CFAES

Department of Food, Agricultural & Biological Engineering

Adsorptive removal of dyes using char derived from anerobic digestate

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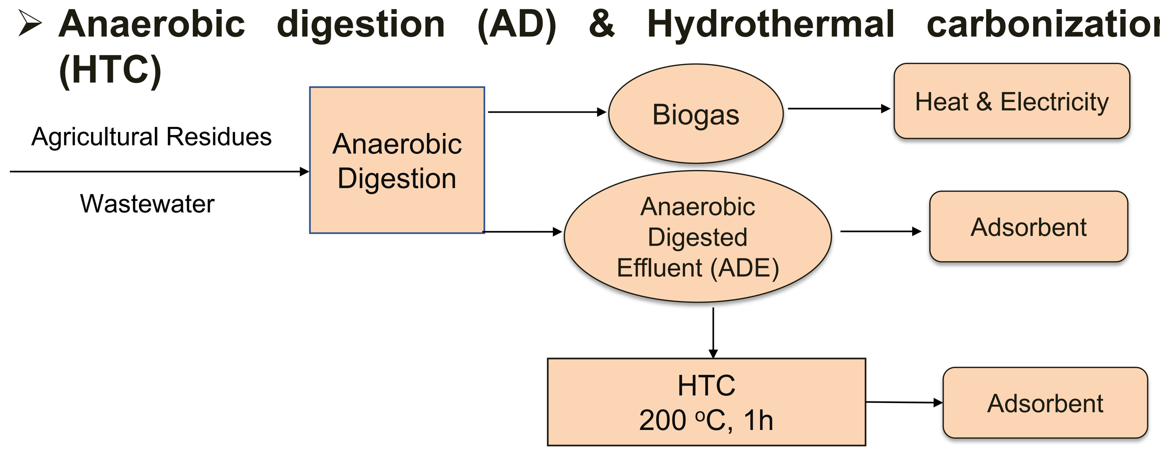
INTRODUCTION

- **Dye market:** Approximately 10,000 different dyes (over 7 x 10^5 tons) are used in food, pharmaceutical, cosmetics, paper and textile industries to impart attractive colors [1] [2]. The current market is about $6.38 billion and is projected that it will expand up to $10.13 billion by 2026 [3].
- **Environmental issues:**

Major Concerns [2] [4]
- Toxic and carcinogenic
- Fish kills
- Retards photosynthetic activity of aquatic plants
- Eye, skin and gastrointestinal irritation to humans

Fig 1- Dyes discharged in waterbody

- **Current dye adsorption methods:** Commercial activated carbon (CAC) adsorption is a widely used technique in comparison to other methods such as flocculation and coagulation [5].
- CAC is generally derived from conventional energy source such as coal, which is a non-renewable fuel source and leads to pollution rendering it to be not environment friendly [6].
- **Alternative dye adsorption methods:** In recent years, there has been a growing research interest to synthesize activated carbon from renewable, cost-effective precursors like agricultural residues such as corn stover, rice and wheat husk and byproducts obtained from industries like steel, wastewater treatment plants etc., [7] Few of the agricultural residues and wastewater are treated by anerobic digestion (AD).
- **Anaerobic digestion (AD) & Hydrothermal carbonization (HTC)**



OBJECTIVE

Investigate the efficacy of different adsorbents derived from activated ADE char (before HTC), HTC char and CAC on cationic and anionic dyes.

MATERIALS & METHODS

EXPERIMENTAL DESIGN

The experiments were performed based on Completely randomized design (CRD)

Adsorbate (Dyes)
- **Methyl Orange** (anionic dye) and **Methylene Blue** (cationic dye) are prevalently used industrial dyes and are considered as representative adsorbate compounds in this study
- Dye Concentrations (ppm)- 10, 25, 50, 100 & 200

Adsorbent (Char)
- Activated ADE char at 200°C (ADE-200) & 400°C (ADE-400)
- Activated HTC char at 200°C (HTC-200) & 400°C (HTC-400)
- CAC
- Adsorbent Dosage- 1 g/L

Process conditions
- Contact time between adsorbate and adsorbent- 24 h
- Temperature- 25 °C

ADSORBENT SYNTHESIS

The adsorbent synthesis protocol is as explained in Fig 2.

