

Removal of Sulfur Dioxide by Carbon Impregnated with Triethylenediamine, Using Indigenously Developed Pilot Scale Setup

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1 Removal of Sulfur Dioxide by Carbon Impregnated with Triethylenediamine,
2 Using Indigenously Developed Pilot Scale Setup

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8 **ABSTRACT**

9 In order to provide protection against extremely toxic gases Activated Carbon (AC) adsorption has
10 long been regarded to be a useful technology in terms of gas removal. AC without chemical
11 impregnation has been considerably less effective than impregnated ACs. AC in present use was
12 modified with an organic amine i.e. triethylenediamine (TEDA) to enhance the physical and
13 chemical properties of AC in order to remove specific poisonous gases. Purpose of this study was
14 to assess the TEDA impregnated AC in terms of adsorption capability for simulant gas like SO₂.
15 Analysis was done in a properly designed setup. By using the scheme reported here, significant
16 adsorption of toxic gas was obtained. Maximum removal capability observed by AC-4 for SO₂ gas
17 was 3.74 g/g-C and its breakthrough time was 264 minutes. Breakthrough time and adsorption
18 capacity of AC-4 was found to be 25 times and 10 times greater as compared to raw AC. Different
19 characterization techniques were also used to study impregnated AC. It was found that chemical
20 adsorption was the crucial means by which TEDA impregnated AC removed the simulant gas.
21 Langmuir model was best to represent equilibrium and adsorption kinetics follow second order
22 model. The process was endothermic, favorable and spontaneous.

23 **Keywords:** Activated carbon, impregnation, adsorption capacity, challenge gas, breakthrough
24 time, adsorption isotherms.

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33 **1. Introduction**

34 Due to high adsorptive properties of AC, it has been employed in a huge range of applications as
35 an easy and safe technique for eliminating contaminants from air stream and from water as well.
36 Of the many carbonaceous materials, activated carbon has gained this special property. This is
37 mainly because of porous nature and huge surface area of activated carbon which makes it
38 functional for removal of irritating and toxic gases from the environment. Impregnating activated
39 carbon (IAC) with warily chosen materials, significantly increases its capacity of adsorption for a
40 large number of gases that raw activated carbon is unable to filter. This marvelous property of
41 activated carbon has been used in the manufacturing of canisters and gas mask filters for the last
42 few decades. With the rising concern on environmental pollution, there has been an increased
43 curiosity in ACs as the means for eliminating pollutants from environment (Abdulrasheed, Jalil et
44 al. 2018, Huve, Ryzhikov et al. 2018, Eskandari, Andalib et al. 2020, Cai, Yang et al. 2021, Wen,
45 Liu et al. 2021). Both the Occupational Safety and Health Administration (OSHA) and
46 Environmental Protection Agency (EPA) have considered AC adsorption as the “gold standard”
47 technology for optimum removal of contaminants on the priority list (Wu, Chang et al. 2007, Yang,
48 Lu et al. 2020).

49 AC is a nice adsorbent for some organic vapors but for polar and low molecular weight gases, it is
50 a poor adsorbent. On the other hand, impregnated ACs which have been modified with chemical
51 reagent react strongly with these kinds of gases, bind them on the surface and thus remove them
52 from airstream (Ho, Moon et al. 2019, Kiani, Faiz et al. 2020, Kiani, Farooq et al. 2021).

53 On the AC surface, pollutant gas molecules can be adsorbed by two approaches, physisorption and
54 chemisorption. Physisorption being a surface phenomenon holds the adsorbate pollutant molecules
55 on the surface of AC by Van der Waal’s forces and classical electrostatic interactions. In

56 chemisorption, adsorbent and adsorbate pollutant molecules are held together on AC interface by
57 means of chemical bond. In case of unimpregnated AC, molecules attach to the surface of AC only
58 by weak physical forces. Owing to the weakness of these interactions between adsorbate and AC,
59 adsorbate can be released into atmosphere easily causing several ecological concerns (Mahle,
60 Peterson et al. 2010, Muzarpar, Leman et al. 2020).

61 Unimpregnated AC does not have the capability to remove contaminants from airstream to a
62 greater extent. Therefore, processes have been developed to coat chemicals on the AC surface to
63 provide essential filtering capabilities. In order to improve removal mechanism of gases from
64 airstream, various treatments were used. Most important one of them is the use of organic coatings
65 (Ho, Chun et al. 2019, Khayan, Anwar et al. 2019). Several impregnating materials i.e.
66 diisopropylamine (DIPA), triethylenediamine (TEDA), piperidine, di-N-propylamine (DNPA),
67 citric acid and tartaric acid have been used for contaminant removal. These “new generation”
68 impregnated ACs can be used for several applications, most important one being used for toxic
69 gases adsorption from air stream. In nuclear testing, most successful combinations to date consist
70 of coal based carbon impregnated with TEDA for the removal of radioactive methyl iodide
71 (González-García, González et al. 2011, Farooq, Irfan et al. 2012, Zhou, Hao et al. 2014, Lee, Lee
72 et al. 2020). In the present work, various types of TEDA impregnated activated carbon samples
73 were prepared by using a very novel and properly developed setup which involves sublimation
74 process for the impregnation of TEDA on activated carbon using Fluidized bed adsorbing tower
75 (FBT). Breakthrough times of IACs were quantified for SO₂ as challenge gases. The intention of
76 present study was to assess the adsorption capacity of AC and TEDA impregnated ACs for SO₂
77 gas. Concentration of gas was measured by using FTIR based gas analyzer. In addition to IACs,
78 an un-impregnated activated carbon was also tested for gas adsorption capacity.

