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Research Article

A COMPREHENSIVE INVESTIGATION INTO THE REMOVAL OF SO_2 FROM AQUEOUS MEDIUM USING CHEMICALLY MODIFIED *HIBISCUS SABDARIFFA* AS A NOVEL ADSORBENT

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Key words: *Hibiscus sabdariffa*, Modified, Adsorbent dosage, Batch studies, Efficiency

ABSTRACT

A green synthetic approach to synthesize HCl-treated *Hibiscus sabdariffa* leaf powder is used as an adsorbent to test feasibility of removing SO_2 efficiency of the improved adsorbent in terms of contact duration, SO_2 solution concentration and adsorbent dose. The optimized ideal conditions are 60 minutes (contact period), 1 gm (adsorbent dosage) and 20 ppm (concentration). HCl-treated *Hibiscus sabdariffa* leaf powder for removal of SO_2 was characterized by FTIR spectroscopy.

The study assesses adsorption kinetics and isotherms in addition to the optimal circumstances of contact time, adsorbent dosage, and SO_2 concentration. The outcomes show that the adsorption procedure adheres to the Temkin isotherm and the first-order kinetic model. This sheds light on the mechanism of adsorption as well as the connection between adsorbate concentration and adsorption capability. The study provides a viable approach for lowering SO_2 pollution in watery environments and emphasizes the significance of using natural waste materials for environmental restoration. Overall, this study adds a thorough understanding of the potential of HCl-treated *Hibiscus sabdariffa* leaf powder as an efficient and long-lasting adsorbent for SO_2 removal, with implications for enhanced public health and cleaner air.

INTRODUCTION

Sulphur dioxide has a subliminal leak of is occurring into the atmosphere. Human respiratory systems are adversely affected by SO_2, leading to respiratory diseases. Our plants, natural systems, and manufactured materials have suffered due to human activity and other methods. Numerous statistical studies demonstrate that SO_2 pollution impacts many urban areas and that there is a strong correlation between respiratory diseases and SO_2 levels (Chen, et al., 2021; Song, et al., 2014; Elder, et al., 2018; Razmkhah, et al., 2020; Hao, et al., 2019). Because of the complex topography of the Deccan Plateau in southern India, air flow systems are altered, and the twin cities of Hyderabad's air pollution are affected by distinct directional qualities or flow patterns. Topography considerations should include while assessing air pollution statistics from the pollution control board. Land cover taken into account when attempting to assess the circumstances of cities (Lee, et al., 2016; Zhang, et al., 2020; Guo, et al., 2021; kang, et al., 2020; Xu, et al., 2021; Zhang, et al., 2019).Urbanization, industrialization, mixed traffic,

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and industrial emissions are examples of human-caused sources of NOx and SOx pollution in cities.According to earlier investigations, industrial complexes in cities have allegedly polluted the city (Li, et al., 2018; Yi et al., 2014; Tailor, et al., 2014; Si, et al., 2019; Wang, et al., 2021; Ahiduzzaman, et al. 2021).In this regard, adsorption factors like duration, concentration, and dosage have been used in adsorption studies to develop and control technology for controlling SO_2 pollution and an aqueous solution of SO_2 by using green absorbent (*Hibiscus sabdariffa*).

Considering the need to reduce the SO_2 in natural sources like aqueous medium, a natural adsorbent is prepared from abundantly available *Hibiscus sabdariffa* leaf powder (non-conventional and biodegradable). *Hibiscus sabdariffa* is a novel adsorbent for adsorption of SO_2 from aqueous solutions. FTIR studies and control technology developed for controlling SO_2 pollution and aqua solution of SO_2 by using green absorbent, which is widely grown *Hibiscus sabdariffa* (Ahiduzzaman, et al. 2021; Jeffery, et al., 2021). In these current studies, adoption studies have been carried out with adsorption parameters such as time concentration dosage and temperature. FTIR studies to develop and control technology for controlling SO_2 pollution and aqua solution of SO_2 by using green absorbent which is widely grown in India, namely *Hibiscus sabdariffa* leaf powder.

MATERIALS AND METHODS

Sodium metabisulphite, para-rosaniline purchased from Sigma Aldrich.and Formaldehyde, Mercurous chloride,and HCl, from Sisco Research Laboratories (SRL). All the reagents of analytical grade and deionized water used for the preparation of all the aqueous solutions.

