MATERIALS AND METHODS

There are three main parts in this research consisting of (1) Nanostructured materials synthesis: Nanopore SUZ-4 zeolite and nanocomposite materials (2) Nanostructured material characterization and (3) Utilization of nanostructured materials: Evaluation of nanostructured sorbents in differential bed reactors for elemental mercury capture and photocatalytic degradation of methyl orange dye for SiO_2-TiO_2 nanocomposite.

1. Nanostructured Materials Synthesis

1.1 SUZ-4 Zeolite from Sol-Gel Synthesis

SUZ-4 zeolite was synthesized by a sol-gel hydrothermal technique carried out in stainless steel bombs (Appendix A: 300 ml stainless steel autoclave Parr Model 4561, USA and 390ml Teflon-lined home-made design stainless steel autoclave with circulating air drying oven (Forced convection BINDER GmbH Model FP240, Germany)) under previously determined optimal conditions (Asensi *et al.*, 1999; Gujar and Price, 2002; Kim *et al.*, 2004).

Different aluminum and silicon sources from several batches were used as raw materials for trying to synthesize SUZ-4 zeolite in each experiment conditions (Appendix A).

For main raw materials of the successful SUZ-4 zeolite synthesis shown in Table 2 (No. 8-17, M1-M5 and M1S-M5S), Tetraethylammonium hydroxide, TEAOH (35 wt. % in water, Aldrich) was used as structure directing agent (SDA) or template and LUDOX AS-40 colloidal silica (40 wt. % SiO_2, Aldrich) was used as the silica source, aluminum metal (99.7% Al, Hi Media) was the aluminum source and potassium hydroxide (85% pellet KOH, Carlo Erba) was used as the potassium source.

There were two types of reactors for synthesis; 1) Stainless steel autoclave-Pressure reactor Parr 300 ml was used to synthesize zeolite powder in No.8-17 2) Stainless steel autoclave pressure reactor with 390ml Teflon-lined home-made design was used to synthesize SUZ-4 zeolite powder and zeolite membrane in No.M1-M5 (without seeding on supporter) and M1S-M5S (with seeding on supporter).

Table 2 Gel compositions for synthesis of SUZ-4 zeolite.

No.	**Gel composition**	**Crystallization**		**Stirring/ Rotating (rpm)**	**pH**
	$\boldsymbol{a\ K_2O:bAl_2O_3:c\ SiO_2:d\ (TEA)_2O:\ eH_2O}$	**Temperature (°C)**	**Time (day)**		
Zeolite powder synthesis with 300 ml stainless steel autoclave Parr Model 4561 (stirring)					
8	$\mathit{7.29}\ K_2O:Al_2O_3:\mathit{33.42}SiO_2:\ \mathit{3.10}\ TEA_2O:\mathit{770.81}\ H_2O$	156	4	80	13.8
9	$\mathit{7.37}\ K_2O:Al_2O_3:\mathit{33.51}SiO_2:\ \mathit{3.09}TEA_2O:\mathit{811.59}\ H_2O$	151	4	300	-
15	$\boldsymbol{\mathit{7.19}\ K_2O:Al_2O_3:\mathit{32.40}SiO_2:\ \mathit{3.05}\ TEA_2O:\mathit{794.60}\ H_2O}$	**154**	**4**	**300**	**-**
10	$\mathit{4.00}\ K_2O:Al_2O_3:\mathit{21.24}SiO_2:\ \mathit{1.30}\ TEA_2O:\mathit{500.80}H_2O$	155	4	300	-
16	$\mathit{3.96}\ K_2O:Al_2O_3:\mathit{21.15}SiO_2:\ \mathit{1.30}TEA_2O:\mathit{498.92}H_2O$	152	4	300	-
11	$\boldsymbol{\mathit{3.96}\ K_2O:Al_2O_3:\mathit{16.26}SiO_2:\ \mathit{0.92}TEA_2O:\mathit{464.10}\ H_2O}$	**155**	**4**	**300**	**-**
14	$\boldsymbol{\mathit{7.30}\ K_2O:Al_2O_3:\mathit{32.69}SiO_2:\ \mathit{3.11}\ TEA_2O:\mathit{783.98}H_2O}$	**169**	**2**	**300**	**13.8**
12	$\boldsymbol{\mathit{3.96}\ K_2O:Al_2O_3:\mathit{21.23}SiO_2:\mathit{1.37}\ TEA_2O:\mathit{502.70}H_2O}$	**169**	**2**	**300**	**13.7**
13	$\mathit{3.99}\ K_2O:Al_2O_3:\mathit{16.73}SiO_2:\ \mathit{0.92}\ TEA_2O:452.85H_2O$	168	2	300	13.5
17	$\boldsymbol{\mathit{4.00}\ K_2O:Al_2O_3:\mathit{16.20}SiO_2:\mathit{0.91}\ TEA_2O:\mathit{450.10}H_2O}$	**168**	**2**	**300**	**13.8**
Zeolite powder and membrane synthesis with 390 ml stainless steel autoclave Teflon-lined owned design (rotation)					
M1 [1]	$\mathit{4.02}\ K_2O:Al_2O_3:\mathit{21.25}SiO_2:\ \mathit{1.30}\ TEA_2O:\mathit{1201.81}H_2O$	155	4	30	13.4
M1S [2]	$\mathit{4.01}\ K_2O:Al_2O_3:\mathit{21.24}SiO_2:\ \mathit{1.30}TEA_2O:\mathit{1201.87}H_2O$	155	4	30	13.4
M2 [1]	$\mathit{3.98}K_2O:Al_2O_3:\mathit{21.22}SiO_2:\ \mathit{1.30}\ TEA_2O:\mathit{1201.58}H_2O$	155	4	30	13.2
M2S [2]	$\boldsymbol{\mathit{4.01}\ K_2O:Al_2O_3:\mathit{21.23}SiO_2:\ \mathit{1.30}\ TEA_2O:\mathit{1201.66}H_2O}$	**155**	**4**	**30**	**13.2**
M3 [1]	$\mathit{4.01}\ K_2O:Al_2O_3:\mathit{21.32}SiO_2:\ \mathit{1.30}\ TEA_2O:\mathit{2554.21}H_2O$	155	3.6	30	11.7
M3S [2]	$\mathit{4.01}\ K_2O:Al_2O_3:\mathit{21.29}SiO_2:\ \mathit{1.31}TEAOH:\mathit{2554.18}H_2O$	155	3.6	30	11.7
M4 [1]	$\mathit{4.00}\ K_2O:Al_2O_3:\mathit{21.17}SiO_2:\ \mathit{1.30}\ TEA_2O:\mathit{1197.77}H_2O$	155	3.9	30	13.4
M4S [2]	$\mathit{3.97}\ K_2O:Al_2O_3:\mathit{21.21}SiO_2:\ \mathit{1.30}\ TEA_2O:\mathit{1199.73}H_2O$	155	3.9	30	13.4
M5 [1]	$\mathit{4.00}\ K_2O:Al_2O_3:\mathit{21.17}SiO_2:\ \mathit{1.30}\ TEA_2O:\mathit{1351.39}H_2O$	155	4.9	30	>14
M5S [2]	$\mathit{3.96}\ K_2O:Al_2O_3:\mathit{21.18}SiO_2:\ \mathit{1.30}\ TEA_2O:\mathit{1351.45}H_2O$	155	4.9	30	>14

