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Use of Waste Plastic Char as Adsorbent for Removal of Arsenic and COD from Aqueous Solution

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Abstract

In present study, the solid char derived from the pyrolysis of waste high-density polyethylene (HDPE) and polypropylene (PP) was tested for removal (adsorption) of inorganic arsenic (As^{5+}) and organic matters (COD) from water and wastewater, respectively. It was observed that the solid char could remove 60% of arsenic (+5) at a dose of 4 gm/L for a contact time of 30 min and the COD removal was 50% at a dose of 4 gm/L with a contact time of 25 min. In both cases the adsorption data was found to fit better with Langmuir model. The adsorption capacity of mixed plastic char for As^{5+} was observed to be in the range of 1.45 – 1.75 mg/gm and in the range of 60.625–67.9 mg/gm for COD. Proximate and ultimate analysis indicated that the pyrolytic char had a large quantity of volatile matter (46.50–48.0%), carbon (41.3–84.7%), and a small amount of moisture (1.2–2.5%). The calorific value and density of plastic char were found to be in the range of 13.50–17.50 MJ/kg and 1.55 – 1.60 gm/m³. FTIR spectra of mixed HDPE and PP waste pyrolytic oil showed the presence of mostly alkanes and alkenes. It was found that with the increase of pyrolysis temperature, the pore size of solid char increased. The XRD pattern of the plastic chars obtained in this study showed sharp diffraction crystalline peaks. The plastic char can be used for further research for removal of other contaminants from aqueous solution.

Keywords: Waste HDPE & PP; Plastic Char; Characterization; Adsorption; Arsenic and COD Removal.

1. Introduction

Plastic pollution is now the biggest concern in the world. UNEP report (2021) confirms that about 300 million tonnes of waste plastics are produced every year. Depending on internal structure and components, the plastic waste materials can take 50 to 500 years or more to complete breakdown (Muller et al., 2001). Plastic waste components have been shown to persist for more than 20 years in landfills (Tansel and Yildiz., 2011). Approximately 78% of household plastic waste is thermoplastics, composed mainly of high-density polyethylene (HDPE), low-density polyethylene (LDPE), polypropylene (PP), and polystyrene (PS). Polyethylene (PE), which includes HDPE, LDPE, and Linear Low-Density Polyethylene (LLDPE), is the most extensively used plastic raw material in India, accounting for 43% of total consumption, while PP accounts for 24%. Pyrolysis is a popular thermal recycling method for converting plastic waste into energy in the form of solid, liquid, or gaseous fuels at a temperature ranging from 300–900 °C. The use of liquid fuel as an alternative source of energy is well documented in various research papers (Dutta and Gupta., 2021; Sharuddin et al., 2016; Kumar and Singh., 2013). A significant amount of non-condensable gas produced during the pyrolysis process can be used in the industrial combustion process (Jung et al., 2010), or production of power from steam cycles through gas engines and turbines (Fernandez et al., 2011; Hossain & Davies., 2013). Several researchers (Martín-Lara et al., 2021; Jamradloedluk & Lertsatitthanakorn., 2014) also used the pyrolytic char as a solid fuel or soil amendment, or as an adsorbent. Several studies compared the properties of various types of biochar derived from the pyrolysis process and found that pyrolysis temperature and feedstock type are crucial factors in determining the effective use of biochar. Still, very few literatures are existing on the use of plastic pyrolytic char for heavy metals removal.

Arsenic (As) has been observed in ground or surface water in many regions of the world (Kobyas et al., 2013; Nidheesh & Singh., 2017). Nearly 108 countries in our world are affected by arsenic pollution in groundwater (Shaji et al., 2020). According to WHO report (2021), in India, arsenic contamination of groundwater beyond the acceptable level has been reported in the states of West Bengal, Jharkhand, Bihar, Uttar Pradesh, Assam, Manipur, and Chhattisgarh (Raessler., 2018). Arsenic exposure in humans from drinking water and food can result in cancer and skin lesions (Hong et al., 2014). Various treatment technologies such as adsorption, coagulation/precipitation, electrocoagulation, adsorption with electrocoagulation, ion exchange, membrane filtration, reverse osmosis have

