Adsorption of acids and bases from aqueous solutions onto silicon dioxide particles

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ABSTRACT

The adsorption of acids and bases onto the surface of silicon dioxide (SiO_2) particles was systematically studied as a function of several variables, including activation conditions, contact time, specific surface area, particle size, concentration and temperature. The physical properties of SiO_2 particles were investigated, where characterizations were carried out by FT-IR spectroscopy, and morphology was examined by scanning electron microscopy (SEM). The SEM of samples showed good dispersion and uniform SiO_2 particles with an average diameter of about 1–1.5 μm. The adsorption results revealed that SiO_2 surfaces possessed effective interactions with acids and bases, and greatest adsorption capacity was achieved with NaOH, where the best fit isotherm model was the Freundlich adsorption model. The adsorption properties of raw SiO_2 particles were further improved by ultrasonication. Langmuir monolayer adsorption capacity of NaOH adsorbate at 25 °C on sonicated SiO_2 (182.6 mg/g) was found to be greater than that of the unsonicated SiO_2 (154.3 mg/g). The spontaneity of the adsorption process was established by decreases in ΔG_{ads}^0, which varied from −10.5 to −13.6 kJ mol^{-1}, in the temperature range 283–338 K.

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1. Introduction

Environmental pollutants increase continuously across the world as industrial processes generate a large variety of molecules that pollute air and water as a result of negative impacts on ecosystems and humans [1]. These contaminants contain many chemicals including heavy metal ions, minerals, colourants and acids and bases. Nearly all these waste materials contain acid and base contaminants directly and/or other contaminants having acidic or basic properties. Acids and bases are ubiquitous in the environment and are hazardous at high levels, eventually falling into water from various sources [2].

Conventional technologies for the removal of contaminants, such as chemical precipitation, electrolysis, ion exchange and reverse osmosis are often neither effective nor economical [3,4]. As a physico–chemical treatment process, adsorption is highly effective, cheap and easy to adapt [5]. Recently, a great many novel adsorption processes have also been developed for enhancing the efficiency of removing organic and inorganic contaminants from water. These methods include adsorption/catalytic oxidation processes, adsorption/catalytic reduction, adsorption coupled with redox [6], oxidation/reduction of adsorbents, demineralization of adsorbents, activation of particles with acid/base treatment and

functionalization of adsorbent for selectivity [7]. The work herein demonstrates the impact of ultrasonication on acid–base adsorption efficiency, particle size and morphology.

Silicon dioxide (SiO_2) particles are widely used in industry as additives and/or fillers [8,9], catalysts, adsorbents, chromatographic separation media, drug delivery supports, oil-spill cleaning [10], separation and purification of matter and the removal of contaminants. Additionally, SiO_2 has been used in the grafting of electroactive species for electrochemical sensors, and for the determination and clarification of pollutants [11]. Due to SiO_2 powders having high free energy, they are easily adsorbed by water at room temperature to undergo hydroxylation [12]. SiO_2 is used as an agent to attract moisture and protect against the aggregation of powders in some powder mixture products due to their high moisture adsorption capabilities. The synthesis of sub-micrometre sized silica particles as hollow silica cuboids have been studied [13]. The adsorption behaviour of various organic adsorbates on silica surface has been reviewed [14].

The adsorption, adhesion, chemical and catalytic properties of silica particles depend on the chemistry of the particle surface. Adsorption by a solid is not a very important process unless the solid has a very large surface compared to its mass. Consequently, SiO_2 is especially effective because it has a highly porous structure. SiO_2 can be activated by being sonicated to highly fine particles in an aqueous suspension, under stirring, at room temperature. This treatment decreases the particles size and increases the surface porosity.

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The aim of this study was to investigate the adsorption of acid and base adsorbates onto SiO_2 particles and to understand the way in which these acid and base adsorbates interact with SiO_2. Adsorption at different temperatures were carried out to investigate the physical interactions of acids and bases on the surface of SiO_2. In an effort to achieve this, the effect of various parameters on the adsorption process was also investigated. Thermodynamic data was calculated to interpret the results. The adsorption capacity of SiO_2 particles by ultrasonication was improved.

2. Materials and methods

2.1. Materials

Hydrochloric acid (37%), acetic acid and ammonium hydroxide solutions (29%, reagent grades), sodium hydroxide, potassium bromide, acetone, methanol, ethanol, diethyl ether, phenolphthalein indicator, SiO_2, and standard equipment were purchased from Aldrich and Merck and used as received.

2.2. Instrumentation

FT-IR spectra of SiO_2 in KBr were recorded using a Shimadzu 5300 FT-IR spectrometer averaging 64 scans at a resolution $1\,cm^{-1}$. SiO_2 particle suspensions were sonicated and homogenized by a Bandelin Sonopuls Model Ultrasonic Homogenizer. To determine the effect of temperature, adsorption experiments were carried out at different temperatures using sonicated SiO_2 particles by a Koehler Model Viscosimeter Set, equipped with a large cylindirical bath filled with water or oil and a temperature-adjustable water circulatory thermostat.

2.3. Physical properties of SiO_2 particles

5 mL solutions of 1 M HCl, 1 M HNO_3, 1 M H_2SO_4, 1 M NH_4OH, 1 M NaOH, 1 M CH_3COOH, H_2O, hexane, methanol, diethyl ether were added to 10 pre-labelled 10 mL cylindirical glass sample tubes, having respective lids, to which weighed SiO_2 particles (50 mg) were added. Each sample tube containing the SiO_2 suspension was closed and vigorously shaken and left to rest to examine the physical changes. The physical changes in each sample tube containing the different suspensions was noted by observation and the results were graded in the range of 1–5, and tabulated accordingly. The physical properties examined were solubility, dispersion, sedimentation and colour change.