[1] without seeding on mullite tubes (in-situ zeolite membrane synthesis)
[2] with seeding on mullite tubes

For zeolite powder synthesis, the effects of corresponding factors: gel composition (SiO_2/Al_2O_3, TEA_2O/Al_2O_3, H_2O/Al_2O_3, K_2O/Al_2O_3), crystallization temperature and time were studied to obtain SUZ-4 zeolite in the first type of reactor. The obtained conditions for powder synthesis were used to synthesize zeolite membrane and powder with and without seeding from the second type of reactor.

Gel preparation for one of several batches is described here (No. M1S): 5.88 g KOH was dissolved in 140 g of distilled water and 0.6 g of aluminum powder was added with the bottle loosely capped (H_2 gas is evolved) and stirred (HTS-1003, Lab & Medical Suppliers) continuously until the aluminum was completely dissolved to form a clear solution. A second solution containing 35.37 g of LUDOX, 12.18 g of TEAOH aqueous solution, and 70 g of water was prepared and stirred for 1 hour and then added successively under stirring at 500 rpm (Model M6, CAT Ingenieurbuero M. Zipperer, Germany) to the dissolved aluminum solution and stirred for 3 hours. A white gel was formed and mixed thoroughly until an even consistency was achieved. The resulting gel had a composition of $3.98\ K_2O:Al_2O_3:21.22\ SiO_2:1.30TEA_2O:1{,}201\ H_2O$ as shown in Table 2. The gel was then transferred to a rotating stainless steel bomb at 30 rpm for crystallization at 155°C under autogenous pressure for 4 days.

For zeolite membrane preparation with seeding, supporters (cylindrical mullite tube ($3Al_2O_3{\cdot}2SiO_2$), HB grade, Nikko Corp., Japan) were cut having 13 mm length with a low speed diamond saw (Isomet, Buchler, IL, USA). The inner and outer diameters and the length of the supporter were 11, 15 and 130 mm, respectively. They were then polished with fine sand paper (No. 800), washed in ultrasonic bath for 15 minutes and calcined at 550 °C for 1 hour. Crushed SUZ-4 zeolite crystals were kneaded with water and then were rubbed on outer surface of supporter. The inner spaces of the supporters were filled with quartz glass wool to prevent the growth of the zeolite layer on the inner surface of the supporter. The supporters were then placed vertically in 390 ml Teflon-lined stainless steel autoclave under the crystallization conditions (Table 2). In order to reduce the homogeneous nucleation of zeolite in the liquid phase, the starting concentrations of the reactants were decreased as compared to those for the usual synthesis of powder zeolites.