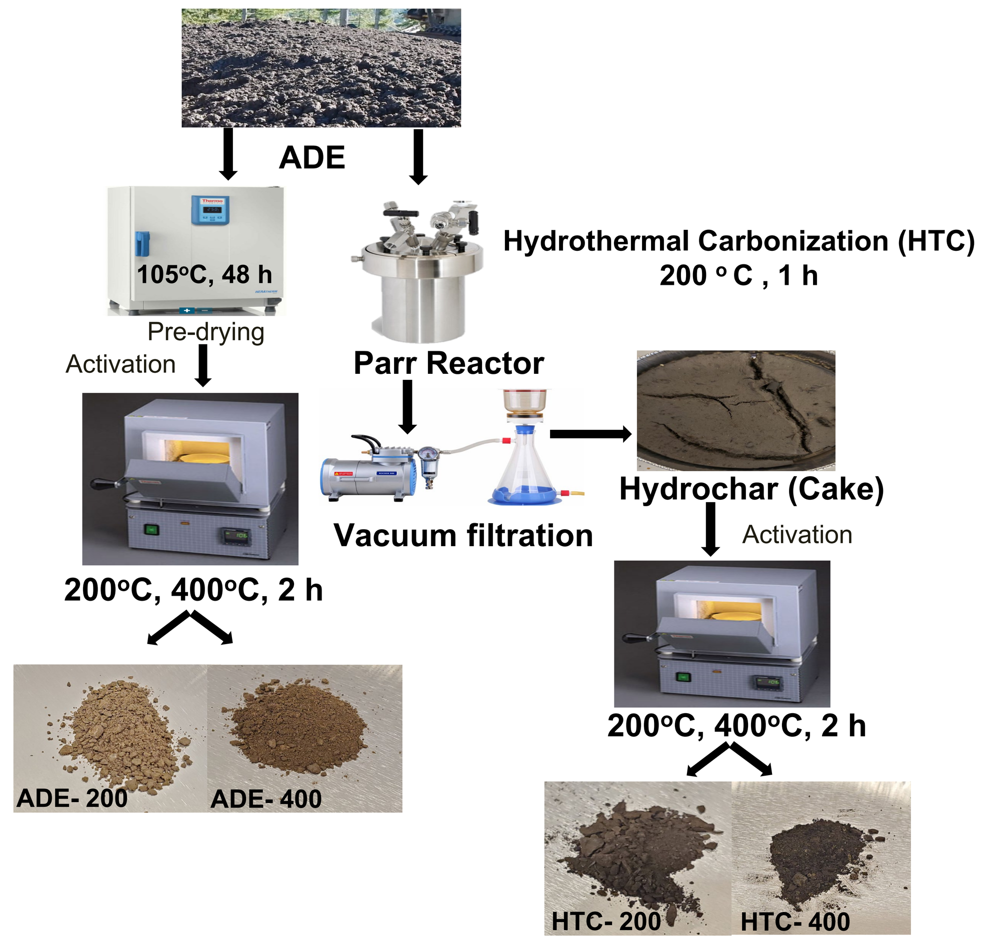


Fig 2- Flow diagram for synthesis of different adsorbents from ADE

ADSORPTION EXPERIMENT PROTOCOL

Batch experiments were performed to determine the concentrations of dye solutions before and after adsorption, as depicted in Fig 3.

