Application of sewage sludge derived hydrochar as an adsorbent for removal of methylene blue dye from wastewater

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Introduction

A huge quantity of sewage sludge (SS) is produced from wastewater treatment plants (WWTPs) due to increasing population, industrialization, and urbanization. The global SS production of 45 million tonnes per year was reported in year 2017 (Liu et al., 2021). The safe disposal of SS is a major management problem due to its inherent moisture, presence of microbes, heavy metals (HMs) and emerging contaminants. Anaerobic digestion (AD) is a preferred option for SS stabilisation because of its energy recovery options. However, it is a slow process and requires higher retention time of 15 to 20 days (Pilli et al., 2015). Hydrothermal pretreatment (HPT) is an emerging technique which may produce easily separable solid and liquid streams having high recovery potential (Malhotra and Garg, 2019). The present study was aimed to examine potential of the sewage sludge derived solid residue, also known as hydrochar (HC) as adsorbent from the dye contaminated wastewater.

Materials and methods

The HC samples were obtained after HTP of SS and centrifuged SS (CSS). Two HCs were produced from SS after HTP at 160°C for durations of 0.5 h and 1 h (denoted as HC_160_0.5 and HC_160_1, respectively). The another HC was produced from CSS at HTP run at 200°C for a period of 3 h (represented as HC_200_3). The HC produced from CSS was further subjected to KOH activation and denoted as HC_200_3_KOH.

The adsorption studies with the HC samples were performed on the synthetic wastewater solution containing methylene blue (MB) dye. Initially, batch MB adsorption experiments with an adsorbent dose of 1 g/L and MB concentration of 200 mg/L were conducted by using adsorbent (HC_160_1) at unadjusted pH (= 3.24) to determine equilibrium time. The equilibrium adsorption time was found to be 24 h and further runs were performed for this much of duration. Subsequently, the effect of initial wastewater pH on the dye removal by various adsorbents was studied. Further, adsorption kinetic, adsorption isotherm and thermodynamic studies were also performed.

Results and discussion

SS, CSS and HC characterisation

The results from proximate and ultimate analyses of the SS, CSS and HC samples are presented in Table 1. HPT resulted in decrease of volatile solids (VS) in the HCs due to either conversion into CO_2 or solubilisation in liquid phase. A slight increase in fixed carbon of HC samples were observed due to volatilisation of VS and polymerisation during HPT. The ultimate analysis results showed loss of hydrogen and oxygen contents in the HC samples indicating occurrence of dehydration and decarboxylation reactions during the HPT. The HC samples were found porous while KOH modification improved homogeneity. Moreover, the presence of major functional group like hydroxyl, carbonyl and ether was also confirmed on the surface of the HC samples.

Adsorption studies

Effect of the initial solution pH

To examine the effect of initial wastewater pH, the adsorptions runs were performed on the MB containing wastewater at an initial pH of 3.24 (unadjusted), 7 and 9. The maximum MB removal was observed for the run conducted with wastewater pH of 7 for all HC samples. The removal of MB was increased from 75% to 95% with a change in pH from 3.24 to 7 and the decreased to 90% with further increase in pH from 7 to 9 for the run with HC_160_1. Similar results were obtained for other HC samples. Therefore, a solution pH of 7 was selected for further adsorption experiments.

Isotherm, kinetics and thermodynamic study

Adsorption isotherms and kinetic studies were conducted to evaluate the mechanism of MB dye adsorption onto sludge-based adsorbent and adsorption rate, respectively. The Langmuir model exhibited better fit to the adsorption data in comparison to the Freundlich model (based on the regression coefficient, R^2 value). Hence, this can be hypothesized that the MB adsorption on the adsorbent surface was monolayer.

The pseudo first and second order models were used to evaluate kinetics of the adsorption process. The MB adsorption data could be fit adequately in both the linear model equations. However, pseudo-second-order kinetic model equation can be suggested more suitable fit to the kinetic data based on R^2 value.

The thermodynamic study was performed to understand the effect of temperature on MB adsorption onto the SS derives adsorbents. The negative values of change in free energy (ΔG°) suggested the occurrence of favourable and spontaneous MB adsorption process. The change in enthalpy (ΔH°) value was found to be maximum for adsorption of MB by HC_200_3_KOH (ΔH° = 15.2 kJ/mol). The value suggests that adsorption process is favourable at higher temperature.

Table 1. Various physico-chemical parameters of SS, CSS and HC

Parameters	SS	CSS	HC_160 _0.5	HC_160 _1	HC_200 _3	HC_200 _3_KOH
Yield (%)	-	-	60	58	57	-
Total solids (w/w)	2.1±.01	10.5 ±1.7	-	-	-	-
Volatile solids (w/w)	57.35±.03	61±0.19	51.2±0.28	52.55±0.21	47.75±0.78	-
Fixed carbon (w/w)	3 ±0.3	4±0.8	5.2±0.09	5.45±0.13	5.25±0.15	-
Ultimate analysis on dry basis						
C (%)	26.7	32.14	26.17	28.13	28.6	24.56
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	35.35±0.2	43.6±0.71	42±0.58	47±0.4	48±0.6

Conclusions

The SS derived HC samples can be used for the removal of recalcitrant pollutants from industrial wastewater streams or sewage. The HTP process improves surface properties of the parent material. Further alkali modification improved the surface properties and resulted in the highest MB removal. The development of waste derived adsorbent will reduce the requirement of activated carbon from natural sources and lessen environmental impacts.

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