The powder product was recovered by filtration (Handy Aspirator Model WP-35 Yamato, Japan and Vacuum Pump 1/8 HP/220V, Oiless Model DOA-V502-BN, GAST Manufacturing, MI, USA). The solid and zeolite membrane was washed with distilled water thoroughly to pH < 10 , dried in an oven (Model DK-42 Yamato, Japan) at 120°C for 2 hours, and calcined in a muffle furnace (Vecstar Model PF3 with EUROTHERM 2416 CG PROGRAMMER, UK) at 550 °C for 4 hours using heating rate for 1 hour from room temperature. The decomposition temperature of the structure directing agent (TEAOH) used was determined by thermogravimetric analysis (TGA) (TA instrument SDT2960 thermal analyzer Simultaneous DTA-TGA Universal 2000) at the heating rate 5°C/min (Appendix A). All experimental conditions for both SUZ-4 zeolite powder and membrane are summarized in Table 3.

Table 3 List of experiments performed for SUZ-4 zeolite powder and zeolite membrane synthesis.

SUZ-4 zeolite synthesis	Parameters	Conditions
Zeolite powder	At $SiO_2:Al_2O_3$ = 33.3	
	- Stirring rate	80 rpm, 300 rpm
	At suitable stirring condition	
	- $SiO_2:Al_2O_3$	33.3, 21.2 and 16.2
	- $TEA_2O:Al_2O_3$	3.1, 1.3 and 0.9
	- $K_2O:Al_2O_3$	7.3, 4.0 and 3.9
	- $H_2O:Al_2O_3$	800, 500 and 460
	- Crystallization time	4 and 2 days
	- Crystallization temperature	151-155°C and 168-169°C
Zeolite membrane	At suitable condition from zeolite powder and rotation at 30 rpm	
	- $H_2O:Al_2O_3$	1,198-2,554
	At suitable condition of $H_2O:Al_2O_3$	
	- Reproducible: crystallization time	3.9, 4 and 4.9 days
	- Seeding	With seed and without seed

1.2 Single Component and Composite Nanomaterials from Flame Aerosol Synthesis (FLAR)

As shown in Figure 3, the experimental setup of FLAR system for nanocomposite synthesis of this research has been developed from a single component synthesis by AAQRL group (Jiang *et al.*, 2007). It consists of three concentric stainless steel tubes in co-flow diffusion burner and a quench/dilution system. The outer diameters of these tubes were 1.23 cm (0.5") for the central tube, 2.45 cm (1") for the middle tube and 3.68 cm (1.5") for the outer tube. All tubes had thickness approximately 0.07 cm (0.03").

Tetra-isopropoxide (TTIP, 97%, Aldrich), tetraethyl orthosilicate (TEOS, purity >99%, Fluka) and aluminum tri-sec-butoxide (ATSB, 97%, Aldrich) dissolved in sec-butanol (99.9%, Fisher Chemical) were used as precursors for the synthesis of TiO_2, SiO_2 and Al_2O_3, respectively.