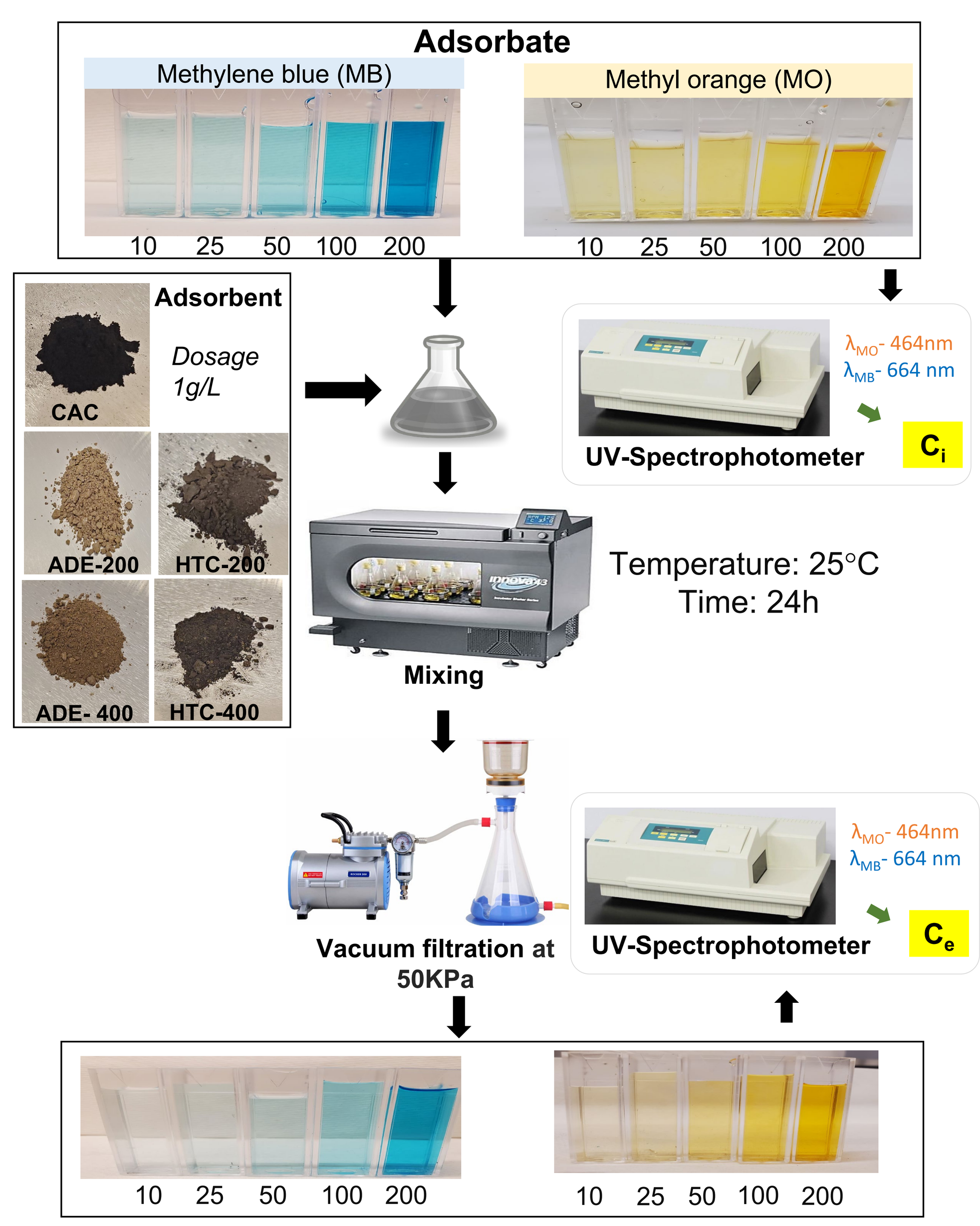


Fig 3- Flow diagram for adsorption experiments of MO & MB

Adsorption Capacity (mg/g) = $\frac{C_i - C_e}{M} * V$

Where,

C_i - Initial concentration of dye solution (ppm)
C_e - Equilibrium Concentration of dye solution (ppm)
V- Volume of adsorbate solution taken (L)
M- Mass of adsorbent used (g)

% Removal = $\frac{C_i - C_e}{C_i} * 100$

RESULTS & DISCUSSION

METHYL ORANGE ADSORPTION

The visual appearance of MO before and after adsorption is as depicted in Fig 4.

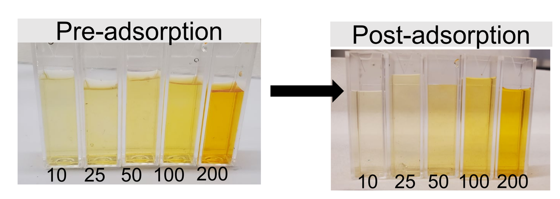


Fig 4- Pre and post adsorption of different concentrations of MO at 1g/L of HTC-400

Table 1 - Statistical analysis of adsorption capacity at 1g/L of different adsorbents for 200 ppm of MO at 95% confidence interval

Treatment	Mean Adsorption Capacity	Grouping based on Tukey- pairwise comparison				
CAC	199.16	A				
HTC-400	35.26		B			
HTC-200	28.14			C		
ADE-400	13.82				D	
ADE-200	6.36					E