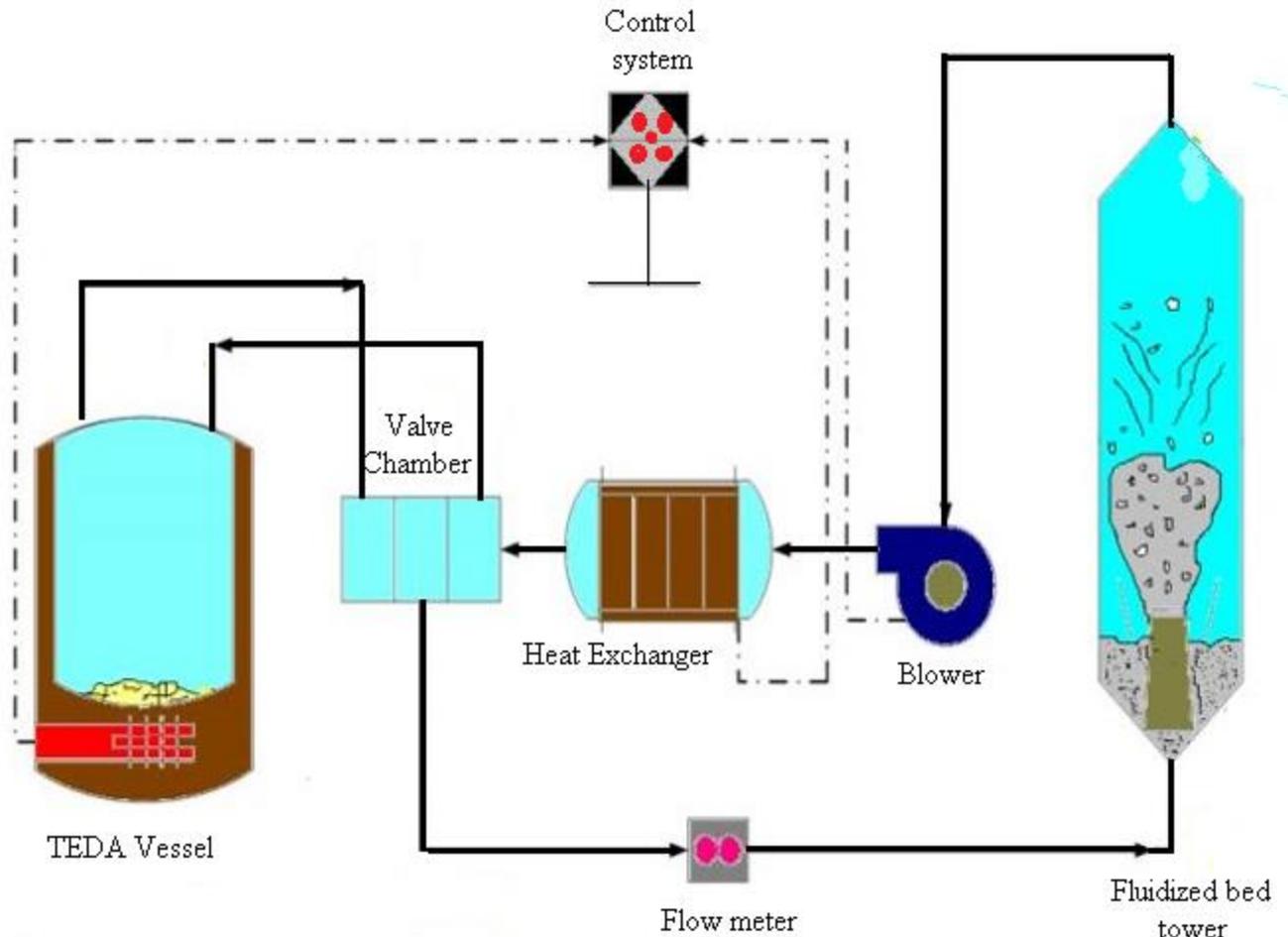
79 **2. Materials and methods**

80 *2.1 Materials/Chemicals*

81 Coal based granular AC having surface area 984 m²/g, total pore volume 0.423 cm³/g, density 6.7
82 g/cm³, moisture content 11% and pH value of 7.8 was used. Chemical used for impregnation was
83 triethylenediamine (C₆H₁₂N₂). Leaching agent used was acetonitrile.

84 *2.2 Design and Scheme of Pilot Scale Impregnation Setup*

85 TEDA was impregnated on AC by using sublimation process. This sublimation process was
86 carried out in a specially designed pilot scale impregnation setup which consists of a fluidized bed
87 adsorbing tower (FBT), TEDA vessel, blower and heat exchanger (HX). These are connected to
88 an electronic control panel (Farooq, Irfan et al. 2012). Design of setup is shown in Fig. 1. Fluidized
89 bed adsorbing tower is the most important part of this setup where TEDA in vapor form
90 impregnates on AC. This technique has the advantage that a uniform impregnant layer can be
91 achieved over all internal and external surfaces of AC.



92

93

Fig. 1 Experimental setup for TEDA impregnation by sublimation

94

2.3 Sample Preparation procedure

95

First of all oil present in the HX is heated by means of heater till it attains 250 °C temperature.

96

Blower is then switched on and air moves towards HX. This hot air then travels directly towards

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FBT. By this manner, air is recirculated till it attains 100 °C temperature within the FBT. AC bed

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present inside the FBT is also heated by this hot air. In the meantime, TEDA vessel heater is also

99

operated to attain the temperature of 100 °C for TEDA sublimation. At this time, valve is opened

100

and 100 °C air flows into TEDA vessel, carries TEDA vapors from the vessel and then moves to

101

the FBT. As a result of fluidization of AC bed in FBT, each and every particle of AC from all sides

102 comes in contact with TEDA laden air. So in this manner, TEDA in vapors form gets impregnated
 103 on external and internal surfaces of AC. This cycle is repeated for a specified time period until all
 104 the TEDA (in the TEDA vessel) is sublimed and gets adsorbed on AC. This method of fluidization
 105 and sublimation by using hot air has a number of advantages over other impregnation methods.
 106 Here, post drying process of impregnated AC is not needed and this process also ensures uniform
 107 impregnation. The samples prepared with various concentration of TEDA are listed in Table 1.

108 Table. 1 Details of TEDA impregnated ACs

Sr. No.	Sample Code	TEDA %	Impregnation temp. (°C)	TEDA vessel temp. (°C)	Activated carbon Amount (kg)	Time (hrs)
1	AC-1	3.2	95	90	2	2
2	AC-2	4	95	90	2	2
3	AC-3	5.5	95	90	2	2
4	AC-4	6.5	95	90	2	2
5	AC-5	7.8	95	90	2	2
6	AC-6	8.5	95	90	2	2
7	AC-7	9.1	95	90	2	2
8	AC-8	10.3	95	90	2	2