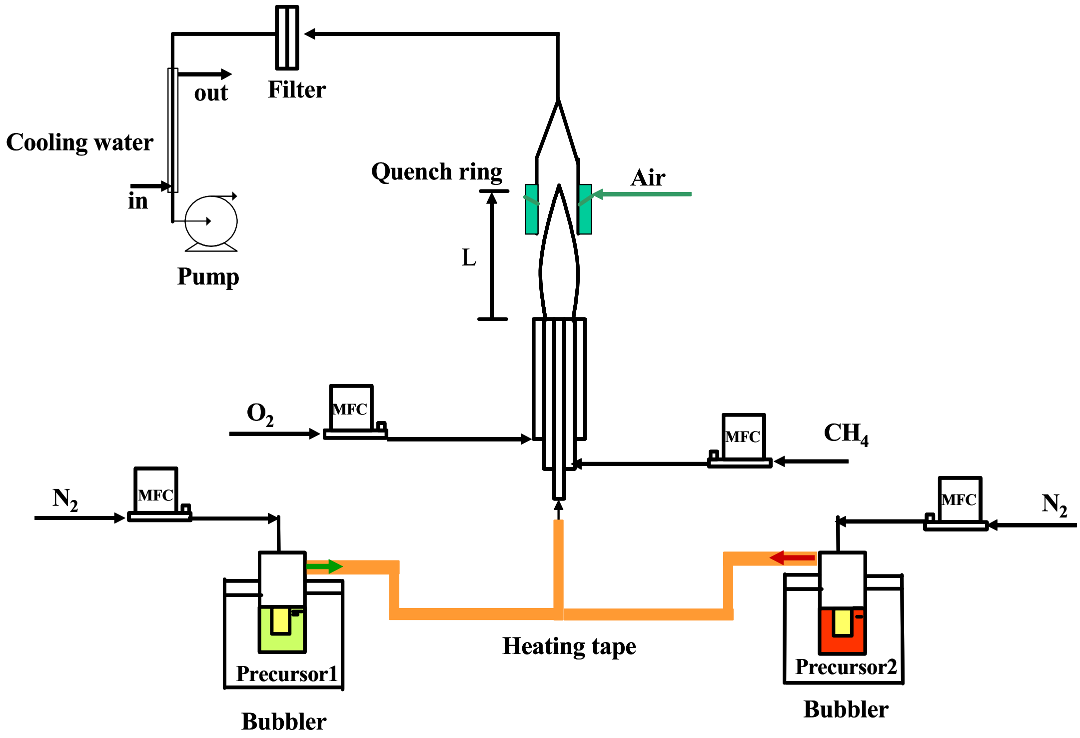

Figure 3 Schematic diagram of FLAR for nanocomposite synthesis.

For SiO_2-TiO_2 system, two bubblers were used to feed TTIP and TEOS precursors with N_2 carrier gas. The precursor delivery tubes to the burner were kept at 210°C to prevent condensation of precursor vapors. The N_2/TTIP and N_2/TEOS were introduced through the central tube of the burner with fuel methane (CH_4) in the first annular space and oxidant oxygen (O_2) in the outer annular. The volumetric flowrates of O_2, N_2/TTIP, N_2/TEOS were 5 lpm, 1.5 lpm and 1.5 lpm, respectively, while flowrate of CH_4 was 1 lpm for varied Si: Ti precursor concentration. Their concentrations were calculated using their known vapor pressured and measurements of their flow rates of carrier gas.

To study the effect of different quench ring positions, a quench ring with inner diameter 1.84 cm (0.72") was placed axially around the flame to control the flame height and particle residence time in the high temperature environment. Compressed cooling air was supplied to the quench ring and entered the flame zone in a radial direction. While Si:Ti molar ratio was kept constantly; positions of the quench ring were varied with respect to the burner outlet from 1 to 8 inch and the flowrates of CH_4 were changed from 1 to 1.4 and 1.8 lpm, sequentially. Mass flow controllers (MKS Instruments, Wilmington, MA) were used to control all gas flowrates in this work. Nanomaterial particles were collected from the downstream by a glass micro fiber filter (EPM 2000, Whatman) in in-line stainless steel filter holder (PN2220, Gelman Science) by a vacuum pump. A cooling water jacket was used before the vacuum pump to cool down the gas stream and protect the pump.

The experimental setup of SiO_2-Al_2O_3 system was similar to that of SiO_2-TiO_2 system. However, a stainless steel atomizer was used in the SiO_2-Al_2O_3 system instead of bubbler in SiO_2-TiO_2 system. Also, 10% of ATSB precursor in sec-butanol was atomized in a stainless steel atomizer with nitrogen carrier gas instead of TTIP precursor in SiO_2-TiO_2 system. All experimental conditions for both systems are summarized in Table 4.

Table 4 List of experiments performed for nanocomposite synthesis.

System	Parameters	Conditions
SiO_2-TiO_2	SiO_2 precursor	Tetraethyl orthosilicate (TEOS)
	TiO_2 precursor	Titania isoproproxide (TTIP)
	O_2 Flow rate	5 lpm
	Si:Ti precursor molar ratio at 4 inch position	0.27, 1.39, 4 and 17.5 (CH_4 flow rate =1 lpm)
	Quench ring position at Si:Ti = 4	1,2,3,4,7 and 8 inch (CH_4 flow rate = 1, 1.4 and 1.8 lpm)
SiO_2-Al_2O_3	SiO_2 precursor	Tetraethyl orthosilicate (TEOS)
	Al_2O_3 precursor	Aluminum tri-sec-butoxide (ATSB) in sec-butanol
	O_2 Flow rate	6 lpm
	CH_4 flow rate	1 lpm
	Si:Al precursor molar ratio at 4 inch position	0.6, 1.4, 2, 24, 30, 48 and 66
	Quench ring position at Si:Al= 2	1,2,4 and 7 inch

The possible mechanism of nanocomposite formation was proposed as shown in Figure 4. Three main morphologies of mixed oxides from the growth process may be formed as small particles discrete on large particles, uniform coating (core-shell structure), and uniform multicomponent (solid solution or solid mixture particles).