2.4. Activation experiment

In this study, unsonicated and sonicated SiO_2 particles were used for the adsorption experiments. Before the adsorption experiments, the SiO_2 particles were activated by ultrasonication. SiO_2 particles were sonicated as described here: SiO_2 (80 g) were added into 1 L Erlenmeyer and then distilled water (500 mL) was added. The resulting suspension was sonicated using an ultrasonic probe at 1000 rpm, with stirring, at room temperature, for 48 h. The temperature of the suspension and the solid-to-liquid ratio was kept constant. The SiO_2 particle suspensions were sonicated and homogenized. The activated samples were rinsed with distilled water and isolated by filtration by a filtration funnel and filter paper. After filtration, the collected sonicated SiO_2 particles were dried in a vacuum oven at 75 °C for 48 h. This sample was used for the sonicated SiO_2 particle adsorption studies.

2.5. Morphology

In this study, the surface morphology and dimensionality of unsonicated and sonicated SiO_2 particles were examined by scanning electron microscopy (SEM). In SEM analyses, samples were attached to carbon tape for surface morphology and dimensionality analyses. These samples were placed onto an aluminium stub and then used for measurements after coating with platinum. The micrographs were taken at an acceleration voltage of 15 kV in a Hitachi S-4700 Field Emission Scanning Electron Microscope.

2.6. Adsorption measurements

100 mL solutions of acetic acid (with concentrations 0.00625, 0.0125, 0.025, 0.0375, 0.05, 0.0625, 0.075, 0.0875, 0.1 and 0.1125 M) were added to 10 pre-labelled 250 mL Erlenmeyers, having respective lids, to which weighed SiO_2 (1 g) was added. Each Erlenmeyer containing the SiO_2 suspensions was closed and vigorously shaken continuously for 15 min and left to rest for 2 h to reach equilibrium. The suspensions were then filtered using a filtration funnel. 25 mL aliquots of the most diluted filtrate and 10 mL aliquots of the other remaining filtrates were taken and titrated against standardized 0.1N NaOH, in the presence of phenolphthalein indicator. In a similar manner, the above procedure was conducted for hydrochloric acid, sodium hydroxide and ammonium hydroxide adsorbates, where for HCl, titrations were run against 0.1N NaOH, and for NaOH and NH_4OH, titrations were run against 0.1N HCl.

Contact time: In order to determine adsorption contact time, adsorption experiments were carried out with variations in time, using sonicated SiO_2 particles. As described for the adsorption measurements, 100 mL solutions of acetic acid (0.1125 M) were added to 10 pre-labelled 250 mL Erlenmeyers with weighed SiO_2 (1 g). The so prepared suspensions after being vigorously shaken for 15 min were left to rest for 10, 20, 30, 60, 90, 120, 150, 180, 210 and 240 min. After subsequent filtration, 10 mL aliquots of each filtrate were titrated against standardized 0.1N NaOH in the presence of phenolphthalein indicator. In a similar manner, the remaining titrations were carried out as described above.

Effect of temperature: In order to determine the effect of temperature, adsorption experiments were carried out at different temperatures using sonicated SiO_2 particles. As described for the adsorption measurements, where 100 mL solutions of acetic acid (with concentrations 0.00625, 0.0125, 0.025, 0.0375, 0.05, 0.0625, 0.075, 0.0875, 0.1 and 0.1125 M) were added to 10 pre-labelled 250 mL Erlenmeyers with weighed SiO_2 (1 g). For the first adsorption experiment, the so prepared SiO_2 suspensions after being vigorously shaken for 15 min and maintained at 10 °C were left to rest in a bath for 2 h to reach equilibrium. After subsequent filtration, as described above in Section 2.6, 25 mL aliquots of the most diluted filtrate and 10 mL aliquots of the other remaining filtrates were titrated against standardized 0.1N NaOH, in the presence of phenolphthalein indicator. In a similar manner, the remaining titrations were carried out as described above. The above procedure was repeated for 25, 45 and 65 °C to complete adsorption study.

3. Results and discussion

3.1. Physical properties of SiO_2 particles

The physical properties of the SiO_2 particles and their characterizations to include FT-IR and morphology by SEM, were investigated prior to the adsorption measurements.

The average size of the original unsonicated SiO_2 particles was 2–3 μm with a size distribution of 99.9% below 23 μm, 75% below 4 μm, and 50% below 2 μm before sonication. The average size of the sonicated SiO_2 particles was 1–1.5 μm with a size distribution of 99.9% below 14 μm, 75% below 3 μm, and 50% below 1 μm after sonication.

Table 1
Results of the physical properties of SiO_2 particles.