been recognized for the arsenic removal from water. But the problems related to higher initial As concentration, varying pH of source water, maximum amount sludge generation, and making it cost-effective compelled the scientists to research more for developing new technology. On the other hand, through domestic and industrial effluents, different kinds of pollutants, such as organic and inorganic pollutants, were continuously introduced into aquatic environments. Because of these pollutants, a large portion of water streams was discarded as wastewater. COD signifies the amount of oxygen required for total chemical oxidation of oxidizable substances that are organic, inorganic, suspended, or dissolved in the water. Adsorption has recently been regarded as the most effective approach due to the low cost of the process, as well as its easy design and wide range of adsorbent options (Yoshitake et al., 2003; Xu et al., 2002). Activated alumina, fly ash, pyrite fines, manganese greensand, amino-functionalized mesoporous silicas, aluminium loaded Shirasu-zeolite, biochar, and other zeolites have been investigated (Kim et al., 2004; Goswami & Das, 2000; Subramanian et al., 1997; Bilici Baskan & Pala, 2011) as adsorbent materials. However, developing affordable and widely available adsorbents remains a major challenge. Adsorption has been extensively used in wastewater treatment to remove organic pollutants and heavy metals (Devi and Dahiya, 2010; Parande et al., 2009). Despite some drawbacks, such as hygroscopicity and pore-blocking, carbon materials have long been regarded as an ideal adsorbent due to their low cost. Martin -Lara et al. (2021) carried out research using a waste mixture of polypropylene (PP), polystyrene (PS), and polyethylene film (PE) and observed that pyrolysis temperature has a great impact on the yield of solid products. With the increase of pyrolysis temperature, the adsorption capacity of solid char obtained from the pyrolysis process also increases reaching a maximum of 7.91 mg/g at 550 °C. Singh et al., (2020) was conducted an experiment for adsorbing arsenic by plastic char derived from pyrolysis of waste Polyvinyl chloride (PVC), Polyethylene terephthalate (PET), and Polyethylene (PE). Among all the plastic char's tests performed, PE and PVC mixed char had maximum As removal rate, ranging from 71.6 to 99.4%, and PE and PET chars showed the lowest amount of sorption ranging from 12.4 to 32.5%. Jamradloedluk and Lertsatitthanakorn (2013) found that the plastic char obtained from HDPE waste plastic pyrolysis had a BET surface area, pore-volume, and pore size of 16.77 m²/gm, 0.2080 cm³/gm, and 496 Å, respectively. Though biochar has been widely used effectively by several researchers for COD removal (Khurshid et al., 2021; Sanou et al., 2017; Hata et al., 2016), the application of solid char in water treatment technologies was not tried by most researchers. The use of plastic char for the organic and inorganic matter removal in water treatment demands further research for use of char as a valuable resource and upscaling the technology more effectively.

The current research mainly concentrated on the use of waste plastic char derived from HDPE and PP pyrolysis as a low-cost and carbonaceous material for As and COD removal, as inferred by pyrolysis of plastic waste. Although a variety of sorbents have been used to remove As and COD from polluted sites, the use of chars derived from waste plastics is a new matter of concern. Furthermore, this is extremely beneficial because solving the problems of managing plastic waste and utilizing existing resources to adsorb heavy metals and organic pollutants. Batch adsorption equilibrium experiments were conducted to determine the optimal conditions for As and COD removal. The predominant mechanisms and sorption efficiency of the plastic char also reveal that it can be used effectively on larger scales for the removal of other heavy metals or organic pollutants.

2. Material and Methods

2.1 Feedstock

Plastic char samples were prepared using waste HDPE and PP as feedstock. The waste plastics of HDPE and PP were collected from the local dumping site. All the plastics were then washed with distilled water and dried in the oven for 24 hours. After that, the moisture-free plastic samples were grinded prior to pyrolysis. The proximate and ultimate characteristics of waste HDPE and PP samples are presented in Table 1.

2.2 Plastic char Preparation

The pyrolysis of waste HDPE and PP was conducted using a laboratory-scale batch reactor comprising of a condenser, and liquid collector (Fig. 1) at 400 °C, 425 °C, 450 °C, 475 °C, and 500 °C under a heating rate of 14 °C/min. In each run, 100 g of feedstock (HDPE: PP= 1:1) was taken inside the reactor. After that, the collected plastic char was sieved to achieve 0.5–1.0 mm in size (Fig. 2). Finally, the chars (in form of pellets) were oven-dried for 24 hours at 105 °C and kept in a vacuum desiccator for further use as an adsorbent.