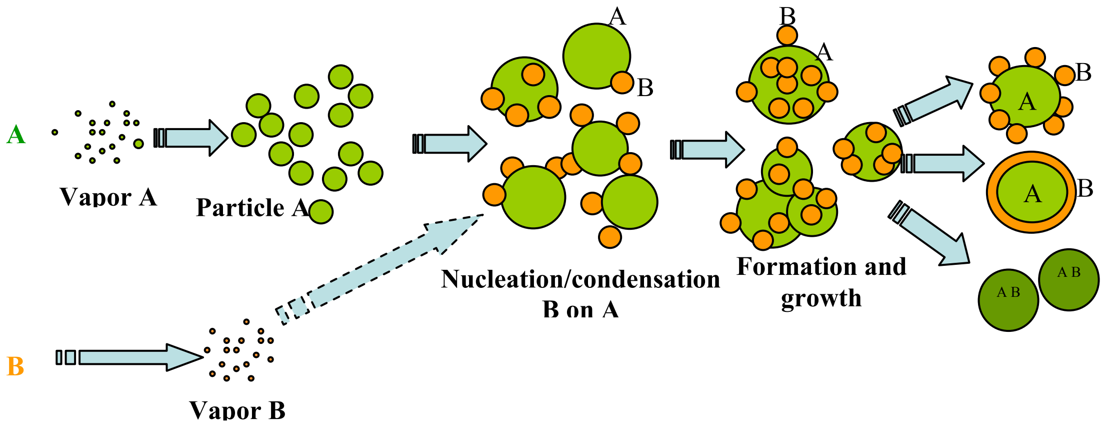

Figure 4 Propose pathway of nanocomposites formation in high temperature environment.

2. Nanostructured Materials Characterization

2.1 X-ray powder diffraction

Phase identification of nanostructured materials were determined by X-ray powder diffraction.

Phillips PW 1830/40 at the Department of Material Engineering, Faculty of Engineering, Kasetsart University was used to determine synthesized SUZ-4 zeolite, using Cu-Kα1 radiation with $\lambda = 1.5406$ Å, generator tension 40 kV, generator current 30 mV in the range 5-50^{o} 2θ and at a rate of 0.01^{o}/min.

Rigaku Geigerflex D-MAX/A at the Department of Physics, Washington University in St. Louis was used to determine synthesized nanocomposite materials, using Cu-Kα1 radiation with $\lambda = 1.5418$ Å, generator tension 35 kV, generator current 35 mV in the range 10-80^{o} 2θ and at a rate of 0.08^{o}/min.

2.2 BET N_2-adsorption/desorption isotherm and pore analysis

Specific surface area (SSA), isotherms and pore size distribution (PSD) of prepared samples were obtained by N_2-adsorption/desorption at -196 ºC. All samples were degassed under flowing N_2 atmosphere to remove adsorbed H_2O from the surface prior to measurement. The SSA was determined by the multipoint Brunauer-Emmett-Teller (BET) method using the adsorption data. The PSD was calculated from the desorption isotherms.

Autosorb 1C, Quantachrome at the Department of Chemical Engineering, Faculty of Engineering, Kasetsart University was used to determine synthesized SUZ-4 zeolite with micropore analysis (74 points N_2 adsorption/desorption) and nanocomposite material with mesopore analysis (39 points N_2 adsorption/desorption).

Autosorb 1, Quantachrome at the Molecular and Nanoscale Analysis Laboratory, Washington University in St. Louis was used to determine synthesized nanocomposite materials with multipoint BET (11-point N_2 adsorption).

PoreMaster 33, Quantachrome at Thailand Institute of Scientific and Technological Research was used to determine porosity and pore diameter of mullite tube in low pressure (0.23-50 psia) and high pressure (20-33,000 psia) with mercury contact angle of 140°.

2.3 Scanning electron microscopy (SEM)

Surface structure of the sample, shape and particle size were taken on scanning electron microscopy (SEM) for three-dimensional appearance with energy dispersive X-ray spectroscopy (EDS) for spot elemental analysis. The powder sample was sprinkled on a carbon sticky tab of aluminum specimen mount and coated with with a nanometre-thick layer of gold (Au) using a sputter coater before being examined and photographs SEMs.

Phillips XL30 SEM with 15-20 kV energy, energy dispersion X-ray analysis (EDX; EDAX Falcon, EDAX Co. Ltd., NJ) and the Edward Scancoat six sputter coater (Edwards Laboratories, Milpitas, CA) for sputtering Au at the Department of Material Engineering, Faculty of Engineering, Kasetsart University were used to determine synthesized SUZ-4 zeolite.

Hitachi S-4500 SEM a field emission scanning electron microscope with 15 kVenergy, a NORAN Instruments Energy Dispersive X-ray (EDX) microanalysis system and the Polaron E5100 SEM Coating System (Polaron Equipment Ltd) for sputterring Au at Molecular and Nanoscale Analysis Laboratory, Washington University in St. Louis were used for synthesized nanocomposite materials.

2.4 Transmission electron microscopy (TEM)

Transmission electron microscopy is a powerful characterization tool that provides information regarding the morphology and crystallography for advanced materials. The samples were dissolved with methanol (99.9%, Sigma-Aldrich, MO) and then sonicated (Model FS60H, Fisher Scientific) for 20 minutes and drop onto TEM grid (300 mesh copper grid, Ted Pella, Inc., MA). TEM of the samples was taken on JEOL 1200 equipped at School of Medicine, Saint Louis University, JEOL JEM-2000FX equipped at Center for Nanoscience, University of Missouri- Saint Louis and JEOL JEM-2100F equipped at Center of materials Innovation, Washington University in Saint Louis.