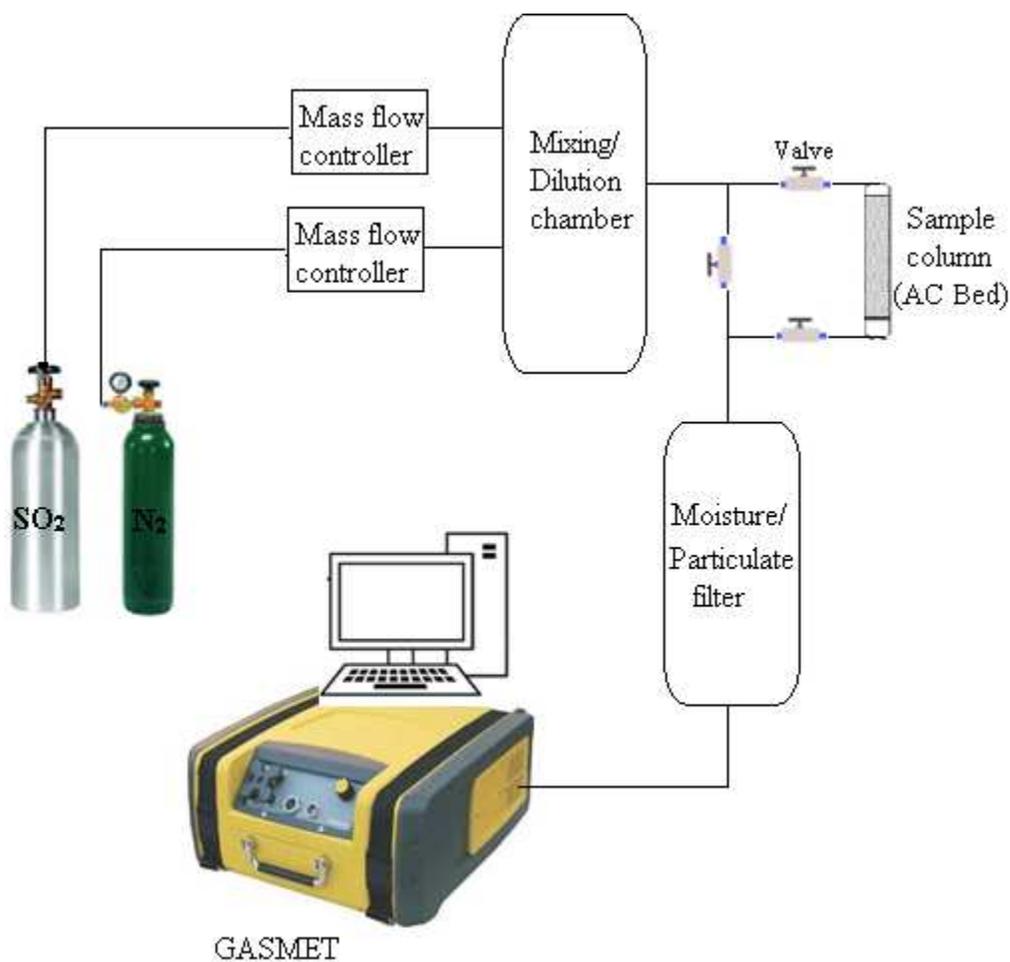
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110 2.4 Sample characterizations

111 A Hitachi S-4800 SEM was used to image the samples. Beam extraction current of 15 μ A,
 112 accelerating voltage 20kV and working distance of 12mm were the characteristic conditions
 113 employed. To attain stability and to facilitate imaging, a conducting carbon paste for fixing the
 114 granules of AC was used. Magnification used was 30-500x.

115 Determination of breakthrough time was done by FTIR based GASMET Analyzer. For gas
116 filtration, samples were tested by using sulphur dioxide (SO₂) as a challenge gas. 0.5g of each
117 sample was tested for SO₂ gas. These were exposed to 57ppmv challenge gas. Total flow rate
118 comprising SO₂ and diluent N₂ was 3L/min. In dilution chamber, SO₂ gets diluted after mixing
119 with N₂ and passed through AC bed for toxic gas adsorption. Breakthrough time (t_b) was measured
120 as the time when challenge gas concentration downstream of AC bed reached a value of 5ppmv.
121 Experimental setup flow chart for SO₂ testing is shown in Fig. 2.

122



123

124

Fig.2 Experimental setup to study SO₂ adsorption on AC

125

126 *2.5 ASTM Standard Tests for AC*

127 ASTM standard tests were performed to calculate the Particle size distribution, Ball-pan hardness
128 number, Water solubles, Apparent density, Total ash content, Moisture content, Iodine number
129 and pH of Raw and TEDA impregnated activated carbon sample (ASTM 1996).

130 *2.6 Adsorption capacity*

131 Experimentally, adsorption capacity was calculated by using breakthrough time curve data by
132 subtracting the area below the breakthrough time curve from the total area. This final area above
133 the curve gives value of adsorption capacity. Area below breakthrough curve was calculated by
134 integration method. Theoretically, breakthrough time was determined by using modified Wheeler
135 Jonas equation and this equation is written as:

$$\frac{t_x}{t_{0.05}} = 1 - \frac{F}{VK_v} \ln \left(\frac{C_o - C_x}{C_x} \right) \quad (1)$$

Where, t_x is the breakthrough time (min), $t_{0.05}$ is saturation time (min), F is total flow rate (cm³/min), V is volume of packed bed (cm³), K_v is adsorption rate constant (min⁻¹), C_o = inlet gas concentration (gm/cm³) and C_x is the concentration at time t_x (gm/cm³).

136 *2.7 Adsorption isotherms*

137 The adsorption data of SO₂ on AC was subjected to three adsorption models i.e. Langmuir,
138 Freundlich and Dubinin-Radushkevich (D-R). Langmuir isotherm was applied in the following
139 linearized form (Lua and Guo 2001):

140

$$\frac{C_e}{C_{ads}} = \frac{1}{Qb} + \frac{C_e}{Q} \quad (2)$$

141 C_e is the equilibrium concentration of gas (SO₂) in ppm, C_{ads} is the adsorbed concentration of gas
142 on activated carbon in ppm. Q is the constant which signifies maximum adsorption capacity at
143 monolayer formation and b is the characteristic Langmuir constant for the adsorption system.

144 Freundlich adsorption isotherm was applied in the following linearized form (Lua and Guo 2001):

$$145 \quad \ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (3)$$

146 q_e is the amount of gas adsorbed, C_e is the equilibrium concentration of gas, K_f is the Freundlich
147 rate constant and $\frac{1}{n}$ is Freundlich adsorption constant strength.

148 D-R adsorption isotherm was applied in the following linearized form (Lua and Guo 2001):

$$149 \quad \ln q_e = \ln q_s - K_D \mathcal{E}^2 \quad (4)$$

150 Where q_s is the constant in D-R isotherm which is related to adsorption capacity, K_D is constant
151 related to mean free energy of adsorption and \mathcal{E} is the Polanyi potential which is given by:

$$152 \quad \mathcal{E} = RT \ln(1 + 1/C_e) \quad (5)$$

153 Where R is gas constant, T is absolute temperature and C_e is equilibrium concentration of gas.

154 2.8 Adsorption kinetic models

155 Mass transfer phenomenon can be best understood by its thermodynamics and kinetics. Pseudo
156 first order and second order models were applied to analyze the adsorption data for kinetic study.

157 Pseudo first order model is the simplest equation which relates dependence of adsorption rate on
158 adsorption capability. Equation is written as (Sumathi, Bhatia et al. 2010):

$$159 \quad \frac{dq}{dt} = k_1(q_e - q_t) \quad (6)$$

160 Linearized form is given as:

$$161 \quad \log(q_e - q_t) = \log q_e - K_1 2.303t \quad (7)$$

162 q_e and q_t are the amounts of gas adsorbed at equilibrium and at time “t” respectively, K_1 is rate
163 constant of pseudo first order and t is contact time.

164 Equation for pseudo second order model is written as:

$$165 \quad \frac{dq}{dt} = K_2 (q_e - q_t)^2 \quad (8)$$

166 Linearized form is given as:

$$167 \quad \frac{t}{q_t} = \frac{1}{K_2 q_e} + \frac{t}{q_e} \quad (9)$$

168 Where t is time in min and q_t is the amount of gas adsorbed at time t , K_2 is rate constant of pseudo
169 second order reaction and q_e is equilibrium adsorption capacity.

