

### **10th International Conference**

on

Sustainable Solid Waste Management 21 – 24 June, Chania, Crete, Greece



# Application of Sewage Sludge Derived Hydrochar as an Adsorbent for Removal of Methylene Blue

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## **Outline**

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# Introduction

- It is estimated that India would produce ~3955 thousand metric tonnes dry sewage sludge, annually (Singh et al., 2020)
- SS generated during wastewater treatment is a huge management problem and responsible for 60% of the total wastewater treatment plant (WWTP) operational cost (Pilli et al., 2015)
- Common sludge disposal techniques in India are landfilling of centrifuged SS and anaerobic digestion (AD)
- Microbiological degradation of sludge to CH<sub>4</sub> and CO<sub>2</sub> by AD is a slow process and requires high retention time and larger digester volume (García-Cascallana et al., 2021)
- Hydrothermal pretreatment (HPT) is an emerging process due to its potential for enhancing resources recovery options from the SS (Barber, 2016; Malhotra and Garg, 2019)
- The hydrochar (HC), a hydrothermally carbonized product, has attracted significant attention in recent years due to its potential applications in various fields including agriculture, energy, and environmental remediation
- One of the simplest ways for HC recycling is in the form of adsorbent within the same or other WWTP
- In the present study, the HC samples recovered after HPTs (thermal hydrolysis and hydrothermal carbonization) of SS and centrifuged sewage sludge (CSS) were tested as an adsorbent

# Methodology (1/2)

Solids fraction of SS after thermal hydrolysis at 160°C for 0.5 h (HC\_160\_0.5) and 160°C for 1 h (HC\_160\_1). Solid fraction of CSS after HTC at 200°C for 3 h (HC\_200\_3) and modified HC\_200\_3 by 2M KOH (HC\_200\_3\_KOH)



Schematic and pictorial view of the TH reactor



Schematic and pictorial view of the HTC reactor

# Methodology (2/2)



Methylene blue removal (Dose = 1 g/L, time = 24 h, pH = 3.24-7, Concentration = 50-500 mg/L, temp = 30°C, Shaker speed = 100 rpm)

Kinetic and thermodynamic studies



Hydrochar (a) HC\_160\_0.5, (b) HC\_160\_1, (c) HC\_200\_3, (d) HC\_200\_3\_KOH

# **Results and Discussion: Characterisations (1/6)**

#### **Proximate and ultimate analysis of SS, CSS and HC samples**

Parameters	SS	CSS	HC_160_0. 5	HC_160_1	HC_200_3	HC_200_3_KOH		
Total solids (w/w)	2.1±.01	10.5 ±1.7	-	-	-	-		
Volatile solids (w/w)	57.3±0.03	61±0.19	51.2±0.28	52.5±0.2	47.7±0.78	-		
Fixed carbon (w/w)	3±0.3	4±0.8	5.2±0.09	5.4±0.13	5.2±0.15	-		
Ultimate analysis on dry basis								
C (%)	26.7	32.1	26.2	28.1	28.6	24.5		
H (%)	4.75	3.4	3.5	3.8	3.2	3.1		
N (%)	1.95	5.6	2.57	2.99	1.86	1.68		
S (%)	0.39	0.64	0.7	0.6	0.53	0.7		
O (%)	26.6	22.9	18.46	17.48	13.81	23.16		
*Ash (w/w)	39.6	35.3±0.2	43.6±0.71	42±0.58	47±0.4	48±0.6		
HHV (MJ/kg)	13.6	13.3			13.8	-		
*Ash = 100 – (C+H+N+S+O)								

### **Results and Discussion: Characterisations (2/6)**



SEM images of sludge and HC samples: (a) SS, (b) HC\_160\_0.5, FTIR spectra of HC and chemically modified HC samples (c) HC\_160\_1, (d) CSS, (e) HC\_200\_3, and (f) HC\_200\_3\_KOH

#### **Results and Discussion: Adsorption Studies (3/6)**



# **Results and Discussion: Adsorption Kinetics Studies (4/6)**

		Pseudo first order model			Pseudo second order model		
Adsorbents	q <sub>e,ex</sub> (mg/g)	q <sub>e</sub> (mg/g)	k₁ (h⁻¹)	R <sup>2</sup>	q <sub>e</sub> (mg/g)	k <sub>2</sub> (g*mg <sup>-</sup> <sup>1</sup> h <sup>-1</sup> )	R <sup>2</sup>
HC_160_1	192.36	133.8	0.103	0.91	200	0.44	0.98
HC_160_0.5	190	134.3	0.122	0.94	200	0.47	0.99
HC_200_3	178	24.5	0.267	0.65	178.6	11.2	1
HC_200_3_KOH	194	22.2	0.193	0.46	192.3	13	1

(initial MB concentration = 200 mg/L, pH = 7, adsorbent dose = 1 g/L, reaction time = 24 h, shaker speed = 100 rpm and temperature =  $30^{\circ}$ C)

Lagergern's pseudo-first order model

$$\log(q_e - q_t) = \log(q_e) - k_1 t$$

Lagergern's pseudo-second order models

$$\frac{t}{q_t} = \frac{1}{k_2 q_e} + \frac{1}{q_e} (t)$$

 $q_{e,ex}$  = Experimental adsorption capacity (mg/g)  $q_e$  = Calculated adsorption capacity (mg/g)  $q_t$  = Amount of adsorbent adsorbed at time t  $k_1$  and  $k_2$  are pseudo first order and second order model rate constant

