Removal of Heavy Metals Ions from Aqueous Solution using Different Pretreatment Techniques of Corn Cob

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Abstract: Water pollution has been a global issue and Malaysian waters are of no exception. Traces of heavy metals have been found in rivers and water sources from industrial and agricultural run-off, apart from improper waste disposal. Hence, this study proposes the application of corn cob to remove Chromium (Cr), Manganese (Mn), and Lead (Pb) metal ions from aqueous solution by different pre-treatment techniques using vinegar and hydrochloric acid (HCl). The experiment was conducted in a water filtration apparatus where each heavy metal of interest were treated separately using the pre-treated corn cob. The samples of metal ions were tested by using Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES), which was later analysed and compared by evaluating the percentage removal of each metal ions, adsorption capacity, and adsorption isotherms. For Cr, Mn, and Pb removal using HCl-treated corn cob, the maximum percentage removal is 58.75%, 98.68%, and 77.18% respectively whilst the maximum percentage removal for Cr, Mn, and Pb using vinegar-treated corn cob is 71.50%, 98.00%, and 74.25%. Further analysis on the equilibrium data shows that this experiment favoured the Freundlich isotherm, as seen from the R^2 values greater than 0.9 for each adsorption experiment. Hence, both corn cob pre-treated using HCl and vinegar was proven to be effective in the removal of Cr, Mn, and Pb ions.

Keywords: Heavy metal adsorption; corn cob; pre-treatment; adsorption isotherm

Introduction

Malaysia is one of the countries experiencing greatest economic growth in the ASEAN region since the 1950s, ranked at 27th out of 63 countries on the Global Competitiveness Index (GCI) in year 2020 (Schwab, 2017; Cecilia, 2020). Parallel to this rapid economic growth comes an increase in pollution. The residential, commercial, and industrial areas discharge illegally wastewater into the natural water sources, where this negatively influences the surrounding environment, its inhabitants (both humans and other living organisms), and the nation's economy (Sharma, 2015). To remove these excessive pollutants from natural sources, advanced technology, which is always available in the market, is used. However, the major drawback is that the advanced technology is usually too costly and ultimately will affect the cost of usable water. As the quality of water deteriorates, the cost of treatment increases and thus affects the economy as water tariffs increases, thereafter (Borneo Post Online, 2011, Jiang et al. 2019). The Department of Statistics Malaysia reported that nearly 64% (RM 1,659.7 million) of all environment protection expenditure goes to protecting the environmental media which included the ground and surface water sources (Crini, 2005; Department of Statistics Malaysia, 2019). Hence, it is of utmost importance to identify cost effective measures to reduce water pollution.

Methods to remove pollutants (both organic and inorganic) are of variety which include membrane processes, biological treatments, chemical, and electrochemical processes, as well as adsorption procedures. Among these methods, adsorption is the most widely used method due to its effectiveness and economical value (Rashed, 2013). Adsorbents play a crucial role in removing contaminants from water sources. Among the adsorbents used, activated carbon (AC) is widely employed and is very effective (Arvanitoyannis, 2008). However, activated carbon is also very costly and is therefore limited in its use for larger-scale applications (Arvanitoyannis, 2008). Due to that, there is a need for alternative low-cost adsorbents. As a result, various studies have been conducted on the use of agricultural waste such as coconut and rice husk, fruit peels, and corn cob as low-cost alternative bio-adsorbents (Abdelfattah et al., 2016).

Corn cob is one of the bio-adsorbents being studied as an alternative adsorbent. It is a by-product of the corn industry. In Malaysia, corn production is about 58,000 metric tonnes per year since 2015 (USDA, 2018). As only the grain is utilized for food, corn cob is considered an agricultural waste. However, this raw, untreated corn cob having a porous structure, is a desirable property in physical adsorption (Vafakhah et al., 2014). Some researchers have shown their interest in the properties of corn cob to be used as an alternative adsorbent. And indeed, the corn cob was proven to be useful and effective by several researchers in removing the dyes and heavy metals from contaminated water. Berber-Villamar et al. (2018) found that corn cob is effective in removing the azo dye Direct Yellow 27 (DY27), a yellow dye from aqueous solutions where the maximum experimental adsorption capacity was found to be 73.7 mg/g. Several other researchers also discovered that corn cob (both treated and non-treated) showed high adsorption capacity in removing heavy metals like Pb, Ni, Zn, and Cu ions (Ali, et al., 2014; Arunkumar, et al., 2014; Muthusamy & Murugan, 2016).