170 2.9 Thermodynamic parameters

171 The primary thermodynamic parameters which are used to calculate the probability and
172 spontaneity of adsorption process are change of enthalpy (ΔH), change of entropy (ΔS) and free
173 energy change (ΔG). Following equations can be used to predict these parameters (Myers 2002):

$$174 \quad \Delta G = -RT \ln K_d \quad (10)$$

175 R is gas constant, T is absolute temperature and K_d is distribution coefficient and is calculated by
176 following equation.

$$177 \quad K_d = (C_o - C_e) / (m_s / V) C_e \quad (11)$$

178 Value of entropy change and enthalpy change was analyzed from intercept and slope of plot
179 between $\ln K_d$ versus $1/T$ respectively.

180 3. Results and Discussion

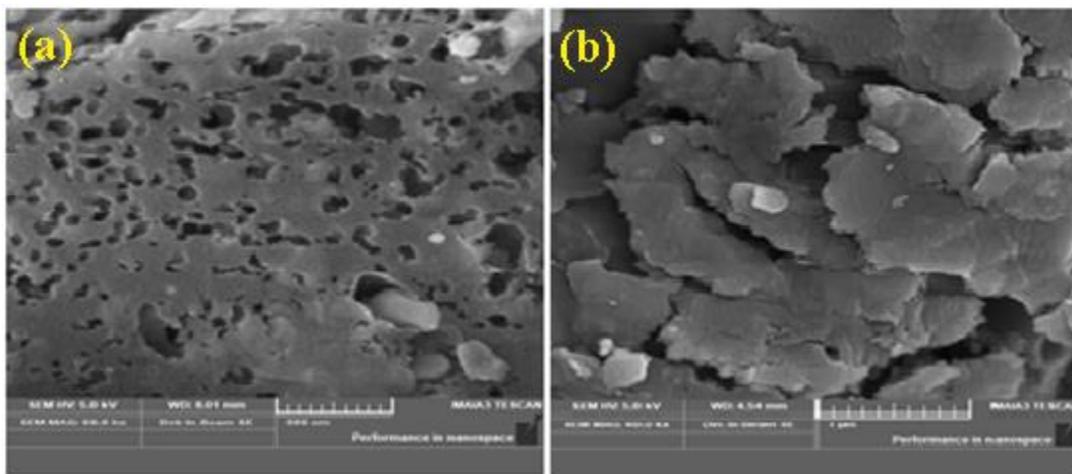
181 Comparison of ASTM standard test results of Raw AC and AC-4 was made and shown in Table
182 2. Results clearly indicate that AC-4 showed an enhancement in properties as compared to the Raw
183 AC. This is mainly because of the impregnant which imparts these improved properties (Al-Qodah
184 and Shawabkah 2009). So we can say that the prepared AC-4 sample might be a sustainable
185 candidate for purification of noxious gases from atmosphere.

186 Table 2 ASTM standard tests for Raw AC and AC-4

ASTM Standard Tests	Raw AC	AC-4
Mean Particle Size (mm)	0.77	0.88
Ball Pan Hardness Number	91.9	94
Water Solubles (%)	0.01	0.35
Apparent Density (gm/cm ³)	0.41	0.43
Total Ash Content (wt. %)	5	5.5
Moisture Content (wt. %)	19.5	0.85
Iodine Number (mg/g-C)	920	1031
Ph	7.8	9.54

187
188 SEM analysis was done to study the distribution of TEDA on AC surface. Fig. 3 (a) and (b) show
189 SEM images of Raw AC at different magnifications which represent cracks and cavities on surface
190 representing a system of complex porous network. Impregnation results in blocking of cavities and
191 cracks and clogging of pore openings (Kiani, Faiz et al. 2020). Fig. 3(c), (d), (e), (f), (g) and (h)
192 represent the distribution of different concentrations of TEDA on surface of AC-1, AC-3, AC-4,

193 AC-5, AC-7 and AC-8. In all these images, it can be seen that the AC surface is immensely covered
194 with TEDA impregnants. Better the distribution of TEDA on surface, better will be its capability
195 to react with toxic gases in atmosphere by adsorbing them on the surface of AC by means of
196 chemical bond with the impregnant. Apart from the chemical adsorption of gases on AC, some
197 pores are also available on AC which are responsible for physical adsorption of gases (Wu, Chang
198 et al. 2007, Arcibar-Orozco, Rangel-Mendez et al. 2013). As TEDA is basic in nature, it plays a
199 significant role in the removal of acidic gases like SO₂ from air.



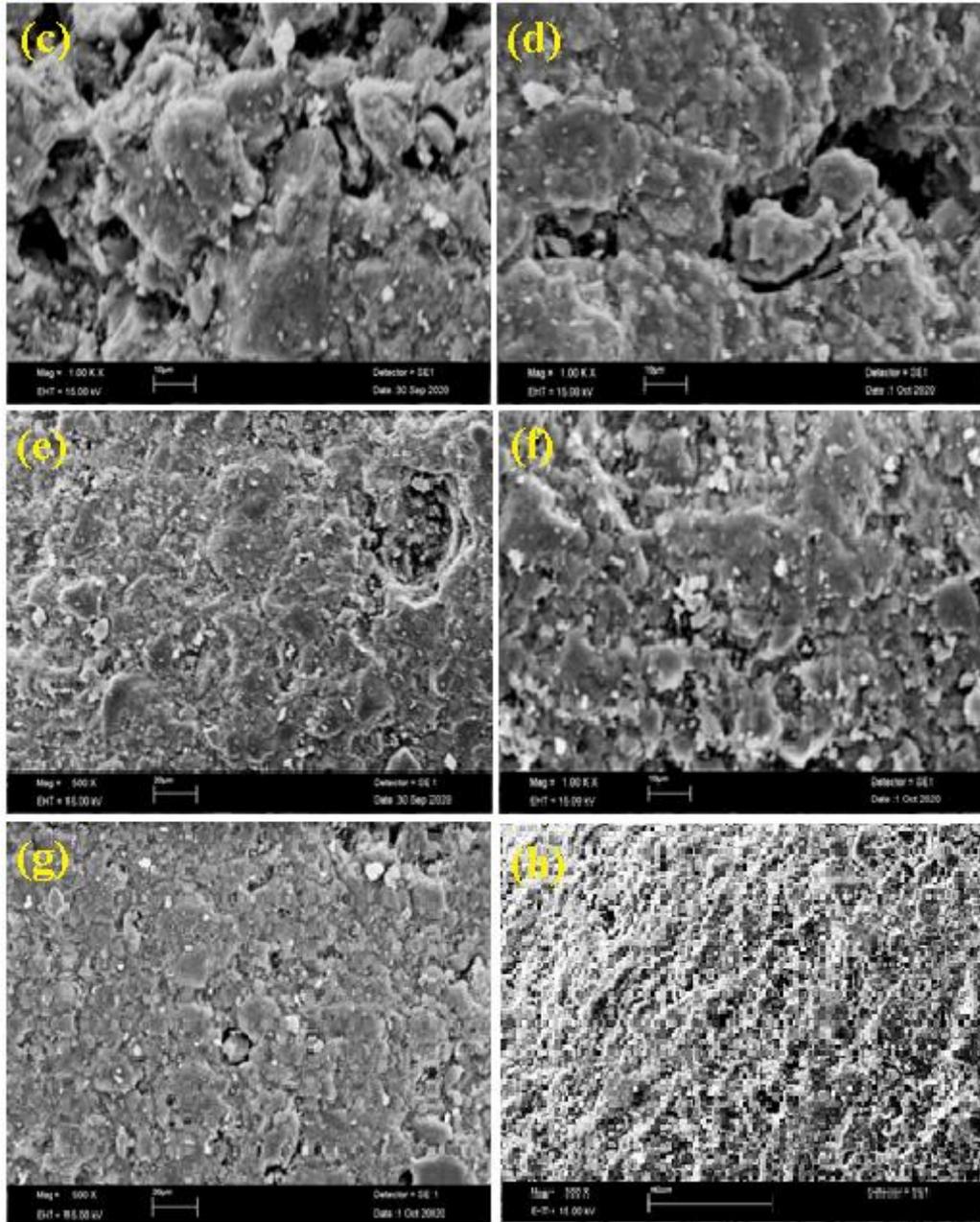
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Fig. 3(a) SEM images of Raw AC at (a) 60kx and (b) 50kx