Solutions or solvents	Solubility		Dispersion		Sedimentation		Colour change	
	a	*b*	*a*	*b*	*a*	*b*	*a*	*b*
HCl	4	3	3	4	2	1	4	5
HNO_3	4	3	3	4	2	1	4	5
H_2SO_4	4	3	3	4	2	1	4	5
CH_3COOH	4	3	4	5	2	1	5	5
NH_4OH	3	2	3	4	3	2	4	5
NaOH	3	2	3	4	2	1	4	5
Hexane	5	5	4	5	2	1	5	5
Methanol	5	5	5	5	1	1	5	5
H_2O	5	5	5	5	1	1	5	5
Diethyl ether	5	5	5	5	1	1	5	5

The physical properties of SiO_2 particles after 1 and 24 h observations were tabulated according to the range 1–5, with 1: very good; 2: good; 3: normal; 4: low; and 5: none. The following results of the physical properties of SiO_2 particles were deduced: (1) surface errosions of SiO_2 particles which occurred in basic solutions were much greater than the other suspensions and solvents; (2) solubility of SiO_2 particles in acidic solutions was less than that for the basic solutions; (3) sedimentation of particles was very good in both polar and apolar suspensions and solvents; (4) solubility and dispersion of particles was very low in apolar suspensions and solvents; and (5) only slight colour changes occurred in acidic and basic solutions. The complete set of results for the physical properties of SiO_2 particles is summarized in Table 1.

3.2. Fourier transform infrared spectroscopy (FT-IR) studies

The FT-IR spectrum of pure SiO_2 particles is shown in Fig. 1. The broad and strong peak at $3471.6\,cm^{-1}$ is due to adsorbed water on SiO_2 particles. The peak at about $832\,cm^{-1}$ belongs to the Si–O band vibration. The original broad and strong peak at about $1136\,cm^{-1}$ is attributed to the overlapping of the combined results of the Si–O band vibrations and/or stretching in SiO_2 particles and Al–O band vibrations and/or stretching in the Al_2O_3 which exists as impurities in SiO_2 particles. The peaks at about $478\,cm^{-1}$ and $998\,cm^{-1}$ may originate from a combination of different bending modes of O–Si–O bonds.
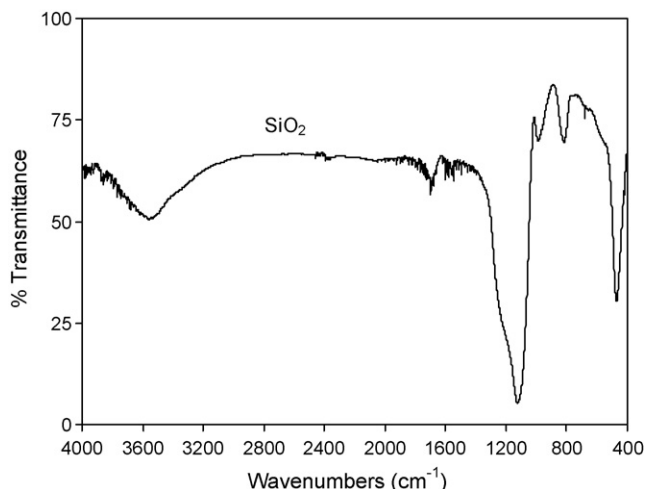
3.3. Morphology studies of SiO_2 particles

The morphology, porosity and the particle size of the unsonicated and sonicated silicon dioxide particles used in the adsorption experiments were examined. The micrographs showing the morphology of the unsonicated and sonicated SiO_2 particles are shown in Fig. 2, where the bar at the bottom of each respective micrograph was used for particle size measurements. The micrographs depicting both unsonicated and sonicated SiO_2 particles revealed that the particles were not wholly spherical, but close to a spherical shape, condensed, unhomogeneous, and of a not so well-ordered structure
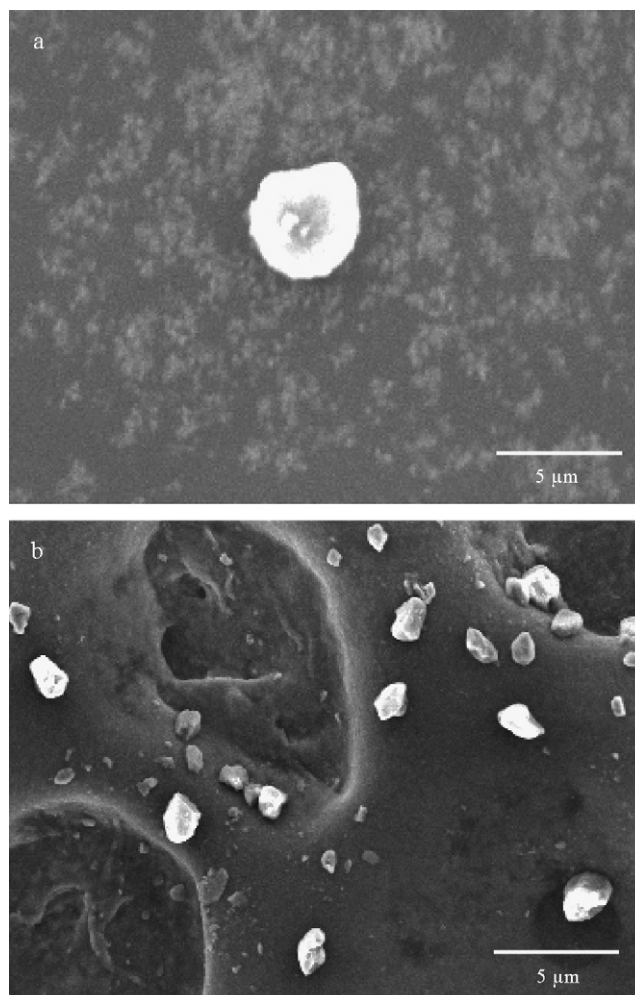

Fig. 2. SEM of (a) unsonicated single and (b) sonicated multiple SiO_2 particles.

