removal and having low adverse effect on the treated water. Many adsorbents have been investigated.

Historically, activated carbon was the primary adsorbent of use because of its high capacity for removal of various pollutants (Jambulingam *et al.,* 2007). The major disadvantage of using this adsorbent is its high price and its high regeneration cost (Ahmaruzzaman, 2008). This has led researchers to look for more economic adsorbents. Large variety of materials have been investigated including; natural zeolites, sludge, red mud, siliceous materials, peat, chitin and chitosan (Ahmaruzzaman, 2008), polyaluminum hydroxide, diatomaceous earth, clay mineral, dolomitic sorbents (Khan *et al.,* 2009), magnetic composite, nano particles (Sheela *et al.,* 2012), chitosan-activated carbon composite (Auta and Hameed, 2013) and organo bentonite (Koyuncu *et al.,* 2011).

Another alternative was to investigate the possibility of using agro-based inexpensive material as adsorbents. These wastes represent two problems; their disposal and being unused resources (Bhatnagar and Minocha, 2006). Tremendous amounts of these materials are produced every year. Bansal *et al.*, (2009) used rice husk to remove nickel ions from aqueous solutions. Garg *et al.*, (2008) used sugarcane bagasse for the same purpose. Jayarajan *et al.*, (2011) investigated the use of Jackfruit peels for removal of Rhodamine dye. Gram husk and groundnut were tried by Chakrabarti *et al.*, (2008) for treatment of water polluted with other textile dyes. Khan *et al.*, (2004) mentioned the use of rice husk, sugarcane bagasse, sawdust, soybean hull, cottonseed hulls, rice barn and straw for the removal of different pollutants.

Other examples of agricultural wastes that have been searched are pistachio hull (Moussavi and Khosravi, 2011), chemically modified coir pith (Suksabye and Thiravetyan, 2012), cedar saw dust (Ismail *et al.,* 2013), crushed brick, garlic peal (Fan *et al.,* 2012), rice husk, peanut shell, barks and dry tree leaves, tea and coffee wastes, wheat bran (Madrakian *et al.,* 2012), mango peel waste (Sheela *et al.,* 2012), apple pomace (Mundhe *et al.,* 2012), jack fruit waste, brewery waste (Anagnostopoulos *et al.,* 2012; Anagnostopoulos and Symeopoulos, 2013) treated sugar cane bagasse, yellow passion fruit peel, jack fruit leaf powder, coconut husk, pine saw dust (Mundhe *et al.,* 2012), and tree products such as fern (Carro *et al.,* 2010).

All these agricultural wastes have the same main chemical compositions namely; cellulose, hemicelluloses, lignin and extractives. Cellulose and hemicelluloses are carbohydrate polymers constituents of simple sugars monomers. Cellulose is the major chemical component of fiber with the degree of polymerization from (DP) from 5,000 to 20,000. The cellulose fibers are held together with hemicellulose and lignin. Hemicelluloses have lower DP (only 50-300) with side groups on the chain molecule and are essentially amorphous. Lignin is a phenyl-propene aromatic compound that cannot be fermented but can be used as a high-energy content boiler fuel. Lignin acts as cementing material between the cellulose and hemicellulose and as a stiffening agent within the fibers. In the production of chemical wood pulps, it is dissolved by various chemical processes, leaving the cellulose and hemicelluloses behind in fibrous form.

Although the cellulose structure is the same in different species, the hemicelluloses vary considerably among species and especially between hardwoods and soft-woods (Browning, 1975; Wyman *et al.,* 2005; Wahab *et al.,* 2013).

To the best of the author knowledge, based on extensive literature survey, none of the researchers discussed the adverse effect of such adsorbents on the treated water. The main focus of the researchers was measuring the adsorption capacity of such adsorbents, investigating the different factors affecting the adsorption process and applying thermodynamic, kinetic and equilibrium models to explain the adsorption process. None of the researchers studied the possible drawbacks of using these biosorbents on the treated water. The goal of this research is to investigate the effect of using biosorbents on the treated wastewater. Three adsorbents namely; dates stone, palm fibers and saw dust were investigated. The effect of dose of adsorbents, pH and particle size on the leaching of soluble substances and on the chemical oxygen demand were investigated.