2.5 Fourier transform infrared spectroscopy (FTIR)

The surface chemical bonding was determined by fourier transform infrared spectroscopy (FTIR, NEXUS470, Thermo Nicolet, France) at Molecular and Nanoscale Analysis Laboratory, Washington University in St. Louis. Diffuse reflectance infrared fourier transform (DRIFT) technique was used for all samples to identify types of chemical bonds (functional groups). Samples were prepared by mixing them with potassium bromide powder (KBr, IR grade, Fisher Scientific, NJ), transparent in the IR, to form a very fine powder. The ratio of sample and KBr is usually 1:20. A mortar and pestle were used to grind the sample and KBr at the same time. The sample powder was then placed onto the sample holder and inserted it into the specimen chamber which can be analyzed. The spectral resolution was 4 cm^{-1} and 256 scans were coded into the mid infrared region (4000-400 cm^{-1}) (Stuart, 1996).

2.6 Zeta potential (ζ)

Zeta potential of a synthesized sample was determined using zetasizer (NanoZS, ZEN3600 and Zetasizer, 3000HS, Malvern instrument) at Aerosol and Air Quality Research Group, Washington University in St. Louis and at Thailand Institute of Scientific and Technological Research. Zeta potential is a good index of the magnitude of the repulsive interaction between colloidal particles. The overview concept of zeta potential is shown in Appendix F. Measurement of zeta potential is commonly used to assess the stability of a colloid (Hunter, 1981; C. Hayashi *et al.*, 1997; Hayashi *et al.*, 1997). NanoZS model was used following these steps. An electrolyte solution of 0.01M NaCl (99+% A.C.S reagent, Aldrich) was used to disperse the powder in de-ionized water and maintain an almost constant ionic strength in aqueous suspensions, which were then sonicated for 20 minutes. The pH value measured by a precision pH meter (Malvern SEN0106), were adjusted by addition of 0.01M HCl (34-37%, Fisher Scientific), 2.5 M HCl or 0.01M NaOH (97+% A.C.S reagent, Sigma-Aldrich) solutions. For Zetasizer 3000HS, 1 M HCl and 1 M NaOH were used to adjust pH and zeta potential was measured in distilled water. This surface charge measurement with different pH will enable us to understand the stability of the samples at solution phase.

2.7 Thermogravimetric Analysis (TGA)

The decomposition of structure directing agent (SDA) for synthesized SUZ-4 zeolite was determined by Thermogravimetric Analysis (TGA) using TA instrument SDT2960 Simultaneous DSC-TGA Universal 2000. In this analysis, the sample was heated from 30 to 900 °C at heating rate 5°C/min in air.

2.8 Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

Trace concentrations of low-level mercury elements for samples on mercury capture testing experiments were determined by ICP-MS using Agilent 7500ce with ChemStation software (Agilent Technology, Inc., CA) at Molecular and Nanoscale Analysis Laboratory, Washington University in St. Louis. Aligent 7500ce ICP-MS is capable of measuring trace elements at levels as low as one part per trillion or quickly scanning more than 70 elements to determine an unknown sample's composition. It is a type of mass spectrometry that is highly sensitive and capable of the determination of a range of metals and several non-metals at concentrations below one part in 10^{12}. It is based on coupling together an inductively coupled plasma as a method of producing ions (ionization) with a mass spectrometer as a method of separating and detecting the ions (Appendix E).

2.9 UV-Visible Spectrometer

Synthesized SiO_2-TiO_2 nanocomposite and SUZ-4 zeolite from photocatalytic of methyl orange were characterized by UV-Vis Spectroscopy using a Perkin Elmer Lamda 2S UV-visible spectrometer (Germany) at the Environmental Engineering Program, Washington University in St. Louis. This measurement involves the spectroscopy of photons and spectrophotometry and the light is split into two beams before it reaches the sample. One beam is used as the reference; the other beam passes through the sample. Samples and blank are typically placed in a transparent quartz cells, known as cuvettes.