Fig. 1. FT-IR spectrum of pure SiO_2 particles.

and shape. The micrographs clearly showed that the particle size of the sonicated SiO_2 particles significantly decreased compared to the particle size of the unsonicated SiO_2 particles. This can be seen in the single particle micrograph (Fig. 2a) and in the multiple particle micrograph (Fig. 2b). Also, the micrographs showed that the porosity of the sonicated SiO_2 particles significantly increased compared to the porosity of the unsonicated SiO_2 particles. Thus, the adsorption experiments showed that the adsorption capacity of sonicated SiO_2 particles increased as a result of their high porous surface area.

3.4. Adsorption of acids and bases on SiO₂ particles

While solids exist because of intermoleculer forces between the repeating units that make up the lattice, these intermoleculer forces are unsaturated or unsatisfied at the surface of the solid. In the interior of a solid, each molecule (that is, if it is a molecular solid) is surrounded on all sides by identical molecules. At the surface of such a solid, however, each molecule is only partially surrounded by identical molecules and in such a case, any approaching molecule or ion becomes adsorbed to its surface; the solid phase is called the adsorbent and the molecules that are adsorbed on the adsorbent are collectively called the adsorbed phase or adsorbate. The adsorbate may be either a gas (molecules) or a solid (molecules or ions) in solution. In this study, the adsorption of different acids and bases on SiO_2 particles in aqueous solution were investigated.

The amount of adsorption, given the symbol Y, has units of moles adsorbate per mass adsorbent. If the adsorbate is a gas, Y may have units of volume adsorbate per mass adsorbent. The amount of adsorption Y increases with the concentration c of the adsorbate. Initially, when the surface of the adsorbent is relatively free the increase is rapid. As the surface fills with adsorbate, the rate of adsorption dy/dc decreases. Eventually, the surface of the adsorbent becomes full with adsorbate, and further increases in the concentration cause no further increase in the amount adsorbed. The amount adsorbed when the surface is just covered with a monomolecular layer of adsorbate is called Y_{max}. At this point, for a given concentration, the amount adsorbed decreases with increasing temperature.

In this study, the Freundlich and Langmuir adsorption equations, given as below, were used for plotting the adsorption isotherms, and for the calculations of the Freundlich and Langmuir constants and thermodynamic parameters. One of the earliest attempts to mathematically describe the adsorption isotherms was the Freundlich equation [15]:

$$Y = kc^{1/n} \tag{1}$$

In this a purely empirical equation, where the units of Y are moles adsorbate per gram adsorbent, c is the concentration of adsorbed liquid (mol/L), and k and n are experimentally determined constants, which depend on the features of adsorbent and adsorbate, and the temperature. Since Eq. (1) is only valid for a given adsorbed phase and adsorbate at a constant temperature, it is sometimes called the Freundlich isotherm. To test the validity of the Freundlich isotherm, the logarithms of Eq. (1) are applied:

$$\log Y = \log k + \frac{1}{n} \log c \tag{2}$$

This equation results, where when $\log Y$ plotted against $\log c$ gives a straight line of slope $1/n$ and an intercept of $\log k$.

To determine whether adsorptions follow the Langmuir equation, and to evaluate some parameters of the adsorption, data was applied to the Langmuir equation [16], which written in the linear form is

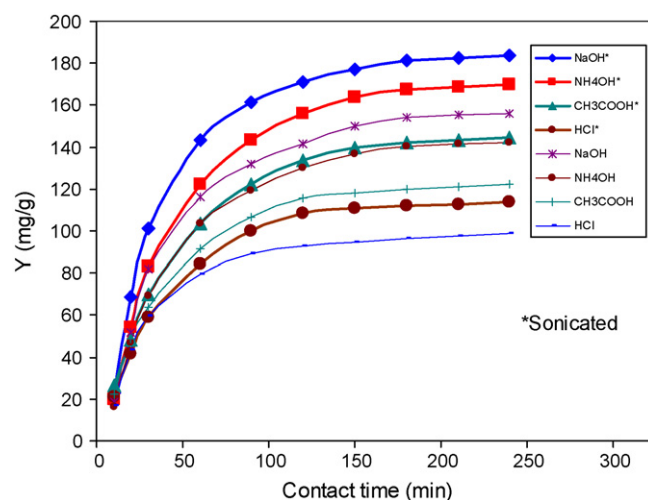$$\frac{c}{Y} = \frac{1}{kY_{max}} + \frac{c}{Y_{max}} \tag{3}$$

Fig. 3. Adsorption isotherms showing effect of contact time of adsorptions of NaOH, NH_4OH, CH_3COOH and HCl on the surface of unsonicated and sonicated SiO_2 particles.

where k is the adsorption constant and Y_{max} is the limiting amount of adsorbate that can be taken up by unit mass of adsorbent. Both k and Y_{max} are constant for the particular system under investigation and for a given temperature. The adsorption constant k can be related to the adsorption free energy, ΔG^0_{ads}, calculated using the equation below [17]:

$$\Delta G^0_{ads} = -RT(\ln k + 4.02) \tag{4}$$

where R is the gas constant and T is the absolute temperature. If a system follows the Langmuir equation, then a plot of c/Y against c (Eq. (3)) gives a straight line with slope $1/Y_{max}$ and an intercept $1/kY_{max}$.