2. Materials and methods

2.1. Adsorbents

Three agricultural wastes were tested; dates stones (DS), Palm fibers (PF) and sawdust (SD). Dates stones were collected from local food processing plant in Madinah, Saudi Arabia. The fibers were collected locally from different types of palm trees and the saw dust was collected from the local sawmills. The method that is usually followed by different researchers for preparation of the adsorbents was applied in this research. The agricultural wastes were washed with tap water to remove dust and any foreign materials (with good rubbing in case of dates stones and palm fibers), filtered out and then soaked in distilled water for ten minutes and filtered out again. The raw materials were oven-dried at 105^{o}C overnight. The raw materials were ground separately in kitchen mixer. They were then sieved to different sizes and kept in covered glass containers for further use.

2.2. Effect of mass of adsorbent

Different known masses of every absorbent were added to 50 ml aliquot of distilled water. The mixtures were agitated using shaker (IKA Yellowline RS/OS 10 Control) for 3 hours at 250 rpm, left to settle for 20 minutes. The solutions were filtered out and filtrates were tested for TDS and COD.

2.3. Effect of pH of water

The effect of initial pH was studied by preparing 3 sets of 150 ml conical flasks containing 50 ml of distilled water. The pH of water in each flask was adjusted at different value using either 1 N H_2SO_4 or 1 N NaOH. To each series, 0.12 g (weighed to the fourth decimal point) of one adsorbent were added. The mixtures were agitated for 3 hours and left to settle for 20 minutes. The mixtures were filtered and the filtrate was analyzed for TDS and COD.

2.4. Effect of adsorbent particle size

To study the effect of the adsorbent particle size on the leaching process, three sets of 150 ml conical flasks were used (one set for each adsorbent). Every set consisted of 6 flasks (one flask for every particle size). 50 ml aliquots of distilled water were added to every flask in the sets. To each flask in the set, 0.14 g (weighed to the fourth decimal point) of the appropriate adsorbent were added. The flasks were agitated for 3 hours at 250 rpm left to settle for 20 minutes and filtered out. The filtrate was analyzed for TDS and COD.

2.5. Analytical method

The chemical oxygen demand (COD) of the water after the agitation process was determined following Hach® Method 8000 of the Hach Water Analysis Handbook (Hach, 1997), using DRB200 Reactor and DPR 890 colorimeter. Total dissolved solids (TDS) were measured using SevenEasy conductivitimeter from Metler Toledo and pH was measured using pH 501, EuTech Instruments. All experiments were performed in a duplicate bases and the average was taken.

3. Results and discussion

3.1. Effect of adsorbent mass

Many organic and inorganic compounds may be leached from different agricultural wastes depending on the nature and structure of this waste. Examples of these organic compounds include carbohydrates, proteins, and lipids (Hansen and Cheong, 2007). As illustrated by Figure 1, increasing the mass of waste resulted in increase in the amount of dissolved solids extracted to the water used. That implies in real situations that when using such agricultural wastes in high quantities to treat industrial wastewater then we are removing a certain pollutant from such water. However, we are adding a new threat to this water. It is clear that a substantial concentration of dissolved solids is extracted from the three tested wastes. The highest concentration is obtained from PF and DS for all used masses, respectively.

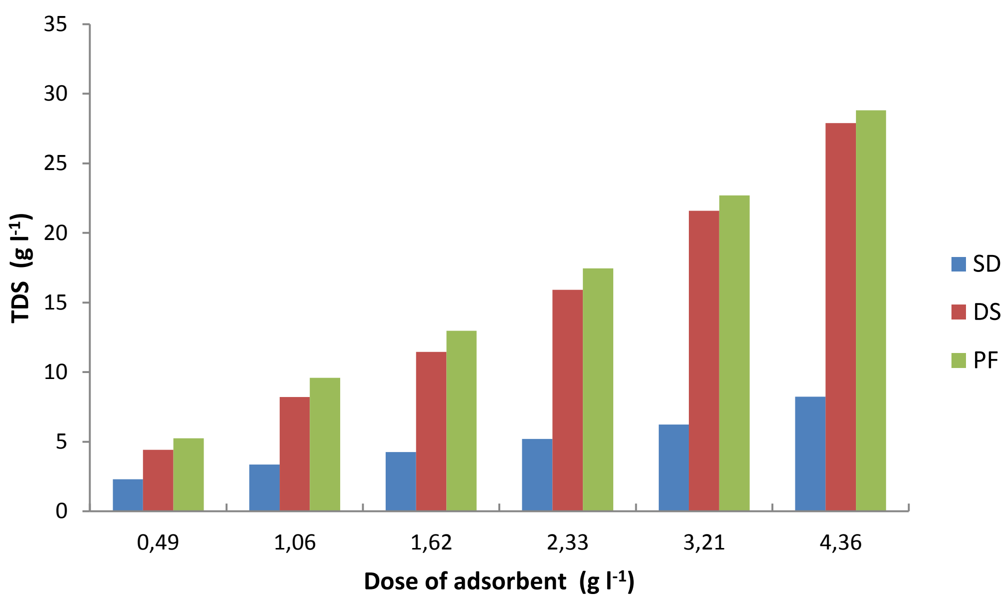

Figure 1. Effect of adsorbent dose on TDS leached to the water

Figure 2 indicates the relationship between the dose of the adsorbent and the amount of TDS leached to the water. It is clear that correlation coefficient, R^2, is greater than 0.99 for all adsorbents which assure the close relationship.