# **Results and Discussion: Adsorption Isotherm Studies (5/6)**

	Langmuir isotherm			Freundlich isotherm		
Adsorbents	q <sub>max</sub> (m g/g)	K <sub>L</sub> (L/mg)	R <sup>2</sup>	K <sub>f</sub>	n	R <sup>2</sup>
HC_160_0.5	370	82	0.996	54	2.53	0.88
HC_160_1	370	84	0.998	53.9	2.5	0.83
HC_200_3	322	40	0.992	65.5	3.4	0.79
HC_200_3_KOH	454	95	0.981	66.2	2.3	0.75

(initial MB concentration = 200 mg/L, pH = 7, adsorbent dose = 1 g/L, reaction time = 24 h, shaker speed = 100 rpm and temperature = 30°C)

✤ Langmuir isotherm

$$q_e = \frac{q_{\max} K_L C_e}{1 + K_L C_e}$$

✤ Freundlich isotherm

$$q_e = k_f C_e^{1/n}$$

- q<sub>e</sub> = equilibrium sorption concentration of solute per gram of adsorbent (mg/g)
- $C_e$  = equilibrium concentration of solute (mg/L)
- $q_{max}$  = maximum adsorption capacity (mg/g)
- $K_L$  = Langmuir constant (L/mg)
- $K_F$  and n = Freundlich constants

## **Results and Discussion: Adsorption Thermodynamic Studies (6/6)**



for MB on HC samples

#### Thermodynamic parameters for MB adsorption

	ΔG°	ΔH°	ΔS°
Adsorbents	(kJ/mol)	(kJ/mol)	(J/molK)
HC_160_0.5	-11	7.7	62
	-11.7		
	-11.9		
HC_160_1	-11.3	4.7	53.3
	-11.8		
	-12.06		
HC_200_3	-10.7	11	72
	-11.4		
	-11.8		
HC_200_3_KOH	-12.1	15.2	90.3
	-13.1		
	-13.4		

 $\Delta G^{\circ} = -RT \ln K$   $\Delta G^{\circ} = \Delta H^{\circ} - T. \Delta S^{\circ}$  $\ln K = (\Delta S^{\circ}/R) - (\Delta H^{\circ}/RT)$ 

 $\Delta G^{\circ}$  = Free energy change;  $\Delta H^{\circ}$  = Heat of adsorption  $\Delta S^{\circ}$  = Entropy change; R = Universal gas constant (8.314 J/mol.K) T = Temperature in kelvin; K = Equilibrium constant

# Conclusions

- Hydrochar obtained from SS and CSS after HPT have MB removal efficiency of more than 90% and can be used for tertiary treatment of wastewater on the site itself
- Langmuir isotherm and pseudo-second-order kinetic models provided the best fit with the experimental equilibrium and kinetic data, respectively
- Thermodynamic analysis confirmed the feasibility of the adsorption process
- The utilisation of waste derived adsorbent will reduce the requirement of activated carbon from natural sources and lessen environmental impacts

# **Acknowledgements**

- Prime Minister's Research Fellow (PMRF) scheme under Ministry of Education, New Delhi, India
- Department of Science and Technology (DST), New Delhi, India
- ESED, Indian Institute of Technology (IIT) Bombay faculty and staff
- ✤ SAIF, IIT Bombay
- Solid and liquid waste research laboratory group



Solid and liquid waste research laboratory group

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**Thank You** 

$$q_e = k_f C_e^{1/n}$$

The model is based on adsorption on heterogeneous surface and is a widely used isotherm. The Freundlich isotherm is derived by assuming that the sites on the adsorbent have different affinities for different adsorbates with each site.

 $q_{\rm e}$  = equilibrium sorption concentration of solute per gram of adsorbent (mg/g)

 $C_e$  = equilibrium concentration of solute (mg/l)

 $K_F$  and n = Freundlich constants

The Lagergern's pseudo-first order model and pseudo-second order models.

$$\log(q_{e} - q_{t}) = \log(q_{e}) - k_{1}t$$
$$\frac{t}{q_{t}} = \frac{1}{k_{2}q_{e}} + \frac{1}{q_{e}}(t)$$

 $q_e$  and  $q_t$  = amount of adsorbent adsorbed at equilibrium and at time t (mg/g)  $k_1$  and  $k_2$  are pseudo first order and second order model rate constant, respectively.

 $q_e = \frac{q_{\max} K_L C_e}{1 + K_L C}$ 

Langmuir adsorption is valid for monolayer adsorption. The solid is assumed to have limited capacity  $(q_{max})$ . All the adsorption sites (i) are assumed to be identical, (ii) each site can retain one molecule of the given compound

 $q_{max}$  = maximum adsorption capacity (mg/g)

- $K_L$  = Langmuir constant
- $C_e$  = equilibrium concentration (mg/l)

#### $\Delta G^{\circ} = -RT \ln K$

Where R is the universal gas constant (8.314 J/(mol.K)), and T is the temperature in Kelvin.

 $\Delta G^{\circ}$  is also related to the entropy change ( $\Delta S^{\circ}$ ) and the heat of adsorption ( $\Delta H^{\circ}$ ) according to the following equation 2.6.  $\Delta G^{\circ} = \Delta H^{\circ} - T. \Delta S^{\circ}$ 

 $\ln K = (\Delta S^{\circ}/R) - (\Delta H^{\circ}/RT)$