Conductometric Studies Of Adsorption Of Sulfide On Charcoal From Aqueous Solution

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Abstract: Adsorption of sulfide (S^{2-}) from aqueous solution on commercial charcoal was studied using conductometric technique. A proportionally constant for concentration of S^{2-} and its conductance was obtained by measuring conductance of S^{2-} solution over a concentration range of 0.0005–0.02 M. The time-dependent measured conductance of S^{2-} solution was converted to concentration using the obtained constant. The adsorption data were analyzed by both Freundlich and Langmuir isotherms. A surface coverage equal to 2.5 mg per gram of charcoal was obtained. The adsorption was found to follow first-order kinetics having rate constant equal to 2.65×10^{-3} s^{-1}.

Index Terms: Adsorption; Charcoal, Conductometric method; Langmuir isotherm, Freundlich isotherm; Monolayer coverage

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1 INTRODUCTION

Sulfide (S^{2-})-containing substances are common malodorous compounds that can be found in volcanic gases, petroleum deposits, natural gas, water and emission from many industrial plants [1]. S^{2-}-containing harmful substances can cause many health problems to human and even as low as one part per million has detrimental effects on chemical catalytic processes [2]. Excessive sulfur can damage kidney, cause headache, throat and stomach discomfort, vomiting, allergic skin diseases, asthma etc. Therefore, removal of S^{2-} is of great importance for both lives and industries. Activated carbon is a highly porous material used for removal of impurities from gases and liquids including gas separation and purification, vehicle exhaust emission control, environmental technology, decaffeination, gold purification, metal extraction, water purification, medicine, sewage treatment, air filters in gas masks and respirators, filters in compressed air and many other applications. Removal of hydrogen sulfide (H_2S) by adsorption or its oxidation using activated carbon as adsorbent/catalyst has received great scientific interest since long [3-10]. For example, F. Abid et al. [6] used different types of wood-based commercial activated carbons as adsorbents for low concentration H_2S and showed that its oxidation efficiently occurred at the mentioned adsorbents. They monitored the amount of emitted H_2S using an Interscan LD-17 continuous monitor system interfaced with a computer data acquisition program. Similarly, activated carbons of various origins such as bituminous coal, wood, coconut shells and peat etc. were used as adsorbents for S^{2-} adsorption/oxidation by T.Z. Bandosz [7]. They intensively investigated the effects of impregnation, relative humidity, temperature, and the inlet S^{2-} concentration on the adsorption process.

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They measured the concentration of S^{2-} using sulfur Microcoulomb Analyzer and Varian 3800 gas chromatograph with a pulsed flame photometric detector permitting the detection levels as low as 0.5 ppm. A Bagreev et al. [8] used four activated carbons of various origins impregnated with different concentrations of sodium hydroxide and used as H_2S adsorbents in an accelerated test. They used the standard dynamic test (ASTM D6646-01) to evaluate the performance of the carbons for H_2S adsorption. R. Sitthikhankaew et al. [9] used commercial and alkaline impregnated activated carbons and tested by the temperature program adsorption of H_2S at various temperatures. At high temperature of adsorption, alkaline activated carbons adsorbed H_2S significantly higher than commercial activated carbon. They employed sulfur analyzer (TruSpec CHNSO, LECO) for measuring content of sulfur in fresh and exhausted activated carbons. A. Hayashi et al. [10] used steelmaking slag in artificial seawater to reduce S^{2-} in it. They analyzed the reaction products with X-ray absorption fine structure and scanning electron microscopy energy dispersive X-ray detector and confirmed corresponding peaks of FeS, FeS_2, sulfur and sulfate. In addition to the above mentioned techniques, temperature-programmed decomposition [11,12], temperature-programmed reduction [13], X-ray photoelectron spectroscopy, X-ray absorption near-edge structure [14-17] spectroscopy etc. have been widely used for monitoring sulfur concentration. Based on our reviews it is seen that great scientific attention has been given to the adsorption / removal of sulfur in gaseous form as H_2S from various sectors. Although charcoal has been very widely used as an adsorbent in many adsorption processes, but its application for the study of adsorption of S^{2-} from aqueous system has not received much attention. Charcoal has been employed to remove halides from water. For example, activated carbon modified by silver aerogels was used by Sanchez et al. [18] to remove bromide and iodide from drinking water. Although many well known techniques are known, but conductometric technique has not received considerable use for investigation of S^{2-} adsorption. Conductometric method could be a very convenient technique for studying adsorption of S^{2-} and other ionic species as well as study of kinetics of ionic reactions. For example, very recently we reported on the study of kinetics of formation of AgCl by the reaction between Ag^+ and Cl^- ions in aqueous solution using very simple conductometric technique [19]. Chemical method for monitoring S^{2-} concentration is not suitable as it involves consumption of a

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lot of chemicals which makes the procedure expensive and also time consuming as it involves many lengthy and tedious steps. In the present article, adsorption of S^{2-} from aqueous solution was carried out on untreated and unmodified commercially purchased charcoal. Conductometric technique was employed for determination of time-dependent conductance. Conductance data was converted into concentration for studding the Freundlich and Langmuir isotherms. Kinetics of the adsorption was also studied.