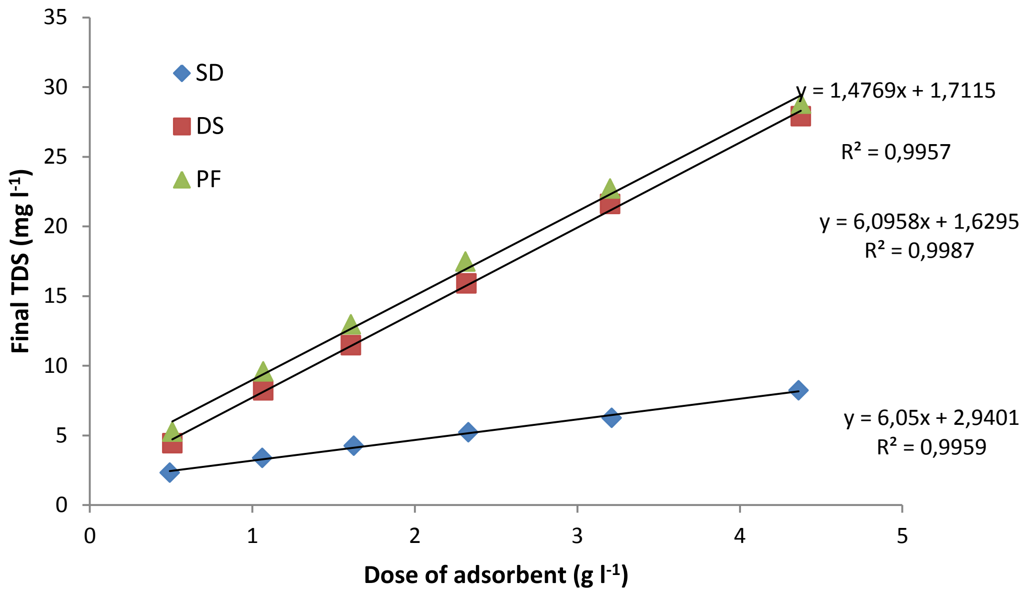

Figure 2. Correlation between the adsorbent dose and TDS extracted to the water

As illustrated by Figure 3 high COD values are obtained when analyzing the treated water which indicates that a considerable part of the dissolved solids are organic material. Again the concentration of these organic materials is directly proportional to the dose of the agricultural waste applied. One important threat of these organic materials is the ability to chelate (Salati *et al.,* 2010) with the heavy metals that may be initially present in the treated water thus decreasing their removal efficiency from water.