2.3 Plastic char Characterization

Physical properties such as calorific value, moisture content, density were measured for the solid char derived from pyrolysis of virgin HDPE and PP samples. The elemental composition of the char was characterized using a CHNS analyzer. The plastic chars derived from pyrolysis at different temperatures (400 °C, 450 °C, and 500 °C) were characterized by Scanning Electron Microscopy (SEM) (Model: JSM-IT200, JEOL) to determine the surface topography and X-Ray Diffraction (XRD) study (Model: PANalytical X-PERT PRO) was performed to determine the crystallographic structure of the material. Calorific value was determined by using a bomb calorimeter (Manufacturer: Mohan Brothers) as per ASTM D 5865. The Brunauer-Emmett-Teller (BET) surface area was determined by the Autosorb-analyzer, Quanta Chrome. Solid char samples were mixed with spectroscopic grade dried KBr and compressed into pellets to obtain FTIR absorption spectra. FTIR spectra were recorded between the wavenumber of 4000 cm^{-1} and 400 cm^{-1} with a resolution of 4 cm^{-1} . Prior to FTIR analyses, all solid char samples and KBr were oven-dried overnight at 60 °C.

Table 1: Proximate and Ultimate analysis for waste HDPE and PP samples

Properties	Waste HDPE Sample (Taking average of 3 replicated experiments)	Waste PP Sample (Taking average of 3 replicated experiments)
Proximate Analysis		
Moisture Content (%)	1.56	1.65
Volatile Matter (%)	89.25	88.25
Fixed Carbon (%)	1.3	1.6
Ash Content (%)	4.65	4.9
Ultimate Analysis		
Carbon (%)	78.20	76.70
Hydrogen (%)	12.875	12.84%
Nitrogen (%)	0.375	0.32
Sulphur (%)	Negligible	<0.1

Fig. 1: Experimental batch reactor setup for the pyrolysis process

Fig. 2: Plastic char

2.4 Chemical Analysis of Aqueous Samples

Parameters of water and wastewater samples like turbidity, pH, chloride, TDS, Alkalinity, hardness, iron were analyzed by following the standard procedures. Arsenic content was measured by SDDC spectrophotometric method (APHA, 1992). COD was determined by the open reflux method. The adsorption studies were carried out with the char derived from pyrolysis of mixed (HDPE:PP as 1:1) plastic to remove arsenic and COD from water and wastewater, respectively. Stock sodium arsenate solution of 100 mg/L of As^{5+} was prepared for the experiments. From this arsenic stock solution, 10 mg/L of the working arsenic solution was prepared which was used for the adsorption experiments. All the solutions were prepared using NIT Sikkim tap water. The pH of the As^{5+} -spiked water was adjusted to 7.0 by the addition of sodium hydroxide (NaOH).

2.5 Arsenic Sorption Kinetics

The uptake capacity of the plastic chars to adsorb As^{5+} and organic matter was analyzed by Langmuir and Freundlich isotherms. The Langmuir model is based on the assumption that the adsorbent has a fixed amount of adsorption sites and that sorption on the adsorbent surface is a monolayer. The Freundlich model, on the other side, assumes that the adsorbent surface is heterogeneous and that sorption on it is multilayer.

Langmuir model is represented as:

$$q_e = \frac{C_e K_a q_m}{1 + C_e K_a} \text{-----(i)}$$

The Langmuir isotherm can be expressed in linear form as:

$$\frac{C_e}{q_e} = \left(\frac{1}{q_m}\right) C_e + \frac{1}{K_a q_m} \text{----- (ii)}$$

where q_m is the monolayer sorption saturation capacity (mg/g) and K_a represents the enthalpy of sorption (L/mg)

On the other hand, the Freundlich isotherm is showed as:

$$q_e = K_f C_e^{1/n} \text{----- (iii)}$$

and also, in the linearized form:

$$\ln q_e = \ln K_f + 1/n \ln C_e \text{----- (iv)}$$

where C_e is the equilibrium concentration (mg/L), q_e is the amount of adsorbate adsorbed (mg/g), and K_f and n are Freundlich constants.