Although raw, untreated agricultural waste can be readily utilized as an adsorbent, pre-treatment is usually needed to improve the efficacy. Pre-treatment methods such as acids, alkalis, detergents, and heat are typically used to increase its surface area and adsorption capacity, as well as to remove any impurities in the material from dispersing into the water (Gong et al., 2005). Thus, bio-adsorbents like corn cob is preferrably to be pre-treated before the application to not only increase the surface area and metal affinity, but as well to prevent its phenolic compounds from dispersing and contaminating the water sample. The most common methods of pre-treatment involve the use of acids and alkaline such as the like of hydrochloride acid (HCl) and sodium hydroxide (NaOH) (Gong et al., 2005; Taty-Costodes et al., 2003).

In view of that, this study aims to investigate the effectiveness of corn cob using vinegar and HCl pre-treatment in removing Cr, Mn, and Pb ions from aqueous solution. Vinegar is known as a basic seasoning in culinary, and is used as preservative due to its acetic acid content and low pH values (Plessi & Papotti, 2003), the acetic acid content of vinegar for corn cob's pre-treatment can be used to compare with the HCl pre-treated corn cob. Besides, the Cr, Mn and Pb ions were selected in the study due to these ions are commonly found in the water discharge. For example, Cr from leather tanning, mining and medicinal industries (GracePavithra et al., 2019); Mn from alloy uses, especially from stainless steel (Khattak et al., 2017); and Pb can be easily found from processing industries such as acid battery manufacturing and ceramic industry (Arbabi et al., 2015). High concentration of these selected ions in the aqueous solution might lead to poisoning. The adsorption performance on selected heavy metal (Cr, Mn, and Pb) ions removal in the aqueous solution can be further analysed for potential new discovery.

Methodology

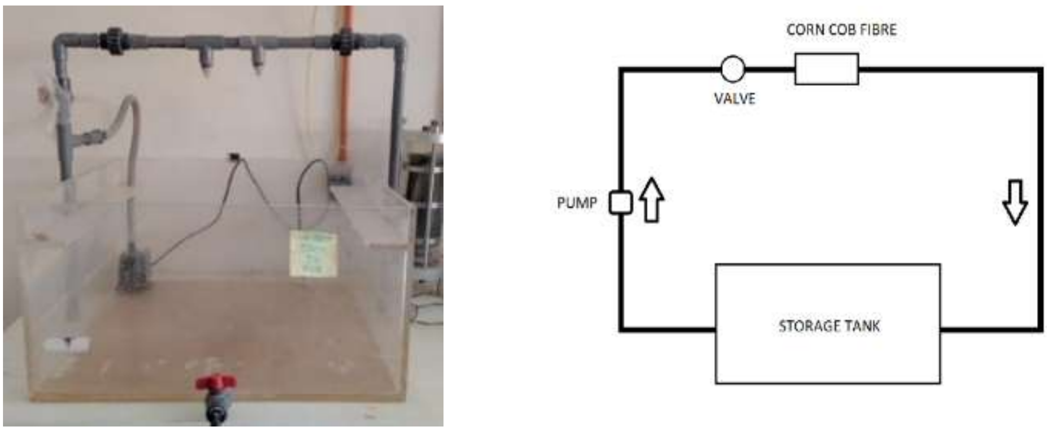
- **Adsorbent and water sample preparation**

The adsorbent material used for the removal of heavy metals in this study is corn cob. The corn cob was sourced from a local supermarket and washed thoroughly to remove any pollutant particles using filtered tap water. It was then ground and dried in an oven at 100℃ for 12 hrs. The corn cob was then sieved using mesh size of 3.5mm. Thereafter, it was treated using white vinegar (5% acetic acid) and 1% HCl for 24 hrs, then washed until clean and dried at room temperature for another 48 hrs (Ali, et al., 2014; Muthusamy & Murugan, 2016).

For the water sample, it was synthesized in the lab. Taking into consideration the biosorption capacity of corn cob of various heavy metals from a previous study, a concentration of 2g/l was used for Cr and Pb, while 80 mg/l was used for Mn (Abdelfattah et al., 2016). All the stock solution preparation is carried out based on EPA method 6010B (EPA, 1996).