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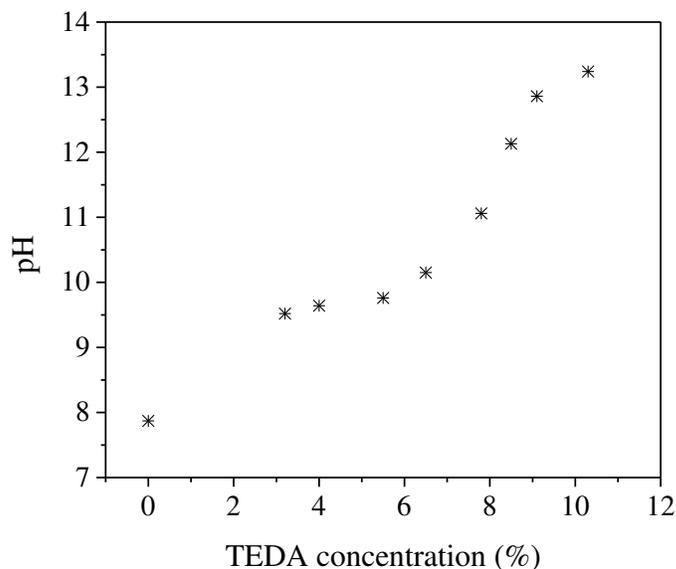


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205 Fig. 3(b) SEM images of impregnated ACs (c): (AC-1), (d): (AC-3), (e): (AC-4), (f): (AC-5), (g): (AC-7) and (h):
 206 (AC-8)

207 pH of samples was measured by ASTM-D3838 method and results are presented in Fig. 4. Results
 208 clearly show that as we increase the amount of TEDA, pH value of ACs also increases. This is due
 209 to the fact that TEDA is basic in nature and its impregnation makes AC more basic. This increased

210 basicity of adsorbent (by means of basic adsorbent) is highly desirable for the chemical adsorption
211 of acidic gases as it leads to the filtration of acidic gases from contaminated environment more
212 efficiently (Wu, Chang et al. 2007).



213

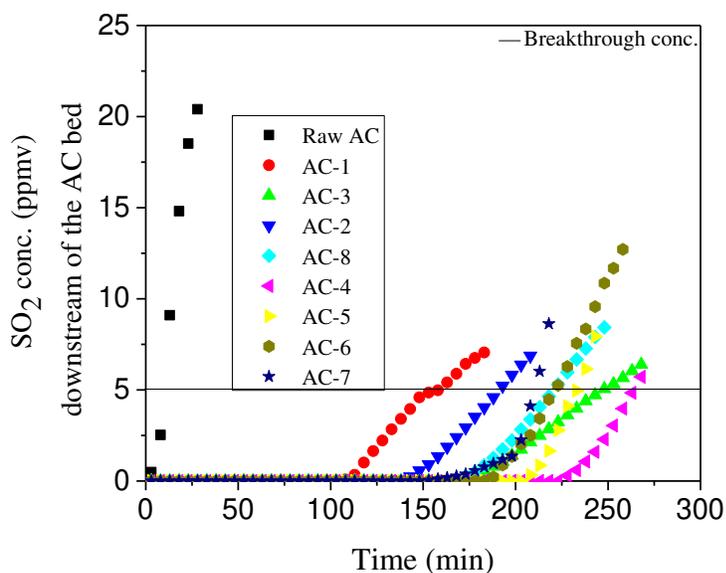
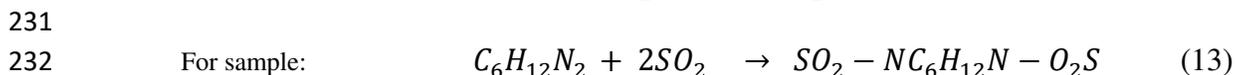
Fig. 4 pH of TEDA impregnated AC samples

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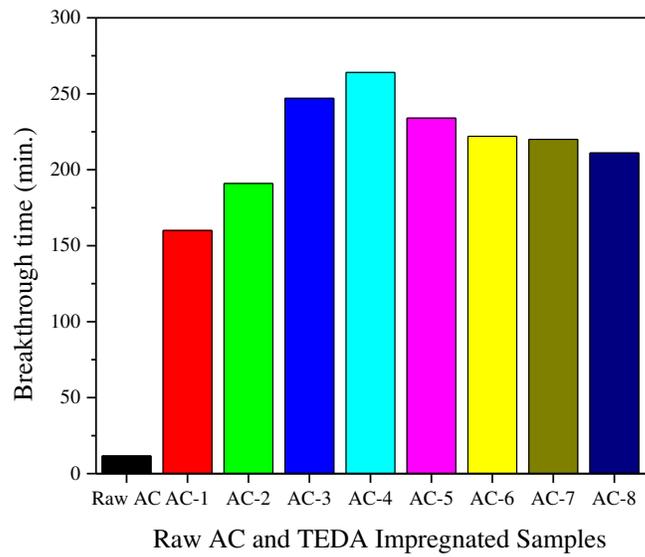
216 Gas filtration capability was tested for SO₂ gas. Comparison of breakthrough time was made
217 between the raw and various TEDA impregnated ACs and shown in Fig. 5(a) and 5(b). These
218 results indicated that Raw AC showed less breakthrough time i.e. 11.6 min as compared to other
219 impregnated samples and so responsible for the purification of toxic gases to lesser extent. In case
220 of TEDA impregnated samples breakthrough time increases initially with the increase in
221 concentration of TEDA but after a certain limit of impregnation, breakthrough time decreases with
222 further increasing the concentration and is shown in Fig. 5(c). The reason behind this is the
223 blocking of pore mouths. Impregnation beyond a certain limit results in the blockage of AC pores
224 and gas molecules do not find more available sites for adsorption, hence its breakthrough time