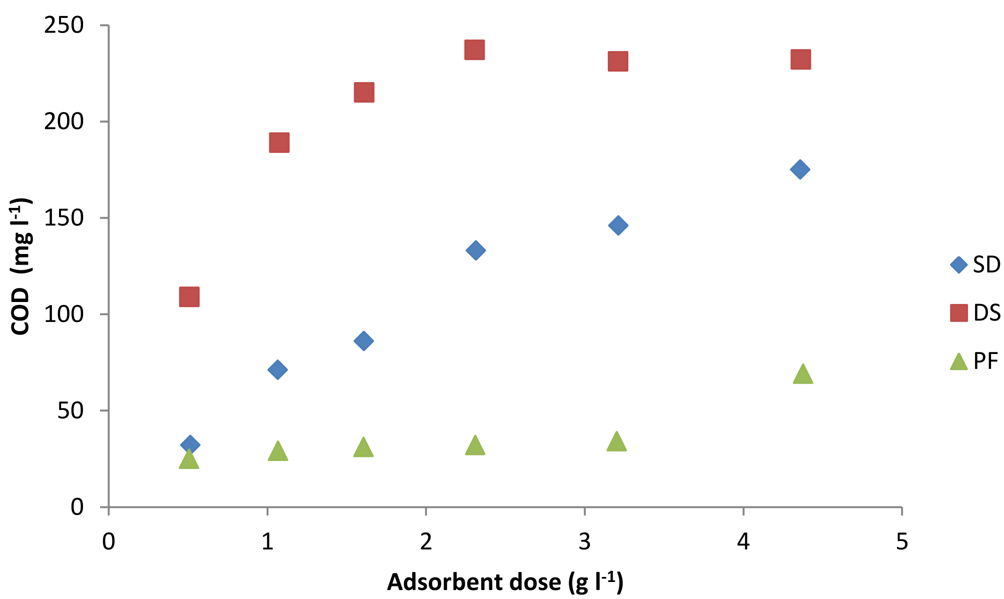

Figure 3. Effect of adsorbent dose on COD leached to the water

3.2. Effect of pH

As indicated by Lai and Idris (2013), the chemical constituents of most lignocellulosic materials are polymeric carbohydrates, which consist of cellulose, hemicellulose, and lignin. Figure 4 indicates that the pH of the water did not have a significant effect on the extraction of the organic compounds unless at very high pH value (pH 12). Usually the extraction of hemicelluloses and lignin is performed at alkaline pH at elevated temperature (Johar *et al.,* 2012). However even at room temperature some of the hemicelluloses and lignin have been extracted (Borrega *et al.,* 2013). The pH of the wastewater is related to the activity producing this wastewater. For instance, pH of the textile wastewater is fluctuating from 6-10 (Kalra *et al.,* 2011). The pH of the wastewater produced from olive mill has a range 4.6-5.8 (Kılıç and Solmaz, 2013). Refinery wastewater may have a value of 8.5 (Yan *et al.,* 2014). Biodiesel wastewater has high pH due to the significant levels of residual alkaline catalyst (Pitakpoolsil and Hunsom, 2013). Wastewater from mining processes usually has low pH (Oncel *et al.,* 2013).

Aside from the cellulose, hemicelluloses and lignin, lignocellulosic materials contain a variety of low molecular weight organic compounds, called extractives. Example of these extractives is fatty acids, resin acids, and waxes. (Mimms *et al.,* 1993). Part of these extractives may account for the dissolved organic in water.

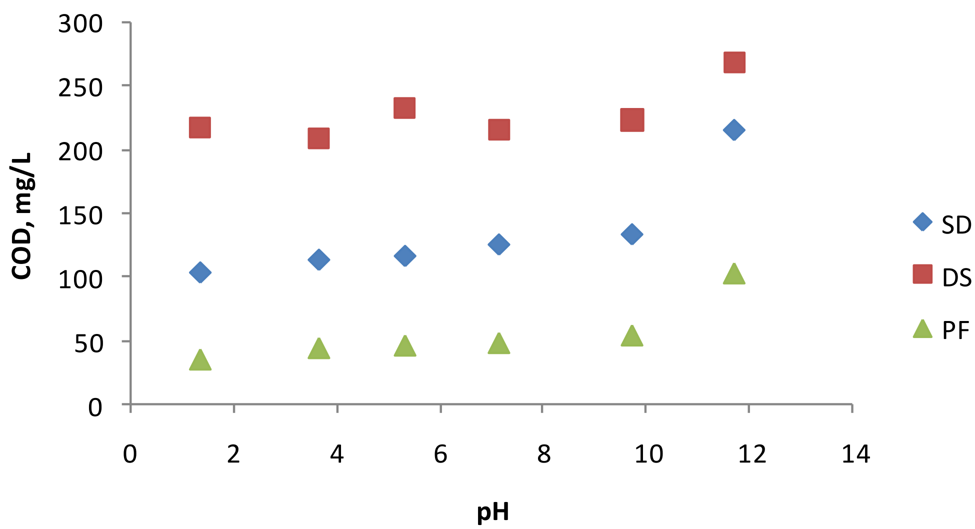

Figure 4. Effect of pH on COD leached to the water

3.3. Effect of adsorbent particle size

Figures 5 and 6 illustrate the relation between particle size of the adsorbent and leaching extent for both TDS and COD. It is clear that the highest leaching of dissolved solids and COD takes place for the smaller particle size of adsorbent. This is due to the increase of surface area by decreasing particle size which facilitates the leaching process. For PF and SD, the values of COD and TDS do not show the same clear significant difference when changing the particle size as DS, however there is a trend of increasing COD and TDS values when decreasing sorbent particle. The same order that was obtained for the previous two properties (dose of adsorbent and pH of water) was kept here. DS has the highest leaching ability, followed by SD and PF