A kinetic study was conducted to find out the required to attain the equilibrium condition. To conduct the kinetic study, 4 gm/L of mixed plastic pyrolysis char was contacted with 10 mg/L of As^{5+} solution or wastewater solution in an Erlenmeyer flask for different contact times of 5 – 35 min. The flasks were put in a horizontal shaker and after the period of contact, the suspensions were filtered through a 0.45- μm filter before analysing for remaining As^{5+} or COD content. For the isotherm adsorption study, a similar procedure was followed with varying doses of adsorbent (pyrolysis char) and was contacted for a period equal to the equilibrium adsorption times obtained from the kinetic studies.

3. Results and Discussion

3.1 Effect of Temperature on Yield of Char

Temperature is the most important operating parameter in pyrolysis because it controls the cracking process of the polymer chain. The van der Waals force attracts molecules together, which prevents them from collapsing. When the temperature of a system rises, the vibration of molecules within the system rises, and molecules tend to evaporate away from the object's surface. The carbon chains break when the energy induced by the van der Waals force along the polymer chains exceeds the enthalpy of the C–C bonds in the chain (Sobko, 2008). Thermal pyrolysis is an endothermic process, i.e., a significant amount of heat is required to bring the feedstock to the reaction temperature. During pyrolysis, polymer materials were heated to high temperatures, and their macromolecules were broken down into smaller molecules, yielding a wide range of hydrocarbons. For the current study, 100 gm of mixed waste (HDPE:PP= 1:1) sample was taken for the pyrolysis process using the laboratory-

scale batch reactor, at temperatures of 400 °C, 425 °C, 450 °C, 475 °C, and 500 °C under a heating rate of 14 °C/min. The liquid, gas, and solid char yield is shown in Fig. 3A, 3B, and 3C by taking the average of three replicate experiments with an error bar (using standard deviation). From Fig. 3A, it was observed that the maximum amount of liquid (60%) was yielded at 475 °C, and then, the liquid yield decreased with the increase of temperature up to 500 °C. The same trend was also observed for thermal pyrolysis of virgin HDPE and PP in another study which was conducted by the author (Dutta & Gupta, 2021). The yield of solid char decreased from 27% to 12.67% at temperatures of 400 and 500 °C (3C).

Fig. 3A: Yield of liquid for pyrolysis of mixed waste HDPE and PP

Fig. 3B: Yield of gas for pyrolysis of mixed waste HDPE and PP

Fig. 3C: Yield of solid char for pyrolysis of mixed waste HDPE and PP

3.2 SEM and XRD Analysis of Plastic Char

The SEM analysis method involves for the examination of changes in material morphology at the micro-scale. Each sample (P1, P2 & P3) was depicted at 1000X, and 5000 X magnifications (Fig. 4A to Fig. 4C). The plastic char samples showed significant changes in the structure when it was prepared at different temperatures (400 to 500 °C). The SEM images of plastic char showed rough morphology and undefined geometry, which was in alignment with the findings of other studies on plastic char (Singh et al., 2020; Singh et al., 2021; Jamradloedluk and Lertsatitthanakorn, 2013). It was noticed that the surface texture of char became rougher and more porous when either the operating temperature or the residence time (25 min to 35 min) was increased. At 400 °C, the sample had a relatively flat surface without clear visible pores. Chars obtained at lower temperatures showed relatively smooth surfaces with tubular shapes. Raising the temperature to 500 °C effectively changed the surface morphology and more pores were observed. The surface structure of the material had lost its smoothness and cracks were evident. Increase of the surface area and pore volume of the solid char material till a maximum temperature due to devolatilization of some biomass components was also reported earlier (Angin et al., 2014; Brunson et al., 2014); however, changes in surface characteristics were also related to other factors such as the feedstock source, experimental conditions, equipment used. Due to the accumulation of charge on the surface of P3 char, a slightly blurred image was formed. Similar blur images caused by charge accumulation were observed in an earlier study conducted by Singh et al., 2020.

Fig. 4A: SEM images of plastic char prepared at 400 °C (P1)

Fig. 4B: SEM images of plastic char prepared at 450 °C (P2)

Fig. 4C: SEM images of plastic char prepared at 500 °C (P3)

The XRD pattern of the plastic chars (P1, P2, & P3) obtained in this study showed sharp diffraction crystalline peaks. In the case of P1, the spectrum showed strong peaks at around 14.11° , 16.79° , 18.57° , 21.5° , and 23.85° , while for P2 at 14.19° , 17.02° , 18.63° , 21.71° , and 24.02° and for P3 at 14.11° , 16.93° , 18.55° , 21.47° , and 23.77° (Fig. 5A, Fig. 5B, and Fig. 5C). Higher counts of the peak were observed at higher temperatures indicating that an increase of temperature increased the crystallinity of solid char.