- The maximum adsorption capacity attained is 35.260 ± 5.586 mg/g for 100 ppm of MO at 1 g/L dosage of HTC-400 as depicted in Fig. 5 (a).
- The maximum removal attained is about 71.808 ± 4.265 % for 10 ppm of MO at 1 g/L dosage of HTC-400 as depicted in Fig. 5 (b).
- The sorption capacity trend saturates at higher concentrations of MO indicating the saturation of active sites present in the adsorbent .
- Order of performance of adsorbents at 200 ppm of MO based on Table 1

CAC > HTC-400 > HTC-200 > ADE-400 > ADE-200

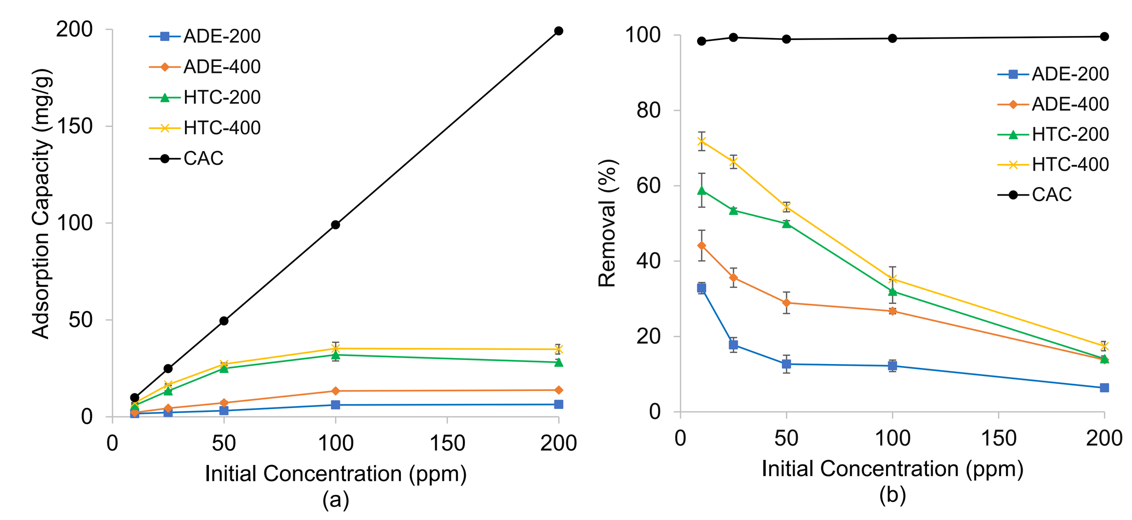


Fig 5- Plot of adsorption capacity & % removal of dye against initial concentration

METHYLENE BLUE ADSORPTION

The visual appearance of MB before and after adsorption is as depicted in Fig 6.

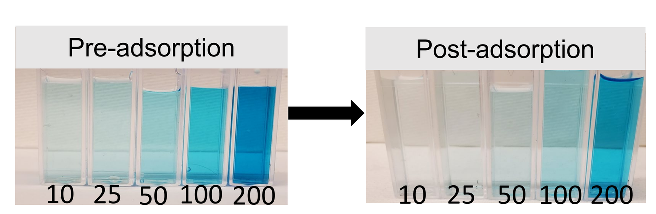


Fig 6- Pre and post adsorption of different concentrations of MB at 1g/L of HTC-400

Table 2- Statistical analysis of adsorption capacity at 1g/L of different adsorbents for 200 ppm of MB at 95% confidence interval

Treatment	Mean Adsorption Capacity	Grouping based on Tukey- pairwise comparison			
CAC	199.78	A			
HTC-400	103.74		B		
HTC-200	88.26			C	
ADE-400	28.18				D
ADE-200	23.27				D

- The maximum adsorption capacity attained is about 103.743 ± 9.264 mg/g for 200 ppm of MB at 1g/L dosage of HTC-400 as depicted in Fig. 7 (a).
- The maximum removal attained is about 91.958 ± 2.604 % for 10 ppm of MB at 1g/L of HTC-400 as depicted in Fig. 7 (b).
- The sorption capacity of ADE char seem to saturate, whereas the sorption capacity of HTC char increases with adsorbate concentration indicating their potential usage at higher concentration of cationic MB.
- The sorption capacity increases with increase in the dye concentration which may be due to enhanced initial mass transfer driving force (chemical potential difference which causes the particles from higher concentration to move towards lower concentration).
- Order of performance of adsorbents at 200 ppm of MB based on Table 2