3. Utilization of Nanostructured Materials

3.1 Elemental Mercury Capture by Nanostructured Sorbents Using Differential Bed Reactor

3.1.1 Nanostructured Sorbents

Eight different sorbents were used in this study. Iron oxide and titanium dioxide were used because they are low cost materials and widely used in a variety of industrial applications. Zeolite was also chosen because it has high surface area and has a connected 3-D networked open pore structure. It is widely used as a molecular sieve, ion exchanger, catalyst and adsorbent (Dyer, 1988; Kongkachuichay and Lohsoontorn, 2006). The sorbents selected were commercial iron oxides (Iron Oxide Red-204M, Trans OxideYellow-AC0544, Trans Oxide Red-AC1005 and Trans oxide Brown-AC3000, Rockwood Pigments), TiO_2 (P25, Degussa), and titania-clay composite (TiO_2-PILC, Triton System Inc.). The crystal phase of each sorbent was determined by XRD as shown in Appendix B. For example, the XRD pattern of TiO_2 indicates that it is a mixture of anatase and rutile; the TiO_2-PILC is primarily composed of the anatase and a mineral like andulasite; and Trans Oxide Brown consists of hematite and a complex structure of Mn (α-Fe_2O_3/$MnFe_2O_4$). SUZ-4 zeolite and magnetite (Fe_3O_4) were synthesized inhouse for this study. SUZ-4 zeolite was synthesized via a sol-gel hydrothermal technique carried out in a stainless steel bomb as previously described (Gujar and Price, 2002). Tetraethylammonium hydroxide, TEAOH (35 wt.% in water, Aldrich) was used as a template, and LUDOX AS-40 colloidal silica (40 wt.% SiO_2, Aldrich), aluminum metal (99.7% Al, Hi Media) and potassium hydroxide (85% pellet KOH, Carlo Erba) were used as the raw materials. One batch of several experiments of synthezised SUZ-4 zeolite was also tested. Magnetite (Fe_3O_4) was synthesized in a furnace reactor by decomposing ferrous oxalate ($FeC_2O_4 \cdot 2H_2O$) in a nitrogen environment at approximately 300^oC (Lin *et al.*, 1996). Micrometer-sized yellow acicular crystals of ferrous oxalate, $FeC_2O_4 \cdot 2H_2O$, were prepared by adding a slight excess of oxalic acid to a heated, dilute aqueous solution of ferrous chloride and were subsequently collected on filter paper and dried in a silica desiccators prior to conversion to Fe_3O_4.

3.1.2 Differential Bed Reactor Experiments

The differential bed reactor (DBR) system set up used in this study is illustrated in Figure 5. Mercury vapor was introduced into the system by passing compressed air at a controlled flow rate (MKS Mass Flow controller, MKS instruments, Inc. and Brooks) through a sealed glass bubbler (mineral oil impinger, ACE Glass, Vineland, NJ) containing liquid mercury at room temperature. Flow rate and temperature were controlled to allow the generation of a stable mercury feed rate. Actual measurements over multiple runs indicated less than 5% variability in the feed rate. The Hg^0 laden air was subsequently mixed with dilution air such that a flow rate of either 500 cm^3/min or 1000 cm^3/min passed through the DBR. The selected sorbent was spread over the glass fiber filter forming a layer having 70-140 μm thickness depending on its density. The sorbent-loaded filter was placed in a holder made from ultraviolet light-transparent borosilicate glass (Filter Support 7519, ACE Glass Inc.). The holder was placed under UV lamp and irradiated with high intensity (365 nm UV light, Blak-Ray Longwave ultraviolet LAMP, 100 W). Mercury capture was measured with and without ultraviolet irradiation. DBR tests were run for durations of 10 and 30 minutes.

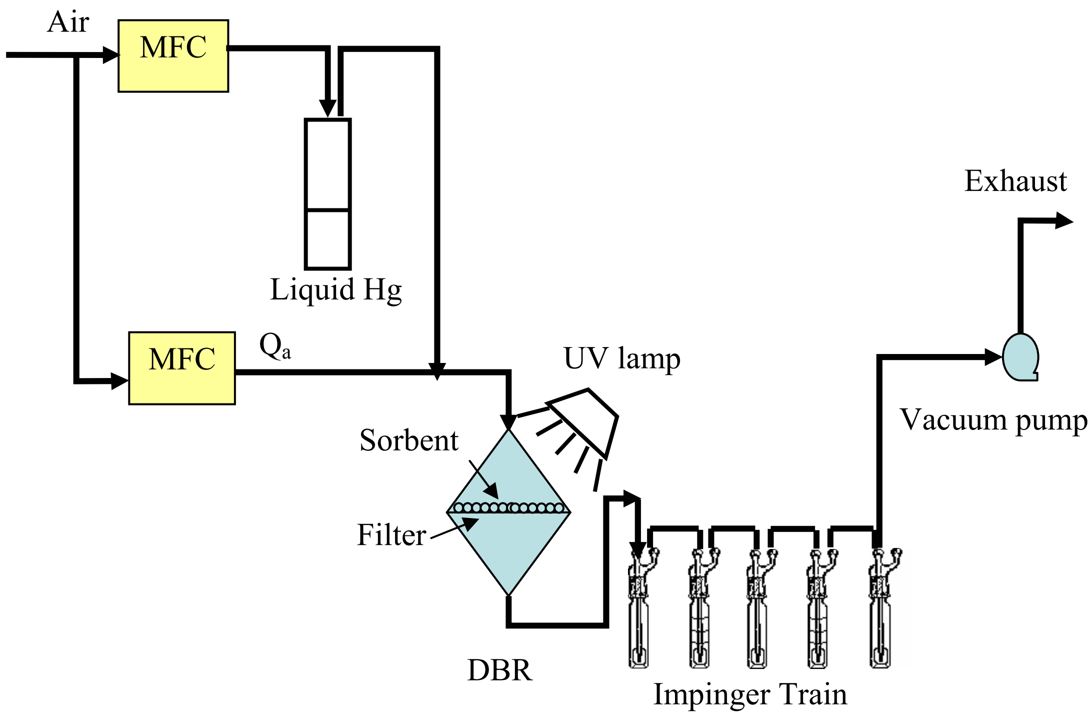

Figure 5 Differential bed reactor (DBR) system used for mercury uptake studies.