225 decreases considerably (Wu, Chang et al. 2007, Bobbitt, Mendonca et al. 2017). After 7% TEDA
 226 impregnation, a considerable decrease in breakthrough time was observed. Breakthrough time of
 227 AC-1, AC-2, AC-3, AC-4, AC-5, AC-6, AC-7 and AC-8 is 160, 191, 247, 264, 234, 222, 220 and
 228 211 minutes respectively. Breakthrough time of AC-4 is almost 25 times greater than Raw AC.
 229 SO₂ adsorption was supposed to occur through subsequent paths (Kiani, Faiz et al. 2020):



233
 234 Fig. 5(a) Breakthrough time curves of TEDA impregnated samples
 235 for 57 ppmv SO₂ as challenge gas

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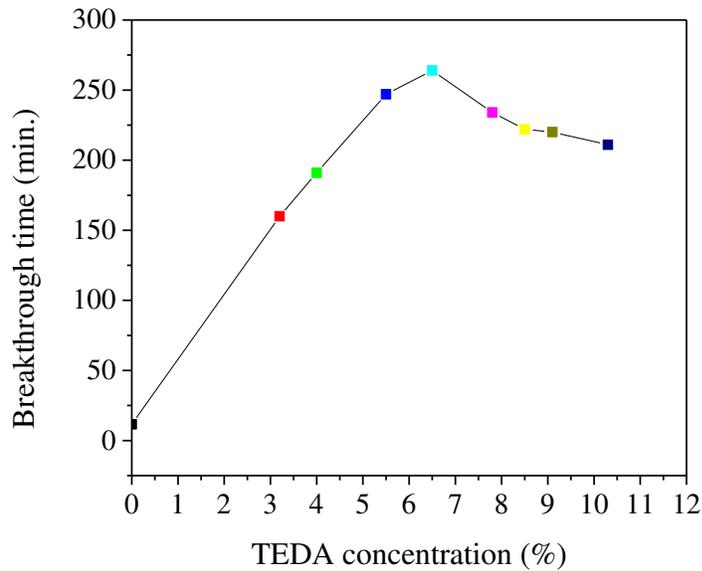


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Fig. 5(b) Comparison of breakthrough time of TEDA Impregnated samples (at 5 ppmv) for SO₂ gas



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Fig. 5(c) Relation between breakthrough time and TEDA concentration

243 Adsorption capacity of Raw AC was found to be 0.41 gSO₂/g-C whereas all other impregnated

244 samples showed higher adsorption capacities. Maximum adsorption capacity was observed for

245 AC-4 which is about 10 times higher than Raw AC as shown in Table. 3. The order of adsorption
 246 capacities of samples was found as Raw AC<AC-1<AC-2<AC-8<AC-7<AC-6<AC-3<AC-
 247 5<AC-4 for SO₂ gas. Impregnation of TEDA on AC surface might be responsible for a greater
 248 resistance or reaction sites (Mahle, Peterson et al. 2010, Perera, Ranjith et al. 2012, Zhou, Su et al.
 249 2018, Hyuncheol Lee 2019).

250 Table 3 Adsorption capacities of Raw and TEDA impregnated ACs

251	Sample	Adsorption capacity
252	Code	(g SO ₂ /g-C)
	Raw AC	0.41
253	AC-1	1.98
	AC-2	2.54
254	AC-3	3.18
	AC-4	3.74
255	AC-5	3.48
	AC-6	3.10
256	AC-7	3.04
257	AC-8	2.97

258

259 Table 4 shows breakthrough time of samples calculated by using modified Wheeler Jonas
 260 equation. A plot of $\frac{t_x}{t_{0.05}}$ vs $\ln\left(\frac{C_0-C_x}{C_x}\right)$ gives a straight line with slope equal to $\frac{F}{VK_p}$ and intercept 1
 261 (Zhou, Feng et al. 2011). Breakthrough time calculated by this method showed almost the same
 262 trend as exhibited by the experimental method, although, the calculated breakthrough times are
 263 slightly on higher side as compared to the experimental ones.

264

Table 4 Breakthrough time by using modified Wheeler Jonas equation

265

266

Sample Code	Calculated Breakthrough Time (min.)
Raw AC	18
AC-1	198
AC-2	241
AC-3	264
AC-4	290
AC-5	259
AC-6	277
AC-7	262
AC-8	249

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275 Fig. 6 shows comparison of breakthrough time calculated by both methods. It can be seen that
276 experimental and model results are linearly varying, but the model breakthrough time is slightly
277 greater than experimental breakthrough time (Lodewyckx, Wood et al. 2004). The reason is that
278 theoretical equations always over predict physical quantities. The regression value is 0.97 which
279 shows a good linear fit between model and experimental results.

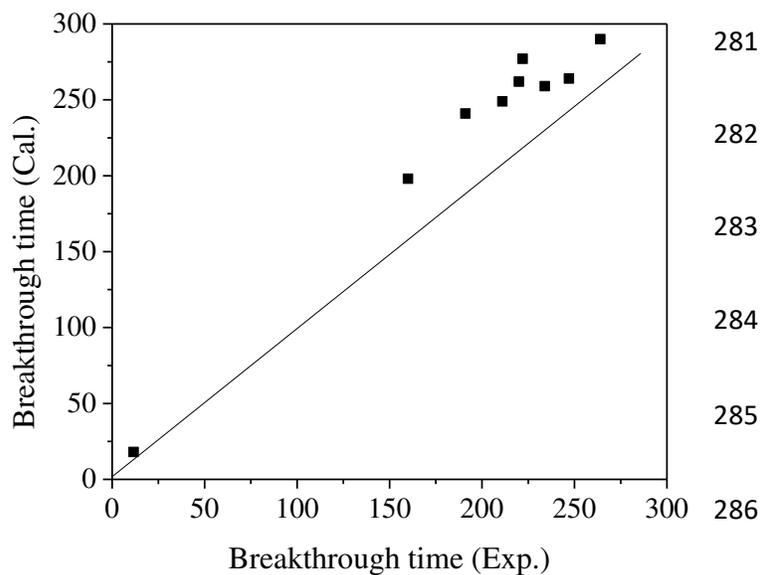


Fig. 6 Plot of Experimental and Model breakthrough time

4. Adsorption isotherms

4.1 Langmuir adsorption isotherm

Fig. 7 shows plot of C_e/C_{ads} vs C_e for SO_2 on AC-4 with initial concentration 57 ppm at 298 K. From the intercept and slope of this plot, values of Langmuir parameters are estimated for the system. Value of R^2 determines the favorability of adsorption process and its corresponding data is given in Table 5. Langmuir isotherm considers that the ions remain adsorbed on certain sites that are mono-energetic and each site binds only one adsorbate molecule without any interaction with the neighboring ions. Moreover, it supports the monolayer adsorption of gas on substrate (Lua and Guo 2001).