In this study, the adsorptions of different acids and bases on the surface of SiO_2 particles were investigated according to the Freundlich and Langmuir adsorption isotherms. Hydrochloric acid, acetic acid, ammonium hydroxide and sodium hydroxide adsorbates were chosen and the physical interactions on the surface of SiO_2 in aqueous solutions were examined.

3.5. Effect of contact time of adsorption on unsonicated and sonicated SiO₂ particles

The effects of contact time for adsorptions of different acids and bases on the surface of unsonicated and sonicated SiO_2 particles were investigated. The adsorption isotherms showing the effect of contact time of the adsorptions of NaOH, NH_4OH, CH_3COOH and HCl on the surface of unsonicated SiO_2 particles are shown in Fig. 3. The times for these adsorptions to reach an equilibrium for these acids and bases were approximately 150, 140, 135 and 125 min, respectively. In general, the rate of adsorption for all the adsorbates was rapid until about 115 min, and the amount adsorbed was high. After 115 min adsorption time, the amount of adsorption varied only slightly and remained approximately at same level to eventually reach a plateau. The effect of contact time on the surface of sonicated SiO_2 particles is also shown in Fig. 3. The times for these adsorptions to reach an equilibrium for these acids and bases studied were approximately 170, 160, 150 and 140 min, respectively. Rapid and high adsorption was observed until about 130 min, after which the amount of adsorption varied only slightly and remained approximately at same level to eventually reach a plateau. The adsorption isotherms for the surface of sonicated SiO_2 particles were then compared against those of the unsonicated SiO_2 particles. It can be clearly seen that the time for adsorptions to
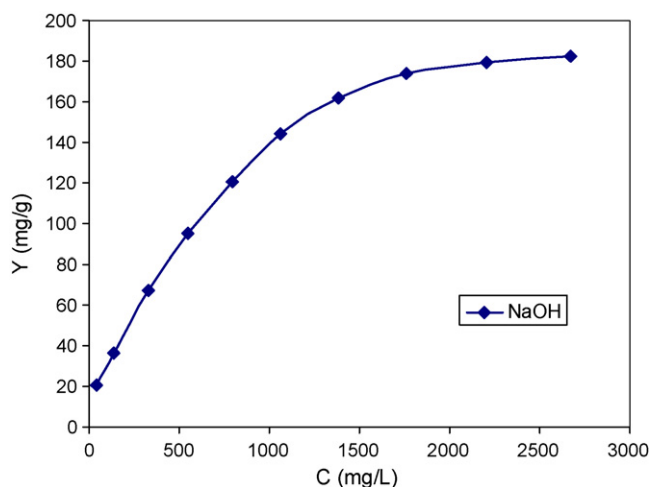
Fig. 4. Freundlich adsorption isotherm of NaOH adsorbate at 25 °C on the surface of sonicated SiO$_2$ particles.

Fig. 6. Freundlich linear adsorption isotherm for NaOH adsorbate at 25 °C on the surface of sonicated SiO$_2$ particles.

reach equilibrium for sonicated SiO$_2$ particles was approximately 15–20 min longer than that of unsonicated SiO$_2$ particles. Further, the amounts of adsorbed adsorbates for sonicated SiO$_2$ particles were obviously more than that of unsonicated SiO$_2$ particles.

3.6. Effect of sonication on Freundlich adsorption isotherms

One of the aims of this study was to investigate the contribution of sonication on the adsorption capacity. For illustration, the Freundlich adsorption isotherm of NaOH adsorbate at 25 °C on the surface of sonicated SiO$_2$ particles is shown in Fig. 4. The maximum amounts of adsorbed NaOH adsorbate on the surface of unsonicated and sonicated SiO$_2$ particles were found to be approximately 160 and 180 mg/g, respectively. These values clearly indicated that the sonication process increased the adsorption capacity by a great amount. The Freundlich adsorption isotherms of all the different acid and base adsorbates showing the effect of sonication on the surface of unsonicated and sonicated SiO$_2$ particles were compared and are shown in Fig. 5. As can be seen from the plots, the amount of adsorbed adsorbates on the surface of sonicated SiO$_2$ particles were found to be greater than those of the unsonicated SiO$_2$ particles. The maximum amounts of adsorbed adsorbates on the surface of unsonicated and sonicated SiO$_2$ particles can be obtained numer-
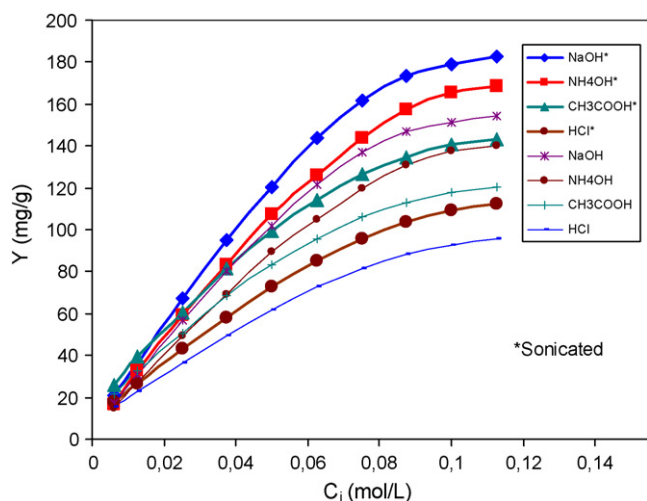
ically from their respective plots. This clearly indicated that the sonication process increased the adsorption capacity by a great amount. For illustration, the Freundlich linear adsorption isotherm of NaOH adsorbate at 25 °C on the surface of sonicated SiO$_2$ particles is shown in Fig. 6. The Freundlich adsorption constants k and n were calculated from the slope and intercept of the linear adsorption isotherms. The parameters for all the adsorbates studied are summarized in Table 2. The adsorption free energies for the sonicated particles were more negative than those of the unsonicated particles, indicating that adsorption was more feasible for the sonicated particles.