- **Adsorption Experiment**

The study was carried out using a water-filtration apparatus in the laboratory, consisting of a water pump, storage tank, and cleaning outlet. The experiment was performed by circulating the synthesized water samples through the adsorbent medium (corn cob). Each water sample was fixed at 25 litres. About 60 g of adsorbent material was used for each iteration, using the optimum value of 2.4 g/l, determined from a range of 0.5 g to 2.5 g (Muthusamy & Murugan, 2016). Each experiment was conducted for 24 hrs and samples were collected four times at 2 hr intervals and once at 24 hrs. The apparatus and the flow of the treatment process is shown in Figure 1.



(a) (b)

Figure 1. Adsorption Apparatus (a) and the Adsorption Experiment Flow (b)

- **Water Sample Testing Method**

After going through the adsorption process, the water samples were sent for testing. The sample was tested according to Method 6010 B, using the Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) by EPA. This method is able to determine trace elements, including heavy metals, in solution. Table 1 shows the recommended wavelengths and estimated instrument detection limits (IDL) for each metal studied within this experiment.

Table 1. Excerpt from Method 6010 B Table of Recommended Wavelengths and IDLs.

Detection Element	Wavelength (nm)	Estimated Instrument Detection Limit (µg/L)
Chromium	267.716	4.7
Lead	220.353	28
Manganese	257.61	0.93

Prior to testing, the samples were first digested or solubilized using the appropriate sample preparation methods. The characteristic emission spectra were then measured by optical spectrometry. The samples were then nebulized and transported to the plasma torch. The intensities of the emission lines were then monitored by photosensitive devices and the corresponding data is collected (EPA, 1996).

- **Analysis Methods**

The results from the tests were analysed using the Freundlich and Langmuir Isotherms. These two isotherms are most widely been used to describe the interaction of pollutants with the adsorbents and are important for analysing and optimising adsorption systems. The Freundlich model is also used in the estimation of adsorption intensity of the adsorbent in relation to the adsorbate (Muthusamy & Murugan, 2016). Langmuir model is used to estimate maximum adsorption capacity with respect to the monolayer coverage on the adsorbent surface (Muthusamy & Murugan, 2016). The adsorption efficiency (qe) was calculated using the general adsorption capacity equation, as shown in Equation 1 (Ribeiro et al., 2014).

$$q_e = \frac{(C_i - C_e)}{m} V \qquad (1)$$

Where
Ce = initial concentration (mg/L)
Ct = final concentration (mg/L)
M = mass of adsorbent (g)
V = volume of adsorbate (L)

Later, the equilibrium between adsorbent and adsorbate can be examined using Langmuir and Freundlich isotherms from Equation 2 and 3, respectively (Chung, et al., 2015).

$$\frac{1}{q_e} = \frac{1}{q_m} + \left(\frac{1}{k_L q_m}\right)\frac{1}{C_e} \qquad (2)$$

$$\ln q_e = \ln k_F - \frac{1}{n} \log C_e \qquad (3)$$

Where:
qe = equilibrium capacity (mg/g)
qm = maximum adsorption capacity (mg/g)
kL = Langmuir constant related to the energy of adsorption (L/mg)
kF = Freundlich constant related to adsorption capacity
n = Freundlich constant related to adsorption intensity
Ce = equilibrium concentration (mg/L)

Result and Discussion

- **Adsorption performance**

On overall, the decrement in concentration of Cr, Mn, and Pb ions were noticed in both corn cob pre-treated with hydrochloric acid and vinegar after the adsorption process. Figure 2 to Figure 4 show the comparison of the percentage removal on Cr, Mn, and Pb ions by two different pre-treated corn cobs. The samples were collected at 2 hr-intervals, with the last collection at 24 hrs. The legends in the graph show the respective heavy metal concentration of each heavy metal in the solution. "HCl" denotes adsorbent pre-treated with hydrochloric acid whilst "V" is adsorbent pre-treated with vinegar.