Characterization

We investigated HCl-treated *Hibiscus sabdariffa* leaf powder's optical properties with a UV–Visible spectrophotometer (UV 1800, Shimadzu, Japan).To investigate the functional groups of the HCl-treated *Hibiscus sabdariffa* leaf powder, Fourier-Transform Infrared (FT-IR) Bruker ATR-FTIR, U.S.A. Experiments are carried out in triplicates.

Adsorbent Preparation from *Hibiscus sabdariffa*

Hibiscus sabdariffa leaves are collected from our house garden as cultivated there. The leaves are air dried, sun dried and powdered using a domestic blender. Then the powder is stored in airtight container for future use and after which it is treated with 0.1 N HCl and further dried.

Preparation of Standard Samples

In 1000 mL standard flask, 15 gms of sodium meta bisulphites is dissolved in deionized water to prepare a 1000 ppm stock solution. Appropriate quantities to prepare working standards, to get the desired concentration of SO_2 from the stock solution.

Experimental Procedure for Percentage Removal of SO_2

The west gaeke method treats the prepared working standards with green adsorbent HCl-treated *Hibiscus sabdariffa*. Batch adsorption experiments are carried out concerning contact time (10,20,30,40,50,60 (in min)), SO_2 concentration (20,40,60,80,100 (ppm)) and adsorbent dosage (0.5,1.0,1.5,2.0 (in gm)) for the removal of SO_2. The initial and final concentrations of SO_2 color determined using the color compatibility method by the West-Gaeke method. Uv-Vis Spectrophotometer recorded the Percentage removal of SO_2. HCl-treated *Hibiscus sabdariffa* leaf powder how effective is at removing SO_2 from aqueous solutions is calculated with this equation

$$\%\,Removal = \frac{(SO2)i - (SO2)f}{(SO2)i}\ X\ 100$$

Where (SO_2) f=Final concentration after adsorption

(SO_2) i=Initial concentration before adsorption.

RESULTS AND DISCUSSION

FT-IR Analysis of Hcl-Treated *Hibiscus sabdariffa* Leaf Powder Treated with Hcl for Adsorption Capacity

For adsorption studies, consider functional group analysis. Figs. 1 and 2 show FT-IR spectra for SO_2 removal, illustrating the adsorbent behavior before and after adsorption. Aliphatic amines($R\text{-}NH_2$), Carbonyl(>C=O), C-H and C=C (Benzene) functional groups at 2998.80, 2936.89, 2872.54 (concerning $R\text{-}NH_2$) and many peaks were smoothened in the range of 2330-3000 cm^{-1} indicating the participation of adsorption by lysine, phenols, flavanoid, lysine groups. The carboxylic acids and acid groups also participate in the adsorption of NO_2 molecules. The decrease in the intensity of the peaks in 1790.16 to 1738.68 cm^{-1},1780.66 cm^{-1} to 1657.18 cm^{-1}, 1634.30 cm^{-1} to 1521.35 cm^{-1} indicates the involvement of aromatic and aliphatic amines and carbonyl groups. There is a tremendous change in the finger print region of FTIR.

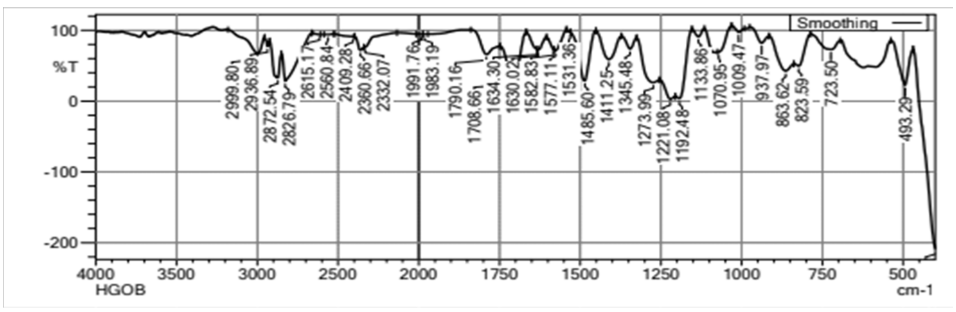

Fig. 1 FTIR of HCl-treated *Hibiscus sabdariffa* leaf powder before adsorption.