Fig. 5A: XRD image of plastic char prepared at 400 °C (P1) Fig. 5B: XRD image of plastic char prepared at 450 °C (P2)

Fig. 5C: XRD image of plastic char prepared at 500 °C (P3)

3.3 Properties of Pyrolytic Char

It was found that with the increase of pyrolysis temperature (400 to 500 °C), the pore size of solid char increased (4.7-4.9 to 6-6.5 nm). Therefore, the solid char obtained from the waste plastic pyrolysis at 500 °C was used for the adsorption study. The obtained char possesses a good calorific value (13.50-17.50 MJ/kg), volatile matter (46.50-48.0%), and is rich in C (41.3–84.7 %), while N and H contents of 0.10–2.78 % and 1.83–5.17 % were relatively low. This was consistent with the characteristics of the chars previously derived by Fang et al., (2016). Proximate analysis of waste plastic char showed less moisture content. Some studies also stated that char obtained at low temperature (300–500 °C) for metal removal is more favourable than char derived from pyrolysis at a higher temperature (700–900 °C). Various Properties of the char (derived at 500 °C) is presented in Table 2.

Table 2: Properties of mixed waste plastics (HDPE and PP) pyrolysis char (P3) prepared at 500 °C

Properties	Experimental Values
Calorific value	13.50-17.50 MJ/kg
Carbon	41.3–84.7%
Nitrogen	0.10–2.78 %
Hydrogen	1.83–5.17 %
Moisture content	1.2-2.5%
Density	1.55 - 1.60 gm/m ³
BET surface area	10.5-12.8 m ² /g
Pore size	6-6.5 nm

3.4 FTIR Analysis of Plastic Char

FTIR analysis was performed to characterize various functional groups on the surface of plastic char (Fig. 6). FT-IR spectroscopy is used extensively for material characterization in the plastics industry. Results revealed that the surface chemistry of plastic char is largely varied with an increase in pyrolysis temperature. Alkanes are identified by absorptions because of C–H bending at 1470-1450 cm⁻¹. The stretching vibration of the C=C bond typically produces a moderate band in the range 1680-1640 cm⁻¹. The strongest bands in the spectra of alkenes in the region 1000-650 cm⁻¹ are those attributed to the carbon-hydrogen bending vibrations of the =C–H group. The –C≡C– stretch appears as a weak band from 2260-2100 cm⁻¹. Indeed, the peaks at 873 cm⁻¹ and 713 cm⁻¹ indicate CO₃ presence (Djebaili et al., 2015). The peak at 1423 cm⁻¹ denotes the presence of C=O and O-H bonds (Pereira et al., 2017); though, it may also indicate the existence of C-O-O stretches in the char (Kumar et al., 2018). The peak at 1030 cm⁻¹ indicates the presence of kaolin in char. The peak at 1241 cm⁻¹ represents the existence of amines in the plastic char (Tang et al., 2018), with the weak peak at 1576 cm⁻¹ also showing the presence of amides. The presence of aliphatic ether C-O or alcoholic C-O is indicated by the peak at 1091 cm⁻¹, although Si-O-Si bonds in the char could also be present (Claoston et al., 2014). A strong peak at 905.415 cm⁻¹ and 717.39 cm⁻¹ denotes the C-H bending. The other peaks of higher intensity identified around 1020 cm⁻¹ and 870 cm⁻¹ correspond to the vibrations of the C-H bonds of aromatic rings. Carboxylic groups consist of C=O and can be found at 1749-1728 cm⁻¹. Lactones can be detected by peaks near 1610 cm⁻¹ (Shen et al., 2018). A medium peak appearance at the region 3700-3584 cm⁻¹ corresponds to O-H stretching also showing the presence of either alcohol or phenol.