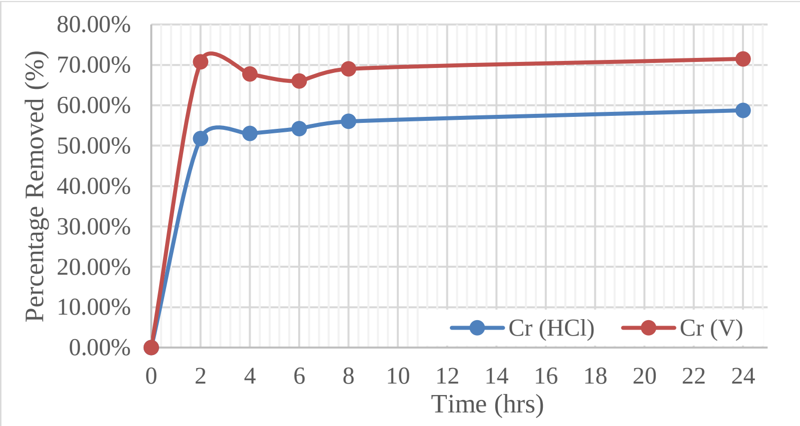


Figure 2. Percentage Removal of Cr ion

From Figure , the percentage removal of Cr using the corn cob pre-treated with HCl was from 51.75% to 58.75% while the percentage removal of using corn cob pre-treated with vinegar was from 66% to 71.5%. This shows similar removal percentage to a study conducted by Garg, et al (2007), where the corn cob adsorbent showed a percentage removal of 62%. It was discussed that this could be improved by decreasing particle size of adsorbent or increasing adsorbent dosage.

From the figure, it can be seen that the adsorbent reached saturation after 2 hrs as seen from the decrease of Cr concentration in the adsorbent from the subsequent readings. Overall, the corn cob pre-treated with vinegar performed better than the corn cob pre-treated with HCl. According to Mao et al. (2012), acetic acid, which is found in vinegar, enhances lignin removal. This, alongside with the removal of hemicellulose allows for more adsorption following increased exposed surface area of the cellulose when compared to HCl pre-treated corn cob, which typically only removes hemicellulose (Lynam, 2011; Pandey et al., 2014). This removal of lignin and hemicellulose exposes more surface area of the interior pores to be used as binding sites of the Cr ions (Albadarina, et al., 2012). In fact, as shown by a study by ALOthman et l., (2012), the percentage removal of Cr could be further increased to around 87.36% to 93.48% by decreasing the particle size of the adsorbent to approximately 37µm. The same study showed that percentage removal of Cr was optimum at 5g/l of adsorbent dosage for an adsorbate dosage of 80mg/l.

Next, the percentage removal of Mn ions by both HCl and vinegar pre-treated corn cob is shown in the Figure 3.

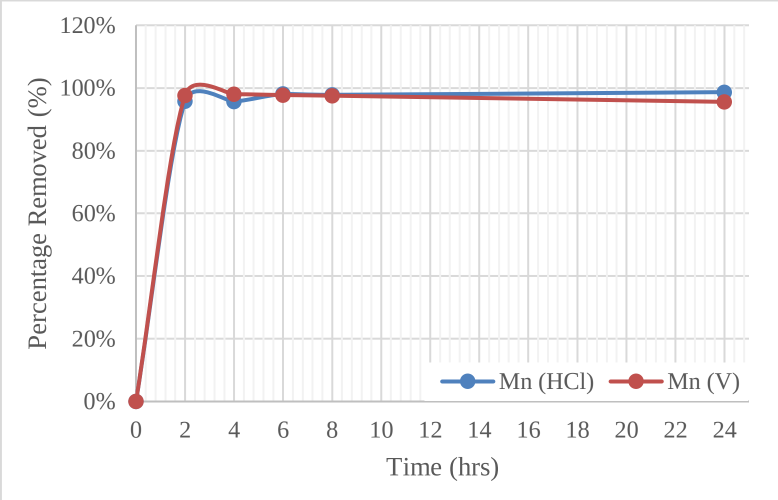


Figure 3. Percentage Removal of Mn

As seen from Figure , the percentage removal of Mn using corn cob pre-treated with HCl was highly efficient from 95.74% to 98.68%. Similarly, the percentage removal of Mn using corn cob pre-treated with vinegar was also similar to that of HCl pre-treated corn cob. The adsorption data shows that maximum uptake for Mn-HCl was 78.94mg/l after 24 hrs of adsorption. Mn-V showed a maximum uptake to be 78.4mg/l at 4 hrs of adsorption. According to an experiment by Norozi and Haghdoost (2016), using similar concentration of Mn, percentage removal at optimum levels was identified to be around 85%.