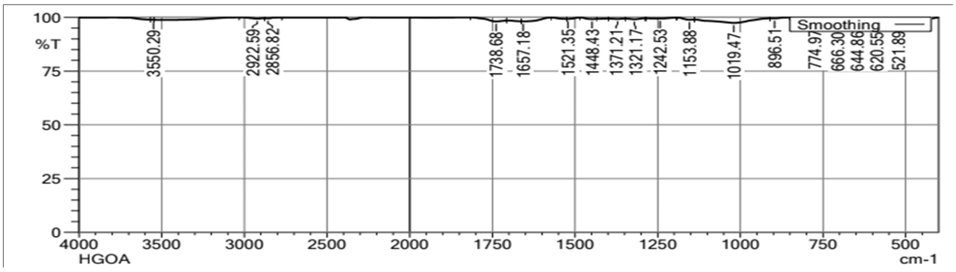

Fig. 2 FTIR of HCl-treated *Hibiscus sabdariffa* leaf powder after adsorption.

Betacyanin pigment in leaf extract has been decreased i.e in the range of 1653.918 cm^{-1} is not observed after adsorption, indicating protonated molecular form Betalanine and participated in the adsorption of NO_2 molecules.

Efficiency Studies of Hcl-Treated *Hibiscus Sabdariffa* Leaf Powder Dosages as Adsorbent for SO_2

We carried out batch adsorption studies with 0.5 gms to 2 gms of chemically treated *Hibiscus sabdariffa* leaf powder for the initial concentration of aqueous solution of SO_2 (Table 1). Fig. 3 shows the removal of SO_2 ions with various doses of chemically treated *Hibiscus sabdariffa* leaf powder, with a dosage optimum of 1.0 gm. The percent removal of SO_2 ions decreased from 1.0 gms to 2.0 gms as the dose increased, indicating that the optimal dose of 1.0 gm.

Tab. 1. Batch adsorption studies for the dosage of the adsorbent.

HCl-treated *Hibiscus sabdariffa* (60 mins, 20 ppm)				
Adsorbent dosage	0.5	1	1.5	2
OD	0.2	0.05	0.07	0.09
Final concentration	30	7	10	13
% Removal	25	82.5	75	67.5

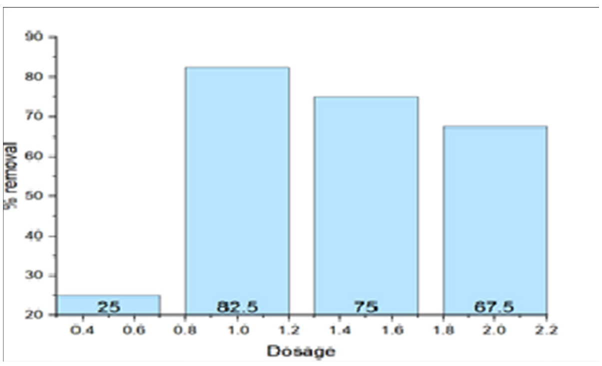

Fig. 3 Effect of HCl-treated *Hibiscus sabdariffa* leaf powder dosages on % removal of SO_2. **Note:** % Removal.

Efficiency Studies of Hcl-Treated *Hibiscus sabdariffa* Leaf Powder With Contact Time Adsorbent for SO_2

A 20 ppm aqueous SO_2 solution with 1 gm of HCl-treated *Hibiscus sabdariffa* leaf powder was used to determine the time intervals (Table 2).

Tab. 2. Batch adsorption studies with respect to the dosage of the adsorbent.

HCl-treated *Hibiscus sabdariffa*(20 ppm, 1 gm Adsorbent)						
Contact time	10	20	30	40	50	60
OD	0.26	0.24	0.2	0.16	0.14	0.05
Final concentration	39	37	30	24	20	7
% Removal	2.5	7.5	25	40	50	82.5

As seen in Fig. 4 the percent elimination increased as contact time increased, with 60 minutes being the optimum contact time with maximum of 82.5% SO_2 removal from aqueous solutions.