Fig. 6: FTIR spectroscopy of mixed waste plastic (HDPE & PP) pyrolysis char (P3) prepared at 500 °C

3.4 Use of solid char as Adsorbent

The solid char obtained from the pyrolysis process was tested for organic matter (COD) removal from wastewater and inorganic matter (arsenic) removal from an aqueous solution by adsorption onto the char. Batch adsorption tests were conducted to study the adsorption of As^{5+} onto mixed plastic pyrolysis char. Laboratory tap water of NIT Sikkim (characteristics presented in Table 3) was spiked with As^{5+} (Na_3AsO_4) for use in the adsorption study. The water was having low TDS, hardness, and alkalinity with mildly acidic pH. Several researchers (Dutta et al., 2021; Sumathi and Alagamuthu., 2014; Ramaswami et al., 2000) reported that the highest removal efficiency for arsenic was observed at pH 7. Therefore, the pH of the As^{5+} -spiked water was adjusted to 7.0 by the addition of sodium hydroxide (NaOH). For the adsorption kinetic tests, char (size 3 – 4 mm) obtained from pyrolysis at 500 °C (P3) was taken (4.0 gm/L) and put in As^{5+} -spiked (10 mg/L) water and shaken for different contact times (5 – 35 min). Arsenic adsorption was found to increase with time and beyond 30 min of contact time, the incremental increase in adsorption was insignificant (Fig. 7). Therefore, the time of equilibrium was considered to be 30 min and As^{5+} removal of 60% was observed. After the equilibrium time, the remaining vacant surface sites are difficult to be occupied by the adsorbate molecules because of repulsive forces between the adsorbate molecules on the solid and bulk phases (Kannan et al. 2010; Das and Mondal, 2011). Isotherm adsorption study was also conducted by varying the dose of mixed plastic pyrolysis char (P3) from 2.0 to 4.50 gm/L in a 10 mg/L solution of As^{5+} keeping the contact time uniform as 30 min (equilibrium time). Arsenic removal by waste plastic char was observed to vary from 35 to 58% (Fig. 8).

Table 3: Characteristics of Tap Water, NIT Sikkim

Parameters	Values
pH	6.5-6.7
Iron (mg/l)	0.00
Arsenic	0.00
TDS (mg/l)	20-30
Chloride (mg/l)	15-25
Hardness (mg/l as CaCO_3)	10-20
Alkalinity (mg/l as CaCO_3)	25-30
Turbidity (NTU)	0

Fig. 7: Removal of arsenic for variation of contact time

Fig. 8: Removal of arsenic for varying doses of char

The experimental data fitted well for both isotherm models and better fit was obtained for Langmuir isotherm ($R^2 = 0.9953$) in comparison to Freundlich isotherm ($R^2 = 0.9849$) (Fig. 9 and Fig. 10).

Fig. 9: Linearized plot for Freundlich isotherm for As removal

Fig. 10: Linearized plot for Langmuir isotherm for As removal

From the linearised plot of Langmuir isotherm (Fig. 10), K_a and q_m values were found 0.596 and 2.141, respectively. The Langmuir isotherm equation can be expressed as:

$$q_e = \frac{1.276C_e}{1+0.596C_e}$$

The Langmuir isotherm is plotted in Fig. 11. The adsorption capacity of mixed plastic char for COD was observed to be quite promising in the range of 1.45-1.75 mg/gm

Fig. 11: Langmuir isotherm for As^{5+} adsorption onto mixed waste plastic (HDPE and PP) pyrolysis char

The pyrolytic char of mixed waste plastic was also tested for removal of COD from wastewater. The char obtained from 500 °C (P3) was used at a dose of 4 gm/L. Rasheed et al. (2017) observed the removal of organic matter when char and biochar were used for wastewater treatment. Several studies were also conducted for wastewater treatment by using biochar (Lewis et al., 1995; Manyuchi et al., 2018; Yaseen et al., 2019). In the present study, the kitchen wastewater was taken from NIT Sikkim hostels, and after adsorption in a batch process, pH and COD were measured at different contact times (05-35 min). The raw wastewater pH and COD were found to be 7.4 and 485 mg/L, respectively. The removal of COD steadily increased with increasing contact time till 25 min, beyond which no further increase in removal was observed (Fig. 12). The isotherm adsorption study was conducted with contact time of 25 min (equilibrium time) with varying doses of char from 2 to 4.0 gm/L (Fig. 13). It was observed with the increase of char dose, the COD removal increased significantly. Maximum 50% removal of COD was observed at a dose of 4 gm/L. Langmuir and Freundlich isotherm models were applied to the isotherm sorption data. The experimental data fitted better with Langmuir isotherm model ($R^2 = 0.91$) and was observed not to fit with Freundlich isotherm model ($R^2=0.562$) (Fig. 14 and Fig. 15).