2 EXPERIMENTAL

2.1 Procedure
The cell of the conductivity meter was thoroughly washed with distilled water to remove any adsorbed / adhered ionic species. The cell constant of the conductivity meter was estimated as 1.0 cm^{-1} using 0.01 M KCl solution that has specific conductance equal to 1408 µS cm^{-1} at 25 °C. The commercially purchased charcoal was thoroughly washed with distilled water and then dried in oven at 120 °C for 1 hour prior to use. Na_2S was used as the source of S^{2-}. 100 ml freshly prepared S^{2-} solution was taken in a clean beaker and the initial conductance of the solution was measured by placing the clean cell into the solution. Then 2.0 g of charcoal was added into the solution and a stopwatch was immediately turned on and the conductance was recorded within possible short time intervals till the conductance attained a steady-state value. The conductance was measured under static condition. The same procedure was repeated for measuring the conductance of all S^{2-} solutions in all investigated concentration range. The concentrations of S^{2-} used was in the range of 0.0005 to 0.008 M for adsorption study. The measurement were performed at 25 °C. All the measurement were done using a conductivity meter DDSJ−308F, China.

2.2 Methodology
Specific conductance of a solution is proportional to the concentration of ionic species and for S^{2-} solution it can be expressed as follows:

$$\kappa = K[S^{2-}] \qquad (1)$$

where κ is the conductance, $[S^{2-}]$ is the concentration of S^{2-} solution and K is a proportionality constant. If the value of K is known then mass of the adsorbed and solution phase S^{2-} can easily be obtained from the conductance data of the solution. Therefore, conductance of S^{2-} solutions in the range of concentration of 0.0005 to 0.02 M was measured and the values of κ were plotted as a function of $[S^{2-}]$ and the result is shown in Fig. 1. The value of the constant K was obtained as 416638 µS cm^{-1} M^{-1} from the slope of the plot. Consequently, the measured conductance during adsorption process was converted into time-dependent solution phase concentration of S^{2-} ($[S^{2-}]_{s,t}$) using the value of K according to Eq. (2):

$$[S^{2-}]_{s,t} = \kappa/K \qquad (2)$$

From the values of $[S^{2-}]_{s,t}$, the amount of sulfur adsorbed with time was calculated in mol L^{-1} ($[S^{2-}]_{a,t}$) and in gram per

gram (x/m) of charcoal using Eqs. (3) and (4):

$$[S^{2-}]_{a,t} = [S^{2-}]_0 - [S^{2-}]_{s,t} \qquad (3)$$

$$x/m = [S^{2-}]_{a,t} * 32.066 * V * 0.5 \qquad (4)$$

where 32.066 is the atomic weight of sulfur, V is the volume of S^{2-} solution used for the adsorption study, m is the mass of charcoal and $[S^{2-}]_0$ is the initial concentration of S^{2-} solution.
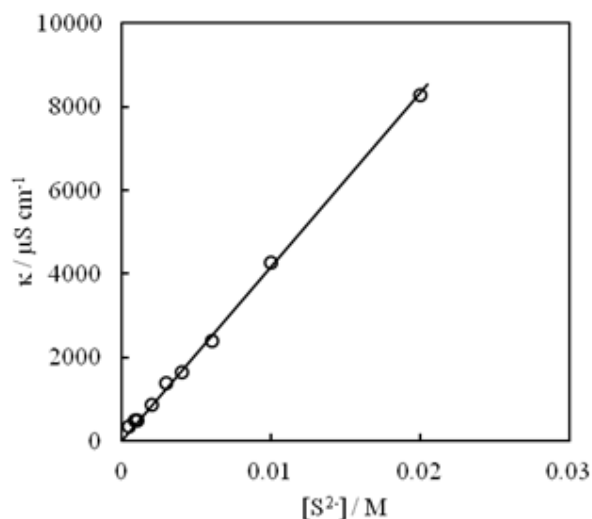

Fig.1. A linear plot of conductance (κ) vs. concentration of sulfide ($[S^{2-}]$) in the concentration range of 0.0005 to 0.02 M.