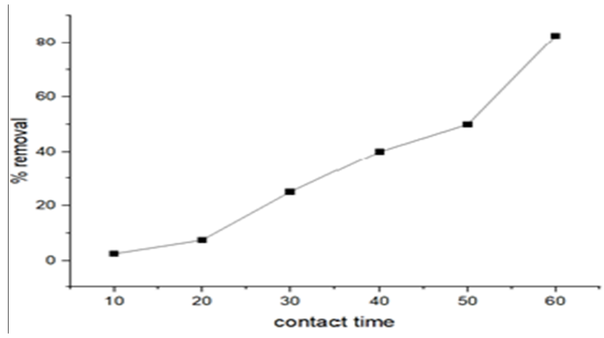

Fig. 4 Effect of HCl-treated *Hibiscus sabdariffa* leaf powder adsorbent contact time on % removal of SO_2. **Note:** (—■—) % Removal.

Influence of Concentration of Working Standard Solution on Removal Percentage of SO_2

With different starting concentrations (ppm) of 20,40,60,80,100 prepared batch experiments (Table 3). As shown in Fig. 5 the percent elimination was 95% at 20 ppm, 82.5 at 40 ppm, and there after declined, indicating acidified *Hibiscus sabdariffa* leaf powder exhaustion (Nenavath Gandhi, et al., 2012).

Tab. 3. Batch adsorption studies for the concentration of working standard solution on removal percentage of SO_2.

HCl-treated *Hibiscus sabdariffa* (60 mins, 1 gm Adsorbent)						
Initial concentration	20	40	60	80	100	1.5
OD	0.01	0.05	0.1	0.14	0.22	1.5
Final concentration	1	7	14	20	33	1.5
% Removal	95	82.5	76.6	75	67	1.5

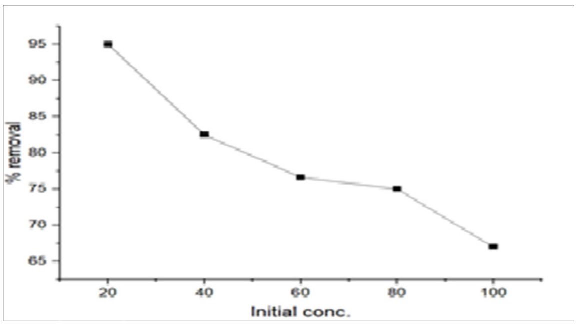

Fig. 5 Effect of concentration of working standard solution on removal percentage of % of SO_2. **Note:** (—■—) % Removal.

Adsorption Isotherms

The critical factor influencing the adsorption of SO_2 molecules by Gongura is temperature. We conducted studies at 20°C, 40°C, 60°C and 80°C and the results by using Langmuir, Freundlich, and Temkin isotherm, shown in Figs 1-3. And adsorption constants are in the Table 4.

Tab. 4. Adsorption isotherm constants.

S. No	Parameters	Temperature (°C)			
		20°C	40°C	60°C	80°C
	Langmuir adsorption isotherm				
1	R^2	0.7998	0.9617	0.9037	0.9969
	Q0	1.095	1	1	1.046
	b2	0.02	0.0047	0.0062	0.0065
	Freundlich adsorption isotherm				
2	Log K	0.8795	0.8155	0.7693	0.775
	R^2	0.9981	0.9974	0.9936	0.9965
	1/n	0.2287	0.2125	0.2659	0.234
	Temkin adsorption isotherm				
3	R^2	0.9975	0.988	0.9815	0.9885
	a	0.745	0.62	0.55	0.52
	b	3.9	7.7	8.8	8.7

The R^2 values are high in the case of Freundlich and Temkin adsorption isotherms ranging from 0.775-0.8795 and 0.9885-0.9975 respectively. The data indicates that it is not following Langmuir adsorption isotherm. The log K values of Freundlich adsorption isotherm decrease with an increase in temperature, showing the lower temperature is favourable (Figs 6 and 7). Adsorption intensity is high at lower temperatures and adsorption capacity is increasing due to the trend indicating the behaviour of adsorption is changing from physical to chemical adsorption. Temkin adsorption isotherms are showing similar results. The bio-charring behaviour of the Gongura provides a large surface area after thermal modification. Adsorption intensity decreases with an increase in temperature (Figs 8 and 9).