Previous study indicates that low pH of solution produces an increasing amount of H^+ ions on the adsorbent surface, which increases Mn hydroxyl (OH^-) ion participation in the adsorption process (Norozi & Haghdoost, 2016). This could explain the high removal percentage of Mn ions in the adsorption experiment. Although the two adsorbents performed similarly, the corn cob pre-treated with vinegar reached maximum capacity slightly earlier before the corn cob pre-treated with HCl. This could be due to the greater availability of binding sites (Lynam, 2011; Pandey et al., 2014; Albadarina, et al., 2012).

On the other hand, the percentage removal of Pb ion by both HCl and vinegar pre-treated corn cob is shown in Figure 4.

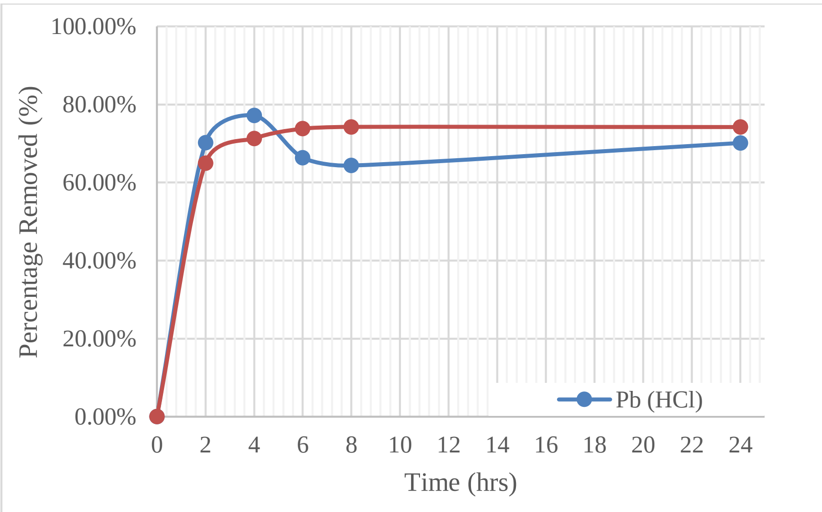


Figure 4. Percentage Removal of Pb

The percentage removal of Pb using HCl treated corn cob fluctuates, reaching optimum removal of around 77% at 4 hrs of adsorption. On the other hand, the percentage removal of Pb using vinegar treated corn cob reached optimum levels of around 74% at 8 hrs of adsorption.

According to Muthusamy & Murugan (2016), the percentage removal of Pb was similarly around 80% at an optimum adsorbent dosage of 2.5g/L. It was noticed that Pb-HCl showed a maximum adsorption of 1544mg/l from initial concentration 2000 mg/L after 4 hrs. The subsequent readings show that the adsorbent had reached saturation and the heavy metal was leaching back into the solution. This can be seen from the reduced uptake at 6 hrs and 8 hrs of 1327mg/l and 1287mg/l respectively from initial concentration 2000 mg/L. On the other hand, Pb-V reached maximum adsorption of 1485mg/l from the initial concentration 2000 mg/L after 8hrs of adsorption, with little decrease in uptake after saturation.

As discussed in this section, the removal percentage of Mn and Pb using both HCl and vinegar pre-treated corn cob was around 95 to 98% and 74 to 77% respectively, while the removal of Cr using both pre-treated corn cob was 51 to71%. The lower percentage removal of Cr compared to the removal of Mn and Pb may be due to the varying biosorption capacities of corn cob for different heavy metals, where the capacity of corn cob to adsorb Cr was significantly lower than Mn and Pb.

- **Adsorption Isotherms**

In order to describe the interaction between both adsorbate (Cr, Mn, and Pb ions) and adsorbent (HCl treated corn cob and vinegar treated corn cob), Langmuir and Freundlich isotherms were used to fit the experimental data modelled adsorption. The parameters for the proposed isotherm models utilizing both HCl and vinegar corn cob was expressed and discussed in Table 2.