3 RESULTS AND DISCUSSION

3.1 Adsorption of S^{2-} on charcoal
The conductances of the S^{2-} containing solutions were recorded under static condition in the presence of 2.0 g charcoal in it. The conductance of the solution was recorded until an equilibrium was established, that is, a steady-state value of conductance was achieved. The same procedure was followed for all the solution under investigation in the concentration range of 0.0005−0.008 M. The measured conductances were then plotted as a function of time and the corresponding results are shown in Fig. 2. The results show that the values of κ_t decrease sharply at lower times and attain a level of trend at higher times, at approximately 40 min. The steady-state value corresponds to the establishment of an equilibrium between the adsorbed and solution phase S^{2-}. The amount of sulfur adsorbed per gram of charcoal was calculated using Eqs. (3) and (4). Then the values of x / m (in g g^{-1}) was plotted as a function of time and the results are shown in Fig 3.
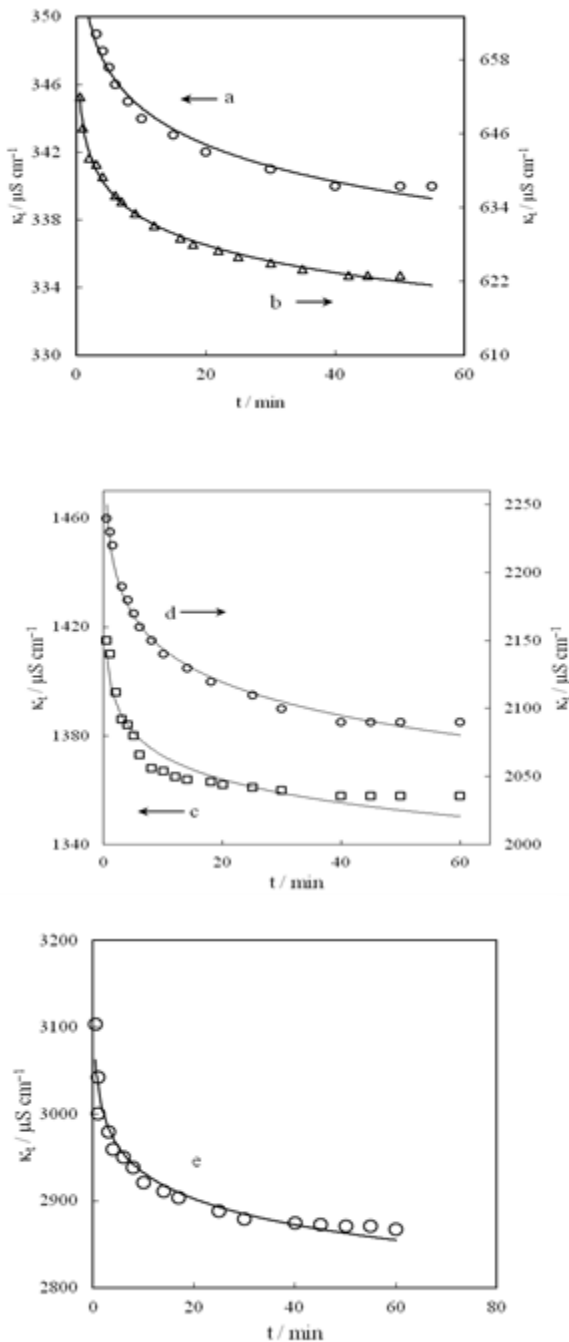
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Fig. 2. Plots of κ_t vs. time for (a) 0.0005, (b) 0.002, (c) 0.004, (d) 0.006 and (e) 0.008 M S^{2-} solutions containing 2.0 g of charcoal at 25 ℃.

The results show that the amount of adsorbed sulfur initially increases, which is followed by a steady- state value. From the steady-state part of the plots, the equilibrium amount of adsorbed sulfur were obtained for all concentrations. The amounts are (a) 0.0003, (b) 0.0008, (c) 0.0012, (d) 0.0016 and (e) 0.0018 g g^{-1} for various initial concentration in range of 0.0005−0.008 M under investigation. The values are summarized in Table 4. The equilibrium concentrations of S^{2-} ($[S^{2-}]_{e,s}$) were also obtained from the steady-state parts of the plots of $[S^{2-}]_{a,t}$ vs. time (not shown).