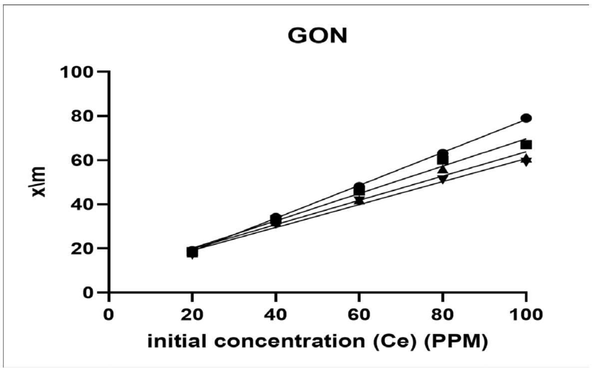

Fig. 6 The graph represents Qe vs. Ce. **Note:** (—●—) x/m (20°C); (—■—) x/m (40°C); (—▲—) x/m (60°C); (—▼—) x/m (80°C).

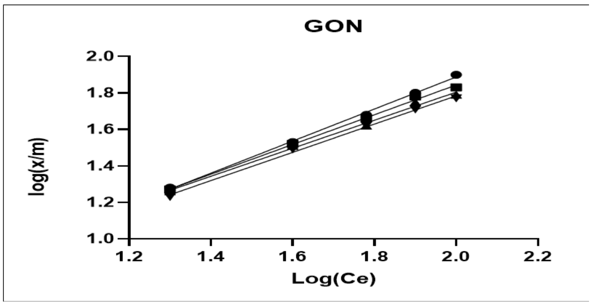

Fig. 7 The graph represents log Qe vs. log Ce. **Note:** (—●—) x/m (20°C); (—■—) x/m (40°C); (—▲—) x/m (60°C); (—▼—) x/m (80°C).

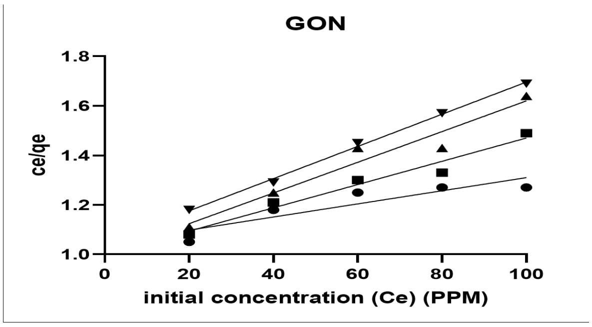

Fig. 8 The graph represents Ce/Qe vs. Ce. **Note:** (—●—) x/m (20°C); (—■—) x/m (40°C); (—▲—) x/m (60°C); (—▼—) x/m (80°C).

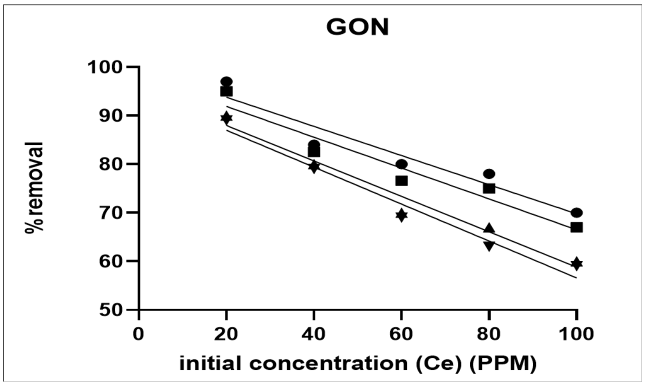

Fig. 9 The graph represents %removal vs. Ce. **Note:** (—●—) x/m (20°C); (—■—) x/m (40°C); (—▲—) x/m (60°C); (—▼—) x/m (80°C).

Adsorption kinetics

R^2 values of pseudo-first-order kinetics is greater than pseudo-second-order kinetic model, which indicates adsorption process is following first order (Table 5).

Tab. 5. The description process is based on the sorbent physical, chemical properties and mass transfer.

The experimental data determined pseudo first order and pseudo second order kinetics					
S. No	**Param-eters**	**At 20 micro gm/lit**	**At 40 micro gm/lit**	**At 60 micro gm/lit**	**At 80 micro gm/lit**
1	**Pseudo first order kinetics model**				
	R^2	0.9632	0.9656	0.958	0.9332
	K	1.377	1.64	1.801	1.927
2	**Pseudo second order kinetics model**				
	R^2	0.771	0.8302	0.7725	0.8671
	K	0.04622	0.05006	0.07646	0.05059
3	**Elovich midel**				
	R^2	0.9806	0.9517	0.928	0.918
	Alpha	3.171	3.1	3.024	3.014
	Beta	-13	-19.67	-21.6	-23.17
4	**Intra particulate diffusion model**				
	R^2	0.9806	0.9517	0.928	0.918
	K	0.2231	0.3491	0.4212	0.4505

In Elovich model R^2 values are ranging from 0.9034-0.7508 at different concentration. The slope (alpha) values are decreasing with increase in concentration (Figs. 10 and 11). Similarly, beta values are also decreasing which are represented by positive and negative values respectively. Similarly inter particle diffusion R^2 values are high compared to Elovich model (Figs. 12 and 13).