3.7. Effect of sonication on Langmuir adsorption isotherms and the determination of the specific surface area of the adsorbent

The contribution and effect of sonication on the surface of SiO$_2$ particles for Langmuir adsorption isotherms were studied. For illustration, the Langmuir adsorption isotherm of CH$_3$COOH adsorbate at 25 and 65 °C on the surface of sonicated SiO$_2$ particles is shown in Fig. 7. The Langmuir adsorption isotherm of all the other adsorbates on the surface of unsonicated and sonicated SiO$_2$ were plotted and evaluated in a similar way. The Langmuir adsorption constants Y_{max} and k, and ΔG^0_{ads} were calculated from the slope and intercept of these linear Langmuir adsorption isotherms for unsonicated and sonicated SiO$_2$. The results of the parameters for all the adsorbates studied are summarized in Table 3.

The effect of sonication and the specific surface area of adsorbents was investigated. It is possible to calculate the area of the adsorbent when the adsorption of the adsorbate leads to a maximum as is the case for a single molecular layer, whereby adsorption is complete as described earlier. The determination of the area of an adsorbed molecule is simple in the case of small adsorbed gas molecules, such as, helium, hydrogen and nitrogen. When the adsorbed molecule is a carboxylic acid, however, the structure is clearly more complex. Nevertheless, studies of the adsorption of straight-chain aliphatic monocarboxylic acids indicate that the number of moles of acid adsorbed per gram adsorbent is independent of the chain length [18]. This suggests that the acid molecules are adsorbed vertically, with the aliphatic chain up and the carboxyl group down attached to the adsorbent. The cross-sectional area A_a of a staight-chain acid may be taken to be about 21×10^{-20} m^2 [18]. The specific area of the adsorbent S (m^2/g) is given by

$$S = A_a N_A Y_{max} \qquad (5)$$

where N_A is Avogadro's number.

Fig. 5. Freundlich adsorption isotherms for different acids and bases showing effects of sonication. C_i: initial concentration.
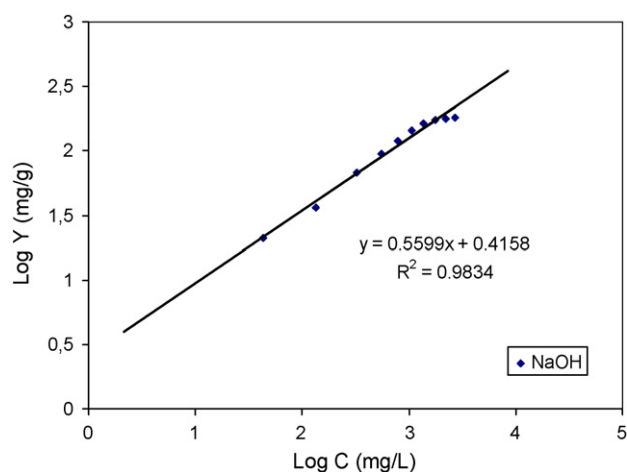
Table 2
Data obtained from Freundlich adsorption isotherms for different acids and bases at 25 °C.

Adsorbate	T (°C)	Slope (L/g)	Intercept (mg/g)	R^2	n (g/L)	k (mg/g)	ΔG^0_{ads} (kJ mol^{-1})
NaOH	25[a]	0.623	0.109	0.983	1.609	1.315	−10.6
	25[b]	0.559	0.417	0.985	1.786	2.719	−12.4
NH$_4$OH	25[a]	0.646	0.015	0.991	1.547	1.165	−10.3
	25[b]	0.615	0.243	0.985	1.626	2.204	−11.9
CH$_3$COOH	25[a]	0.512	0.195	0.995	1.954	1.071	−10.1
	25[b]	0.481	0.391	0.993	2.078	1.812	−11.4
HCl	25[a]	0.531	0.145	0.991	1.883	1.032	−10.0
	25[b]	0.487	0.373	0.985	2.053	1.604	−11.1

[a] Results for unsonicated SiO$_2$ particles.
[b] Results for sonicated SiO$_2$ particles.

Table 3
Data obtained from Langmuir adsorption isotherms for different acids and bases at 25 °C.

Adsorbate	T (°C)	Slope (g/mol)	Intercept (g/L)	R^2	Y_{max} (mol/g)	k (L/mol)	ΔG^0_{ads} (kJ mol^{-1})	S (m^2/g)	%S increase (m^2/g)
NaOH	25[a]	231.9	7.086	0.967	0.0043	31.85	−18.5		
	25[b]	207.7	3.266	0.967	0.0048	65.81	−20.3		
NH$_4$OH	25[a]	253.2	9.440	0.988	0.0039	27.10	−18.1		
	25[b]	225.9	5.177	0.995	0.0044	47.28	−19.5		
CH$_3$COOH	25[a]	311.9	9.195	0.982	0.0032	24.01	−17.8	405.4	12.2
	25[b]	275.4	5.712	0.981	0.0036	37.42	−18.9	459.3	
HCl	25[a]	401.8	12.483	0.965	0.0025	21.28	−17.5		
	25[b]	345.9	8.074	0.965	0.0029	30.58	−18.4		

S: specific surface area.
[a] Results for unsonicated SiO$_2$ particles.
[b] Results for sonicated SiO$_2$ particles.