TABLE 1
Summarization of values of $[S^{2-}]_0$ / M, $[S^{2-}]_{e,s}$ / M, (x/m) / gg^{-1}, ln($[S^{2-}]$ / M), ln(x/m /gg-1) and $[S^{2-}]_{e,s}$ /(x/m) /M /gg^{-1} for solution of various concentrations

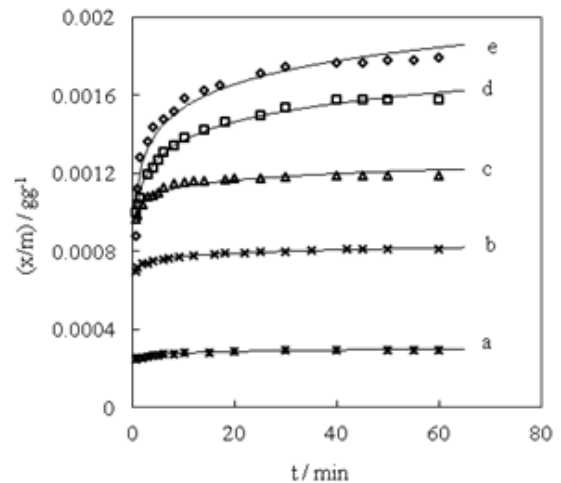| $[S^{2-}]_0$ / M	$[S^{2-}]_{e,s}$ / M	x/m / gg^{-1}	-ln ($[S^{2-}]_{e,s}$ / M)	/-ln(x/m / gg^{-1})	$[S^{2-}]_{e,s}$ /(x/m) / M /gg^{-1}
0.0005	0.0003	0.0003	8.1	8.1	1.1
0.002	0.0015	0.0009	6.5	7.1	1.9
0.004	0.0033	0.0012	5.7	6.7	2.7
0.006	0.0050	0.0016	5.3	6.4	3.1
0.008	0.0071	0.0018	4.9	6.3	3.9

Fig. 3. Plot of x/m vs. t for S^{2-} solutions of different concentrations: (a) 0.0005, (b) 0.002, (c) 0.004, (d) 0.006 and (e) 0.008 M in the presence of 2.0 g of charcoal at 25 ℃.

3.2 Study of adsorption isotherm

Adsorption isotherm is basically important to describe how adsorbates interact with adsorbents and is critical in optimizing the use of adsorbents. Adsorption isotherm can be used to relate the adsorbate concentration in the bulk and the adsorbed amount at the interface at equilibrium. In this study, the obtained data were fitted to Freundlich and Langmuir isotherms.

3.2.1 Freundlich adsorption isotherm

The values of $-\ln(x/m)$ were plotted against $-\ln[S^{2-}]_{e,s}$ for various concentrations of S^{2-} and the result is presented in Fig. 4. The values fall on a straight line. The values of Freundlich constant K_f and n were calculated from the intercept and the slope of the straight line as 29.3 and 1.7, respectively. The obtained value of n is greater than 1 suggesting that the data hold good for Freundlich adsorption.
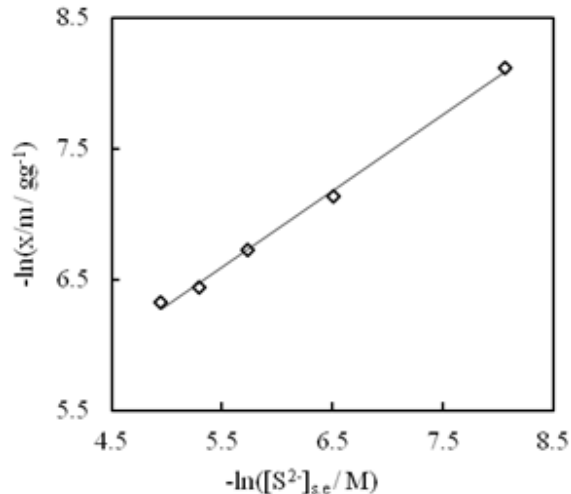
Fig. 4. *Linear plot of -ln(x/m /gg⁻¹) vs. -ln([S²⁻]ₑ,ₛ / M) for the adsorption of S²⁻ on charcoal from aqueous solution at 25 °C.*