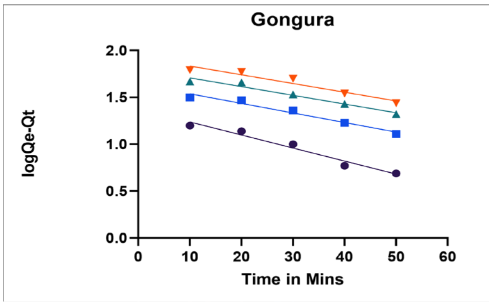

Fig. 10 The graph represents log Qe-Qt vs. T(Time in mins). **Note:** (-●-) log(Qe-Qt)(20 ppm); (-■-) log(Qe-Qt)(40 ppm); (▲) log(Qe-Qt)(60 ppm); (-▼-) log(Qe-Qt)(80 ppm).

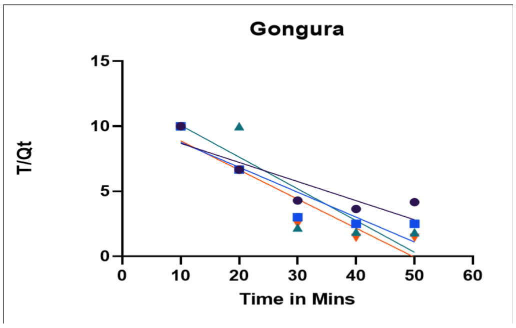

Fig.11 The graph represents T/Qt vs. T(Time in mins). **Note:** (-●-) % Removal(20 ppm); (-■-) % Removal (40 ppm); (▲) % Removal (60 ppm); (-▼-) % Removal (80 ppm).

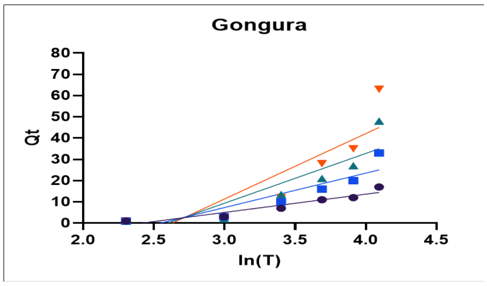

Fig. 12 The graph represents Qt vs. ln (T). **Note:** (-●-) Qt (20 ppm); (-■-) Qt (40 ppm); (▲) Qt (60 ppm); (-▼-) Qt (80 ppm).

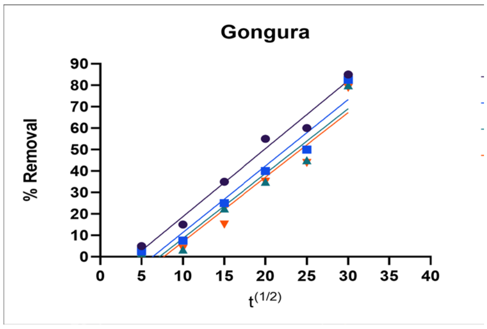

Fig. 13 The graph represents % Removal vs. t(1/2). **Note:** (-●-) % Removal(20 ppm); (-■-) % Removal (40 ppm); (▲) % Removal (60 ppm); (-▼-) % Removal (80 ppm).

The experimental data fits Inter particle diffusion model and Pseud- first-order kinetic model.

CONCLUSION

HCl-treated *Hibiscus sabdariffa* leaf powder were successfully employed as adsorbent for removal of SO_2 from aqueous solutions. The degree of SO_2 removal by HCl-treated *Hibiscus sabdariffa* leaf powder increased with increasing contact time, with 60 minutes being found to be the optimum. The percent removal of SO_2 declined as the concentration increased, with the greatest percent removal occurring at 20 ppm, and greater percent SO_2 removal was achieved using a 1.0 gm adsorbent dose. The use of plant waste is a critical advance in preserving a sustainable environment. The quality of our natural resource. Such as air and water, can be improved by employing these low-cost, environmentally friendly biosorbents. It follows temkin isotherm and first order kinetics.