Fig. 12: Removal of COD for varying contact time

Fig. 13: Removal of COD for varying doses of char

Fig. 14: Linearized Freundlich isotherm for COD removal Fig. 15: Linearized Langmuir isotherm for COD removal

From the linearized plot of Langmuir isotherm, K_a and q_m values were found 0.01 and 84.03, respectively.

Therefore, the Langmuir isotherm equation can be expressed as:

$$q_e = \frac{0.8403C_e}{1+0.01C_e}$$

The Langmuir isotherm is plotted in Fig. 16.

Fig. 16: Langmuir isotherm for COD removal onto mixed waste plastic (HDPE and PP) pyrolysis char

The adsorption capacity of mixed plastic char for COD was observed to be quite promising in the range of 60.625-67.9 mg/gm (Fig. 16).

The char should also be tested with arsenic-contaminated natural water samples in both batch and column studies to ascertain its effectiveness as an adsorbent for practical applications. Similarly, column studies with wastewater samples for removal of COD would be necessary to evaluate char as an effective adsorbent for practical applications of wastewater treatment.

The As sorption and COD removal experiments were statistically analyzed using Analysis of Variance (ANOVA). ANOVA was applied to examine the hypothesis regarding the need for the char dose applied and to confirm the sorption capacity of different plastic char. The study analyzed the influence of independent variables (applied char dose) on dependent variables (As or COD sorption). p-values were used to denote statistically significant values. The level of significance was set at $p < 0.05$. For As removal, the value of F for a single way adopted was

found to be 26.555, which is greater than the F critical value of 5.987. This confirmed that the null hypothesis is rejected with a 95 percent confidence level. Similarly, For COD removal, the value of F for a single way adopted was found to be 145.7, which is greater than the F critical value of 5.32. This confirmed that the null hypothesis is rejected with a 95 percent confidence level and therefore, the applied dose char has a major influence on the adsorption process.

4. Conclusion

Batch sorption experiments were used to explore the effect of plastic char on As and COD removal. Pyrolysis temperature has been found to be the most effective factor in controlling the surface properties of samples. It was found that with the increase of pyrolysis temperature (400 to 500 °C), the pore size of solid char increased (4.7-4.9 to 6-6.5 nm). The solid char obtained from the waste plastic pyrolysis at 500 °C was found to have a density of 1.55 - 1.60 gm/m³ with BET surface area 10.5-12.8 m²/gm. The plastic char samples showed significant changes in the structure when it was prepared at different temperatures (400 to 500 °C). It was noticed that the surface texture of char became rougher and more porous when either the operating temperature or the residence time (25 min to 35 min) was increased. The XRD pattern of the plastic chars (S1, S2, & S3) obtained in this study presented sharp diffraction crystalline peaks. Higher counts of peak in XRD of solid char at higher temperatures indicated increased crystallinity of char with increase of pyrolysis temperature. FTIR analysis was applied to characterize the various functional elements present in plastic char. The highest peak was observed at 717.39 cm⁻¹. Carboxylic groups and lactones were identified from the FTIR spectra of the char. The solid char was tested for removal (adsorption) of inorganic (As⁵⁺) and organic matters (COD) from water and wastewater, respectively. It was observed that the solid char could remove 60% of arsenic (+5) from an aqueous solution at a dose of 4 gm/L for a contact time of 30 min. The COD removal was 50% at a dose of 4 gm/L with a contact time of 25 min and the adsorption data was found to fit better with Langmuir model. The adsorption capacity of mixed plastic char for As⁵⁺ was observed to be in the range of 1.45 – 1.75 mg/gm and in the range of 60.625-67.9 mg/gm for COD. Langmuir isotherm fitted well than Freundlich isotherm. The use of plastic char for the organic matter removal and inorganic components from water solutions demands further research for upscaling the technology more effectively for removal of other contaminants. The char should also be tested with arsenic-contaminated natural water samples in both batch and column studies to ascertain its effectiveness as an adsorbent for practical applications. Similarly, column studies with wastewater samples for removal or COD would be necessary to evaluate char as an effective adsorbent for practical applications of wastewater treatment.

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