Table 2. Parameter of Adsorption Isotherm for HCl and vinegar treated corn cob

		Cr-HCl	**Cr-V**	**Mn-HCl**	**Mn-V**	**Pb-HCl**	**Pb-V**
Freundlich	**1/n**	-0.807	-0.452	-0.027	-0.033	-0.402	-0.433
	log K_f	8.394	5.754	0.278	0.204	5.716	5.628
	R^2	**0.998**	**0.999**	**0.980**	**0.994**	**0.990**	**0.998**
Langmuir	**KL**	-38.940	-16.306	-0.039	-0.065	-9.459	-14.872
	Q_{max}	0.098	0.084	0.793	0.868	0.059	0.083
	R^2	**0.993**	**0.995**	**0.905**	**0.971**	**0.962**	**0.990**

For Cr-HCl and Cr-V, the R^2 values show high correlations at 0.998 and 0.999 respectively for Freundlich isotherm, and 0.993 and 0.995 respectively for Langmuir isotherm. Although both isotherms seem suitable, it ultimately shows that Freundlich isotherm is more appropriate in this experiment for the adsorption of Cr using both pre-treated corn cob adsorbents. Similarly, Garg, et al. (2007) showed that Freundlich isotherm was more suitable for the adsorption of Cr ions using corn cob.

For Mn-HCl and Mn-V, the R^2 values for Freundlich isotherm were 0.980 and 0.994 respectively, while the R^2 values for Langmuir isotherm were 0.905 and 0.971 respectively. Similarly, a study by Nassar, et al. (2004) showed that the adsorption of Mn ions using corn cob showed high correlation (R^2 = 0.97 and 0.99) to Freundlich isotherm.

Lastly, the R^2 values for Pb-HCl and Pb-V were 0.990 and 0.998 respectively for Freundlich isotherm, and 0.962 and 0.990 for Langmuir isotherm. Thus, the shape of the Freundlich isotherm is more favourable in the adsorption of Pb using HCl and vinegar pre-treatment. A study by Muthusamy & Murugan (2016) also showed that the adsorption of Pb using corn cob showed suitable correlations to both Freundlich and Langmuir isotherms.

As discussed earlier, the correlation coefficient for each adsorption experiment indicates that Freundlich isotherm is the most suitable isotherm. The Freundlich isotherm assumes that adsorption takes place on a heterogenous surface, occurring on sites at varying degrees of adsorption energy (Gautam and Chattopadhyaya, 2016). These points to the heterogeneity of the adsorbent, making the Freundlich isotherm the best model for this adsorption experiment.

Table shows that for Freundlich isotherm constant 1/n, all the values are less than 1. This indicates that the adsorption is a chemical process, meaning that the adsorption relies heavily on chemical bonding of the adsorbate on the adsorbent (Ajenifuja, et al., 2017). Values greater than 1 for K_f indicate a greater affinity for adsorption of metals (Al-Senani et al., 2018). Hence, the values of K_f for Cr (8.394 & 5.754) and Pb (5.716 & 5.628) indicate a favourable adsorption. On the other hand, Mn (0.278 & 0.204) does not seem to show favourable affinity according to the Freundlich isotherm.

Conclusions

In this study, it was identified that the corn cob using HCl and vinegar pre-treatment are effective in removing Cr, Mn, & Pb ions from aqueous solution. The usage of vinegar as a pre-treatment method of the adsorbent are proven successful, and in the case of the removal of Cr ions performed better than those pre-treated with HCl owing to the more surface area of the interior pores to be used as binding sites of the Cr ions.

For the adsorption isotherm models, the Freundlich isotherm was found to be more suitable than the Langmuir isotherm in the removal of Cr, Mn, and Pb ions from aqueous solution, proving the heterogeneity of corn cob as an adsorbent where the R^2 value is more than 0.98 for all the heavy metal ions removal. This indicated that the Freundlich equation agreed with the experimental data which the adsorption mechanism as chemical adsorption for Cr, Mn, and Pb ions from aqueous solution.

Thus, the results show that corn cob pre-treated with HCl and vinegar are indeed effective, and can be used in the removal of Cr, Mn, and Pb ions in optimum conditions. Hence, further study could be done on the optimal pH, adsorption time, and adsorbent particle size for increased adsorption capacity and efficiency of the adsorbent.

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