The effect of sonication on a specific surface area of adsorbent was examined. For illustration, the Langmuir adsorption isotherm of CH$_3$COOH adsorbate at 25 °C on the surface of sonicated SiO$_2$ particles is shown in Fig. 7. The specific surface area of unsonicated and sonicated SiO$_2$ particles was calculated using the Langmuir adsorption isotherms of CH$_3$COOH adsorbate and the specific surface area using the slope and intercept of the linear Langmuir adsorption isotherms. The data obtained from the Langmuir adsorption isotherms for NaOH, NH$_4$OH, CH$_3$COOH and HCl adsorbates at 25 °C on the surface of unsonicated and sonicated SiO$_2$ is summarized in Table 3. As a result of sonication, the specific surface area of sonicated SiO$_2$ particles using CH$_3$COOH adsorbate increased by approximately 12.2%.
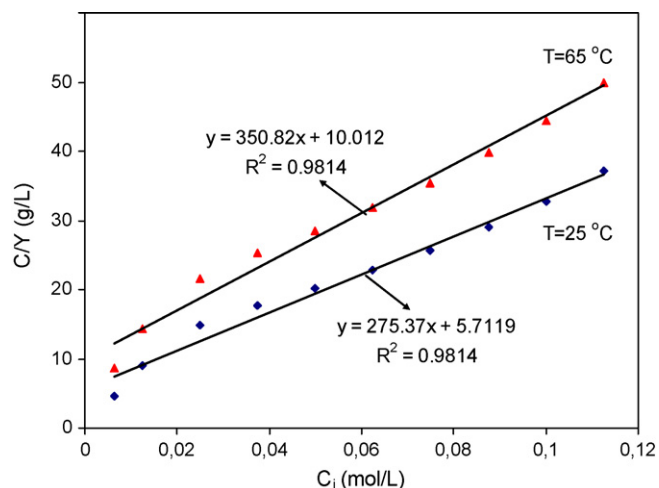
3.8. Effect of temperature on Freundlich adsorption isotherms for different acids and bases using sonicated SiO$_2$ particles

To examine the effect of temperature on the Freundlich adsorption isotherms for different acid and base adsorbates, the adsorptions carried out at 10, 25, 45 and 65 °C on the surface of sonicated SiO$_2$ particles were investigated. For illustration, the Freundlich adsorption isotherm of NaOH adsorbate at 10, 25, 45 and 65 °C on the surface of sonicated SiO$_2$ particles is shown in Fig. 8. The Freundlich adsorption constants were calculated at different temperatures from the slope and intercept of the linear Freundlich adsorption isotherms for sonicated SiO$_2$ particles. As can be seen from the plots, the amount adsorbed on the surface of sonicated particles decreased as the temperature of adsorption

Fig. 7. Langmuir adsorption isotherm for CH$_3$COOH adsorbate at 25 and 65 °C on the surface of sonicated SiO$_2$ particles. C_i: initial concentration.
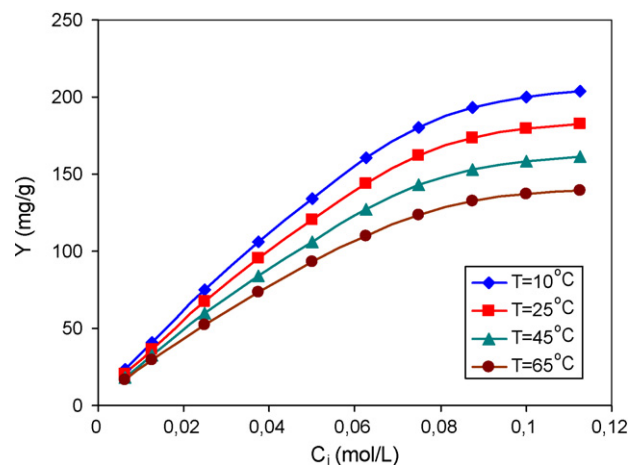

Fig. 8. Freundlich adsorption isotherm of NaOH adsorbate at different temperatures on the surface of sonicated SiO$_2$ particles. C_i: initial concentration.

Table 4
Data obtained from Freundlich adsorption isotherms of NaOH, NH$_4$OH, CH$_3$COOH and HCl adsorbates at different temperatures on the surface of sonicated SiO$_2$ particles.

Adsorbate	T (°C)	Slope (L/g)	Intercept (mg/g)	R^2	n (g/L)	k (mg/g)	ΔG_{ads}^0 (kJ mol^{-1})
NaOH	10	0.484	0.731	0.984	2.068	5.852	−13.6
	25	0.559	0.417	0.985	1.786	2.719	−12.4
	45	0.610	0.172	0.984	1.638	1.351	−11.4
	65	0.609	0.082	0.987	1.639	0.761	−10.5
NH$_4$OH	10	0.557	0.502	0.986	1.795	4.166	−12.8
	25	0.615	0.243	0.985	1.626	2.204	−11.9
	45	0.657	0.029	0.985	1.523	1.204	−11.1
	65	0.626	0.029	0.994	1.597	0.736	−10.4
CH$_3$COOH	10	0.455	0.538	0.991	2.201	3.122	−12.1
	25	0.481	0.391	0.993	2.078	1.812	−11.4
	45	0.503	0.261	0.994	1.989	1.072	−10.8
	65	0.522	0.125	0.995	1.915	0.712	−10.3
HCl	10	0.441	0.578	0.974	2.269	2.636	−11.7
	25	0.487	0.373	0.985	2.053	1.604	−11.1
	45	0.518	0.218	0.989	1.931	1.001	−10.6
	65	0.546	0.059	0.992	1.833	0.685	−10.2

Table 5
Data obtained from Langmuir adsorption isotherms of NaOH, NH$_4$OH, CH$_3$COOH and HCl adsorbates at different temperatures on the surface of sonicated SiO$_2$ particles.