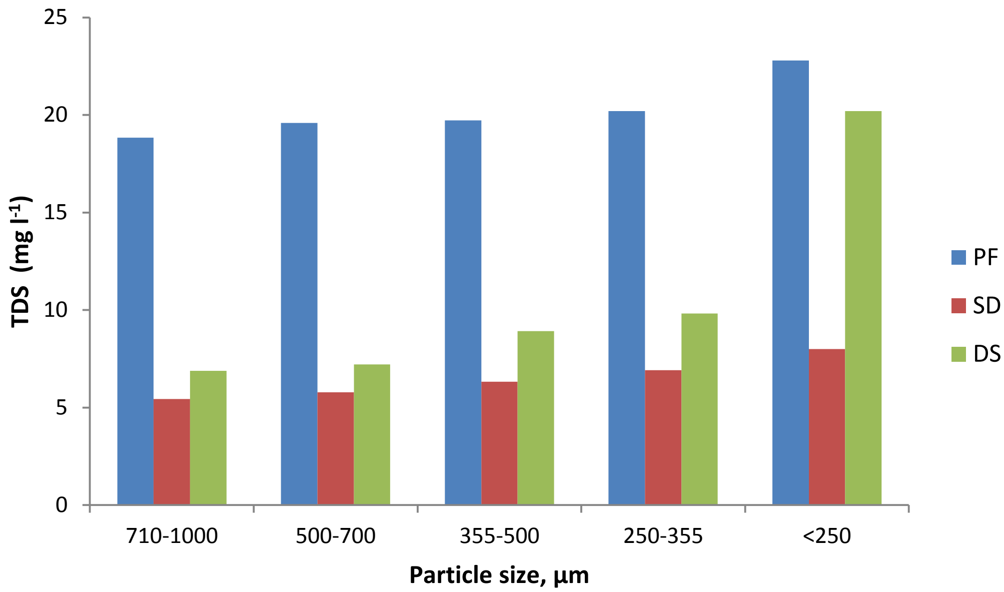

Figure 5. Effect of adsorbent particle size on TDS change of the water

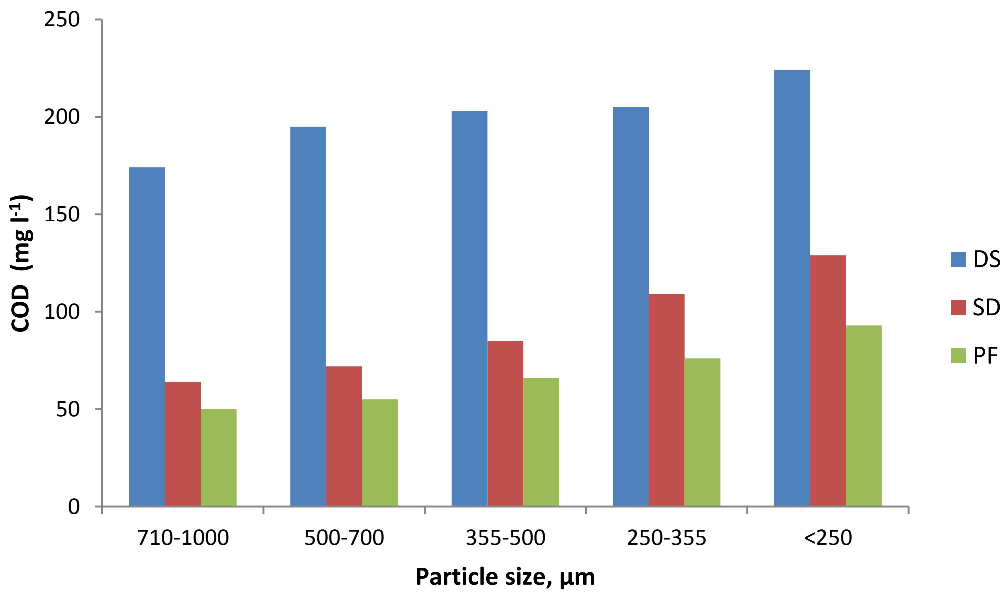

Figure 6. Effect of adsorbent particle size on COD leached to the water

4. Conclusion

By examining the extraction behavior of TDS and COD from the tested agricultural wastes to the aqueous solution it can be concluded that under the study conditions all the tested adsorbent are capable of polluting the treated water by TDS and COD. The dose of adsorbent is directly proportional to the concentration of TDS and COD introduced to the water. These concentrations are highly increased at high alkaline pH of the aqueous media and small particle sizes of the adsorbent. More study is required to study this process using other adsorbents and at different working conditions.

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