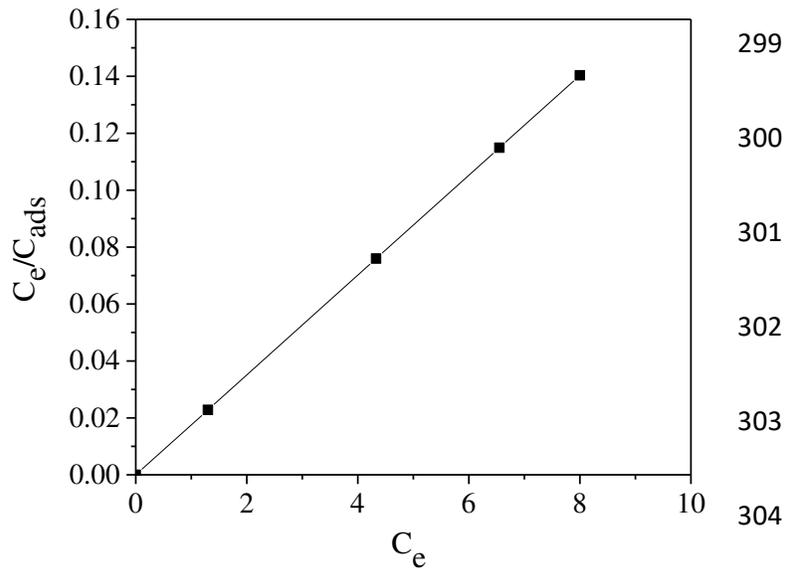
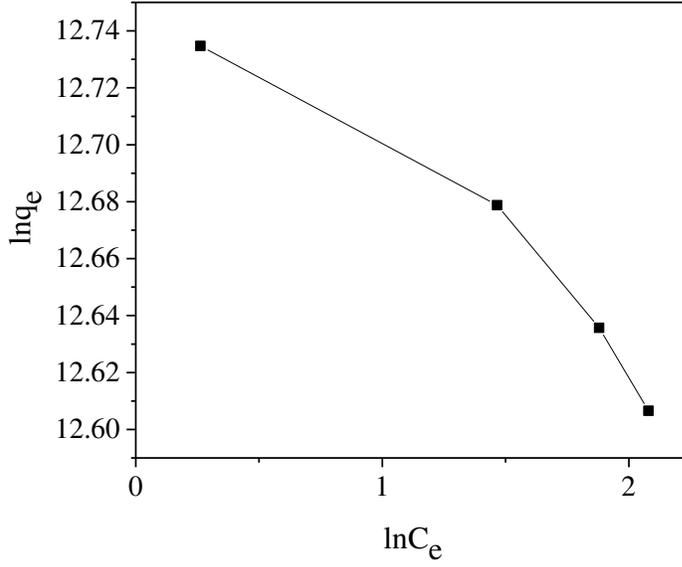


Fig. 7 Langmuir plot of SO₂ adsorption on AC-4

4.2 Freundlich adsorption isotherm

Fig. 8 shows the plot of $\ln C_e$ vs $\ln q_e$ for the adsorption data of SO₂ gas on AC-4 at initial concentration of 57 ppm and 298 K. Slope and intercept were used to determine the Freundlich constant (Muzarpar, Leman et al. 2020). Value of R^2 determines the favorability of adsorption process and its corresponding data is given in Table 5.



311

312

Fig. 8 Freundlich plot of SO₂ adsorption on AC-4

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4.3 D-R isotherm

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Fig. 9 shows the plot of lnC_{ads} vs \mathcal{E}^2 for adsorption data of toxic gas on AC-4 surface at initial

315

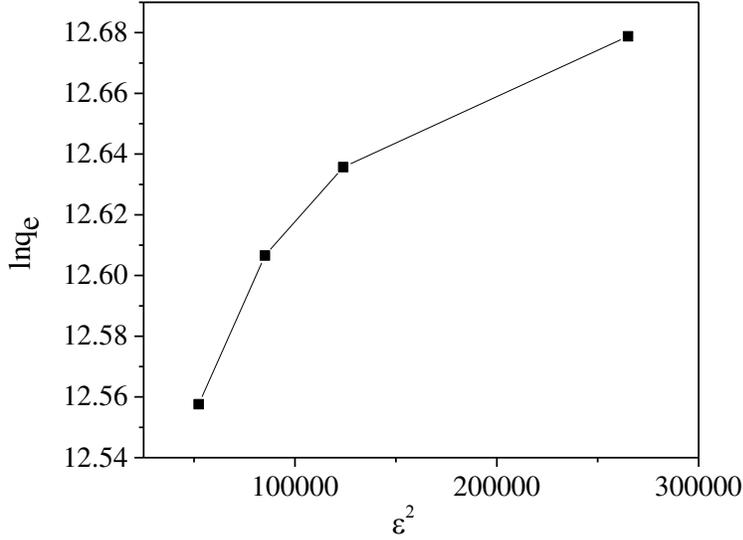
concentration of 57 ppm and 298 K. From intercept and slope of plot we get value of D-R

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parameters (Sumathi, Bhatia et al. 2010). R² value provides information about the favorability of

317

adsorption process. Fig. 9 shows D-R isotherm plot and its corresponding data is given in Table 5.



318

319

Fig. 9 D-R plot of SO₂ adsorption on AC-4

320

5. Adsorption Kinetics

321

Plot of $\log (q_e - q_t)$ vs t for pseudo first order reaction is shown in Fig. 10 and plot of t/q_t vs T for

322

pseudo second order reaction is shown in Fig. 11 for the adsorption of SO₂ gas on AC-4. Kinetics

323

of adsorption can be predicted from the corresponding value of R^2 (Yi, Wang et al. 2014). Value

324

of R^2 for pseudo first order reaction is 0.7223 and for second order is 1. This concludes that pseudo