3.2.2 Langmuir adsorption isotherm

Langmuir adsorption isotherm for the present study can be expressed as follows:

$$[S^{2-}]_{e,s}/(x/m) = 1/K_L K_m + [S^{2-}]_{e,s}/K_m \qquad (5)$$

where K_L is the equilibrium constant and K_m is another constant equal to the monolayer coverage. The derived values of $[S^{2-}]_{e,s}$ / (x/m) were plotted as a function of $[S^{2-}]_{e,s}$ for all the concentration of S^{2-} and the results are shown in Fig. 5.
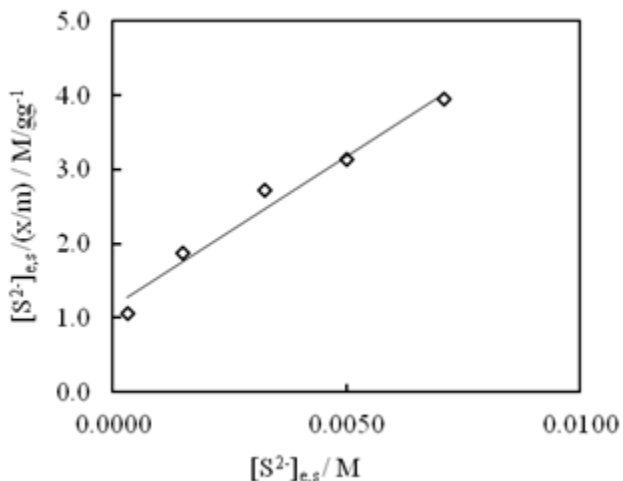

Fig. 5. *Linear plot of $[S^{2-}]_{e,s}$ /(x/m) vs. $[S^{2-}]_{e,s}$ for adsorption of S²⁻ on charcoal from aqueous solution at 25 °C.*

It shows that the values nicely fall on a straight line. From the intercept and slope of the straight line, the equilibrium constant was obtained as 350 and the monolayer coverage was obtained as 2.5 mg g⁻¹. The result thus implies that the adsorption also followed Langmuir isotherm satisfactorily.

3.3 Kinetic study of S²⁻ adsorption

First-order rate equation (Eq. (6)) can be written in term of conductance as shown in Eq. (7):

$$\ln C_t = \ln C_e - kt \qquad (6)$$

$$\ln \kappa_t = \ln \kappa_\infty - kt \qquad (7)$$

where κ_∞ is the steady-state conductance of S^{2-} solution and k is the first-order rate constant. Therefore, $\ln\kappa_t$ were plotted as a function of time for two different concentrations of (a) 0.006 and (b) 0.008 M. The values fall on their respective straight lines suggesting that the adsorption of S^{2-} on commercial charcoal used in the present study followed a first-order kinetics. The average first-order rate constant was calculated as 2.65×10^{-3} s⁻¹ from the slopes of the straight lines.

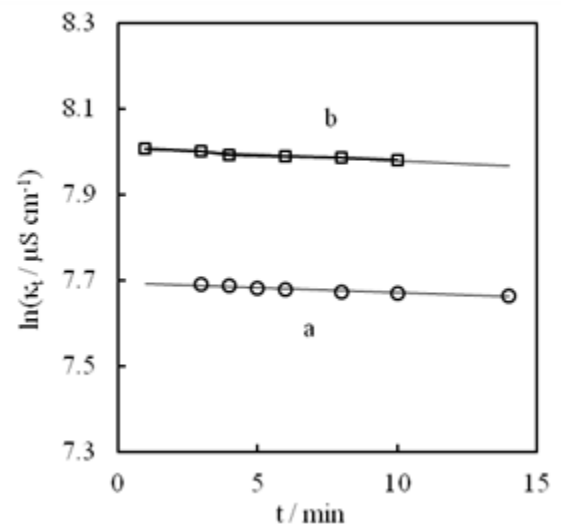**Fig. 6.** *Linear plots of $ln(\kappa_t/\mu S\ cm^{-1})$ vs. time for adsorption of S²⁻ from (a) 0.006 and (b) 0.008 M S²⁻ solutions.*

4 CONCLUSIONS

A linear calibration curve for S^{2-} in the concentration range of 0.0005-0.02 M was obtained. The calibration curve was successfully employed to monitor the variable concentrations of S^{2-}. Adsorption of S^{2-} on charcoal was monitored conductometrically. The adsorption of S^{2-} on charcoal was found to follow both the Freundlich and Langmuir isotherms. The values of K_f and n were obtained as 29.3 and 1.7, while the adsorption equilibrium constant K_L was calculated as 350 at 25°C. The amount of sulfur adsorbed leading to the formation of monolayer was calculated as 2.5 mg per gram of charcoal. The adsorption of S^{2-} on charcoal was found to follow a first-order kinetics. The average first-order adsorption rate constant was calculated as 2.65×10^{-3} s⁻¹. The present work thus successfully demonstrate the studies of S^{2-} adsorption on charcoal using a simple conductometric technique. The method could be utilized for monitoring concentration of ionic species in many physical and chemical processes, specially for removing harmful ions from drinking water during crisis period.

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