CAC > HTC-400 >HTC-200 >ADE-400 >=ADE-200

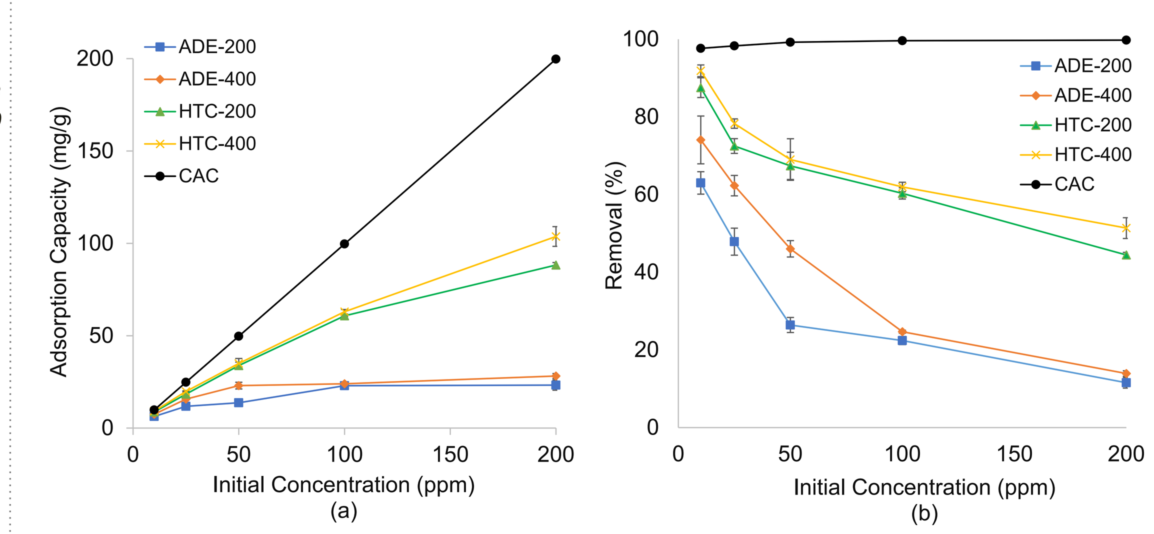


Fig 7- Plot of adsorption capacity & % removal of dye against initial concentration

PLAUSIBLE MECHANISM FOR ADSORPTION OF MB

- Electrostatic interaction seemed to play the major role. There is enhanced force of attraction between the positive charges in cationic dye and the negative charges present on the surface of the adsorbent which promotes better adsorption as depicted in Fig 8.

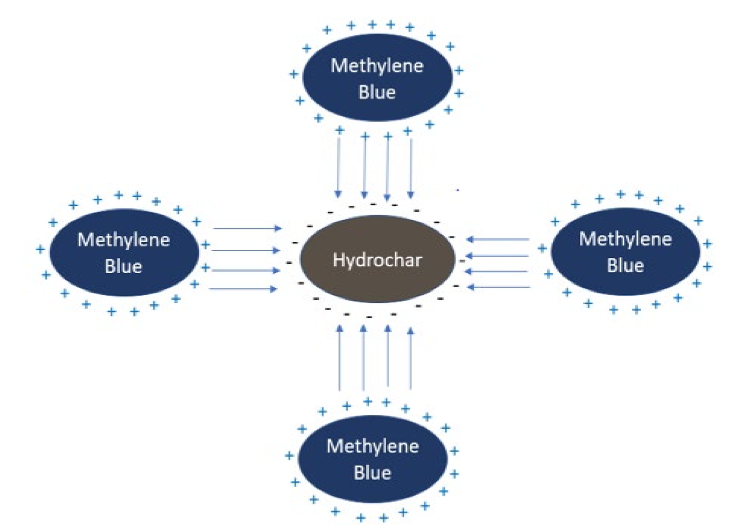


Fig 8- Electrostatic Interaction

CONCLUSION

- The adsorption performance of the HTC & ADE char was better in the case of MB
- The adsorption potential of HTC char was better owing to the enhanced porosity & surface area
- The performance of CAC was best in both the cases and colorless solution was attained in less than 2 hours

FUTURE WORK

- Enhance the sorption performance by chemical impregnation method
- Assess the potential of char to sorb dyes from industrial wastewater
- Investigate the efficacy of HTC char for nutrient and heavy metal reclamation

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