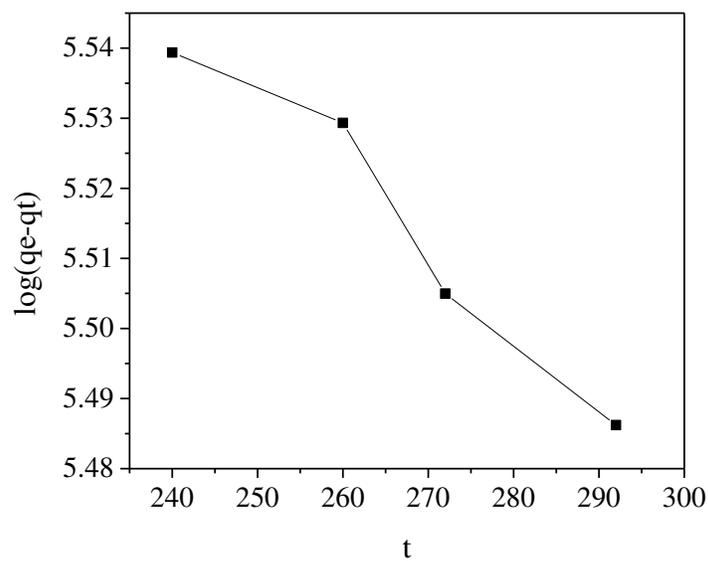
325

second order reaction is the most favorable path for adsorption of SO₂ on AC-4 and fits best to

326

adsorption process (Sumathi, Bhatia et al. 2010).

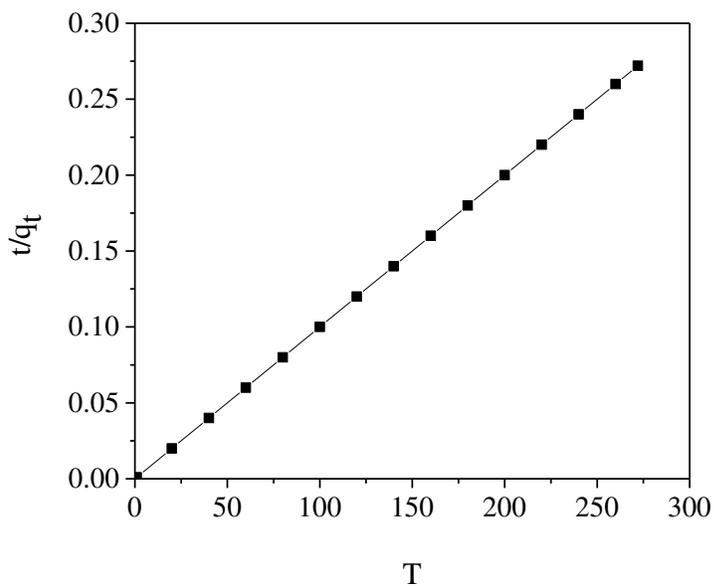
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Fig. 10 Plot of pseudo first order for SO₂ adsorption on AC-4



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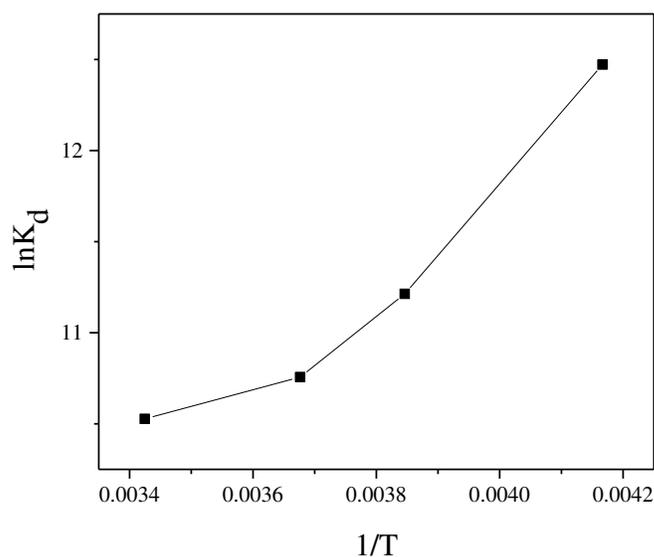
Fig. 11 Plot of pseudo second order for SO₂ adsorption on AC-4

332

6. Thermodynamic parameters

333 Plot of $\ln K_d$ vs $1/T$ is shown in Fig. 12. From the slope and intercept of this graph value of ΔG and
 334 ΔH have been computed respectively. Positive value of ΔS proposed an increased randomness at
 335 the interface in the adsorption process. Positive enthalpy value shows the endothermic reaction
 336 while negative free energy indicates the spontaneous nature of adsorption process respectively
 337 (Zhou, Yi et al. 2012). Corresponding values are shown in Table 5. Comparison of three isotherm
 338 models shows that Langmuir adsorption isotherm model is the best fitted model as compared to
 339 Freundlich and D-R isotherms.

340



341 Fig. 12 Plot of $\ln K_d$ vs $1/T$ for thermodynamic parameters

342 Table 5 Parameters for Langmuir, Freundlich and D-R isotherms for SO_2 adsorption

Gas adsorbed	Models	Parameters	ΔH (kJmol^{-1})	ΔS ($\text{JK}^{-1}\text{mol}^{-1}$)	ΔG (kJmol^{-1})	
SO_2	Langmuir	Q	0.017	6628.2	9.42	-26.08
		B	0			
		R^2	1			
		K_f	12.7			
	Freundlich	$1/n$	-0.057			
		R^2	0.941			

	q_s	2.5
D-R	K_D	5×10^{-7}
	R^2	0.864

343 **Conclusion**

344 In this study different TEDA impregnated ACs were prepared by using sublimation method. All
345 samples displayed higher breakthrough times and gas adsorption capacities to a considerable
346 amount as compared to the Raw AC. Moreover, AC-4 prepared in this work is a sustainable
347 candidate for the purification of toxic gases from contaminated air by chemisorption on porous
348 carbon surface. Its breakthrough time and adsorption capacity was found to be 264 minutes and
349 $3.74 \text{gSO}_2/\text{g-C}$ respectively for 57 ppmv SO_2 . Being basic in nature, TEDA played a dynamic role
350 in the purification of acidic gases from air. Gas adsorption data are reliable with Langmuir,
351 Freundlich and D-R isotherms. Adsorption data strongly follow Langmuir adsorption isotherm and
352 pseudo second order kinetics. Thermodynamic parameters ΔH , ΔG and ΔS have been calculated.
353 However the positive enthalpy change showed the endothermic reaction for adsorption of SO_2 on
354 AC. While negative free energy change confirmed the spontaneous nature of adsorption process.

355 **Ethics approval and consent to participate**

356 Not applicable

357 **Consent for publication**

358 Not applicable

359 **Availability of data and materials**

360 Not applicable

361 **Declaration of competing interest**

362 The authors declare no competing financial interest.

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366 **Author contribution**

367 Sidra Shaoor Kiani: Literature review, Writng original manuscript

368 Atif Ullah: Experimentation

369 Amjad Farooq: Reagents and other analysis tools, Methodology, Validation, Investigation,

370 Formal analysis, Reviewing manuscript

371 Naseem Irfan: Instrumentation

372 Masroor Ahmed: Instrumentation

373 Mohsan Nawaz: Conceptualization

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