Adsorbate	T (°C)	Slope (g/mol)	Intercept (g/L)	R^2	Y_{max} (mol/g)	k (L/mol)	ΔG_{ads}^0 (kJ mol^{-1})
NaOH	10	186.7	1.745	0.966	0.0054	125.75	−20.8
	25	207.7	3.266	0.967	0.0048	65.81	−20.3
	45	224.0	6.032	0.967	0.0045	33.76	−19.9
	65	262.1	8.205	0.971	0.0038	18.74	−19.5
NH$_4$OH	10	201.9	2.329	0.976	0.0049	85.58	−19.9
	25	225.9	5.177	0.995	0.0044	47.28	−19.5
	45	244.3	8.441	0.998	0.0041	25.84	−19.2
	65	293.4	11.247	0.997	0.0034	14.61	−18.8
CH$_3$COOH	10	247.7	4.128	0.981	0.0041	65.32	−19.3
	25	275.4	5.712	0.981	0.0036	37.42	−18.9
	45	307.7	7.553	0.981	0.0033	20.63	−18.6
	65	350.8	10.012	0.981	0.0029	12.06	−18.3
HCl	10	315.2	5.553	0.965	0.0032	51.54	−18.7
	25	345.9	8.074	0.965	0.0029	30.58	−18.4
	45	380.6	10.823	0.965	0.0026	17.75	−18.2
	65	428.1	14.558	0.965	0.0023	10.97	−18.0

increased. This clearly indicated that the temperature negatively effected and decreased the adsorption capacity. The maximum amount of adsorbed adsorbates on the surface of sonicated SiO$_2$ can be obtained numerically from their respective plots. The Freundlich adsorption isotherms of NaOH, NH$_4$OH, CH$_3$COOH and HCl adsorbates at different temperatures on the surface of sonicated SiO$_2$ particles were plotted. The data obtained from the Freundlich adsorption isotherms for NaOH, NH$_4$OH, CH$_3$COOH and HCl adsorbates at different temperatures on the surface of sonicated SiO$_2$ particles is summarized in Table 4. The NaOH adsorbate showed the greatest reduction in the amount adsorbed for sonicated SiO$_2$ particles, while the HCl adsorbate showed the least reduction in the amount adsorbed for sonicated SiO$_2$ particles. The adsorption free energies for the low temperature adsorptions were more negative than the high temperature adsorptions, indicating that adsorption was more feasible at lower temperatures.

3.9. Effect of temperature on Langmuir adsorption isotherms for different acids and bases using sonicated SiO$_2$ particles

To examine the effect of temperature on the Langmuir adsorption isotherms of NaOH, NH$_4$OH, CH$_3$COOH and HCl adsorbates, the adsorptions carried out at 10, 25, 45 and 65 °C on the surface of sonicated SiO$_2$ particles were investigated. For illustration, Langmuir adsorption isotherm for CH$_3$COOH adsorbate at 25 and 65 °C on the surface of sonicated SiO$_2$ particles is shown in Fig. 7.

The Langmuir adsorption isotherms for all the other adsorbates at different temperatures on the surface of sonicated SiO$_2$ particles were plotted. The Langmuir adsorption constants Y_{max} and k, and ΔG_{ads}^0 were calculated from the slope and intercept of the linear Langmuir adsorption isotherms for sonicated SiO$_2$ particles. The data obtained from the Langmuir adsorption isotherms for NaOH, NH$_4$OH, CH$_3$COOH and HCl adsorbates on the surface of sonicated SiO$_2$ particles at different temperatures is summarized in Table 5. The adsorption free energies for the lower temperature adsorptions were more negative than those of higher temperature adsorptions, indicating that adsorption was more feasible at lower temperatures.

4. Summary

The physical properties of SiO$_2$ particles were investigated and characterization and morphology of the particles were carried out by FT-IR and SEM. The SEM images of the samples showed good dispersion and uniform silica particles with an average diameter of about 1–1.5 μm. According to the adsorption results, the SiO$_2$ surfaces possessed effective interactions with acids and bases, and the greatest adsorption capacity was found to be with NaOH. The adsorption properties of raw SiO$_2$ particles were further improved by ultrasonication. Langmuir monolayer adsorption capacity of the NaOH adsorbate at 25 °C on sonicated SiO$_2$ (182.6 mg/g) was found to be greater than the unsonicated SiO$_2$ (154.3 mg/g). The high performance exhibited by adsorbate was attributed to increased

surface area and higher negative surface charge after sonication. The SiO_2 particles using a homogenizer showed a greater specific surface area ($459.3\,m^2/g$) than the unsonicated particles ($405.4\,m^2/g$).

Acknowledgments

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