REFERENCES

Chen Z, Yin H, Wang C, Wang R, Peng Y,Y,ou C and Li J. 2021. New insights on competitive adsorption of No/So_2 on Tio2 anatase for photocatalytic No oxidation. *Environ Sci Technol*. 55 (13): 9285–9292.

Song X, Wang S, Hao C and Qiu J. 2014. Investigation of So_2 gas adsorption in metal–organic frameworks by molecular simulation. Inorg Chem Commun. 46(8): 277-281.

Elder A, Bhattacharyya S, Nair S and Orlando T. 2018. Reactive adsorption of humid So_2 on Metal–Organic Framework Nanosheets. J Phys Chem C. 122(19): 10413-10422.

Razmkhah M, Moghadam S, Pourafshari CM and Moosavi F. 2020. Potential of diamines for absorption of So_2: Effect of methanol group. J Mol Liq. 319(12): 114163.

Hao J, Xi Z, Liu T, Lin Y and Xu. 2019. Investigation of low concentration So_2 adsorption performance on different amine-modified merrifield resins. Atmos Pollut Res. 10(2): 404-411

Lee H, Lee K, Kim M, Suh Y and Kim H. 2016.ACS Sustainable Chemistry and Engineering. 4(4): 2012-1019

Zhang Y, Chen Z, Liu X, Dong Z, Zhang P, Wang J, Deng Q, Zeng Z, Zhang S and Deng S. 2020. Efficient So_2 removal using a microporous metal–organic framework with molecular sieving effect. Ind Eng Chem Res. 59(2): 874-882.

Guo L, Feng X, Gao Z, Krishna R and Luo F. 2021.Bimetal–Organic framework for efficient removal of trace So_2 from So_2/Co2 and So_2/Co2/N2 mixtures. Inorg Chem. 60(3): 1310-1314.

Kang L, Han L, Wang P, Feng C, Zhang J, Yan T, Deng J, Shi L and Zhang D. 2020. So_2-Tolerant NOx reduction by marvelously Suppressing So_2 adsorption over FeδCe1−δVO4 catalysts. Environ Sci Technol. 54(21): 14066-14075.

Xu X, Wu P, Li C, Zhao K, Wang C, Deng R and Zhang J. 2021. Reversible removal of So_2 with amine-functionalized ZIF8 dispersed in n-heptanol. Energy amp Fuels. 35(6): 5110-5121.

Zhang Y, Zhang P, Yu W, Zhang J, Huang J, Wang J, Xu M, Deng Q, Zeng Z and Deng S. 2019. Highly selective and reversible sulfur dioxide adsorption on a microporous metal–organic framework via Polar Sites. ACS Appl Mater Interfaces. 11(11): 10680-10688.

Li B and Ma C. 2018. Study on the mechanism of So_2 removal by activated carbon. Energy Procedia.153(10): 471-477.

Yi H, Zuo Y, Liu H, Tang X, Zhoa S, Wang Z, Gao F and Zhang B. 2014. Water Air and Soil Pollution.225(5): 1-7.

Tailor R, Ahmadalinezhad A and Sayari A. 2014. Selective removal of So_2 over tertiary amine-containing materials. J Chem Eng. 240(3): 462-468.

Si T, Wang C, Yan X, Zhang Y, Ren Y, Hu J and Anthony E. 2019. Simultaneous removal of So_2 and Nox by a new combined spray-and-scattered-bubble technology based on preozonation: From lab scale to pilot scale. Appl Energy. 242(5): 1528-1538.

Wang Y, Wang Z and Liu Y. 2021. Review on removal of So_2, Nox, mercury, and arsenic from flue gas using green oxidation absorption technology. Energy Fuels. 35(12): 9775-9794.

Ahiduzzaman M, Jamini, Sadia T, Islam and Aminul AKM. 2021. Chapter 4-Roselle (*Hibiscus sabdariffa* L.): processing for value addition. Roselle. 53-65.

Jeffery, Tia D, Richardson and Matthew L. 2021. A review of the effectiveness of hibiscus for treatment of metabolic syndrome. J. Ethnopharmacol. 270(4): 113762.

Nenavath Gandhi, V. Mary Priyanka and D. Sirisha. 2012. Adsorption studies on mixed algae to control So_2 and No_2 pollution. Environ Res Eng Manag. 62(4): 53-56.