Downstream of the reactor, mercury vapor mixed with dilution air was passed through a series of five impingers with sintered glass filter tips (25 ml Midget bubblers, Ace Glass Inc.). The sampling train consisted of five impingers with 15 ml of solutions of the following: the first two impingers contained 1.0 M tris(hydroxymethyl) aminomethane (Tris, Molecular Biology Grade, Fisher Biotech) and 9.94x 10^{-4} M ethylenediamine tetraacetic acid (EDTA, Certified A.C.S, Fisher Scientific), the third impinger contained 10% hydrogen peroxide (H_2O_2, 50 % solution, EMD) and 2% hydrochloric acid (by volume), and the last two impingers contained 0.05 M potassium iodide (KI, Certified A.C.S., Fisher Scientific) in 2% hydrochloric acid. The solution in the fourth impinger was oxidized with 50 µl of 10% hydrogen peroxide to form I_3^- just prior to sampling.

The first two impingers were used to determine the amount of oxidized Hg and the last three impingers were used to determine the amount of elemental mercury (Hedrick *et al.*, 2001; Smallwood, 2005) as shown in Table 5.

Table 5 Impinger solution for sampling.

Impinger#	Solution	Species captured
1	1.0 M tris (hydrosymethyl) aminomethane +9.94x 10^{-4} M ethylenediammine tetraacetic acid	Hg^{2+}
2	1.0 M tris (hydrosymethyl) aminomethane +9.94x 10^{-4} M ethylenediammine tetraacetic acid	Hg^{2+}
3	10% hydrogen peroxide + 2 % nitric acid	Hg^0
4	0.05 M potassium iodide + 2% hydrochloric acid (oxidized with 50 µL of 10% hydrogen peroixide just prior to sampling)	Hg^0
5	0.05 M potassium iodide + 2% hydrochloric acid	Hg^0

Source: Hedrick *et al.* (2001)

The tris solutions and the acidified hydrogen peroxide solution have been extensively tested as part of other methods (EPA Method 101A and Tris Buffer Method, respectively) to effectively capture oxidized and elemental mercury, respectively, and these solutions are amenable to ICP-MS. In 2001, the iodine based impinger solutions were developed to oxidized elemental mercury and retain it in solution as HgI_4^{2-} (Hedrick *et al.*, 2001). It was previously found that more than 98% of elemental mercury was captured in the first oxidizing impinger (4th impinger) (Hedrick *et al.*, 2001), hence Hg^0 was determined by measuring the mercury concentrations in the 4th and 5th impingers. The sampling solutions from the impingers were kept in plastic tubes (BD Falcon Blue Max Jr., Becton Dickinson Labware, Franklin Lakes, NJ) and stored at 4°C until they were analyzed by ICP-MS.

Experimental conditions for the screening study of nanostructured sorbents are summarized in Table 6. The inlet concentration of Hg^0 (determined from impinger samples taken without sorbent in the DBR) was varied from 16-610 µg/m^3. The DBR was held at ambient room temperature.

Table 6 Experimental condition for screening study of nanostructured sorbents

Run No.	**Sorbent**	**Mass [c] (g)**	**Air flow rate through Hg feed bottle; Q_{Hg} (cm^3/min)**	**Reactor running time (min)**
1	Baseline (no sorbent)	-	20^a, 5^{a-b}, 3.33^b, 1.67^b	10^{a-b}, 30^a
2	Iron Oxide Red	0.264±0.053	20^a,5^{a-b}	10^{a-b}, 30^a
3	Trans Oxide Yellow	0.240±0.080	20^a,5^{a-b}	10^{a-b}, 30^a
4	Trans Oxide Red	0.176±0.001	5^{a-b}	10^{a-b}
5	Trans Oxide Brown	0.173±0.047	20^a,5^{a-b}, 3.33^b, 1.67^b	10^{a-b}, 30^a
6	Titanium Dioxide	0.028±0.009	20^a,5^{a-b}, 3.33^b, 1.67^b	10^{a-b}, 30^a
7	Titania Pillared Clay	0.317±0.018	20^a,5^{a-b}, 3.33^b, 1.67^b	10^{a-b}, 30^a
8	Synthesized SUZ-4 Zeolite	0.178±0.019	20^a,5^{a-b}, 3.33^b, 1.67^b	10^{a-b}, 30^a
9	Synthesized magnetite Fe_3O_4	0.243±0	20^a	30^a

[a] Total flow rate in the system (Q_a) = 1,000 cm^3/min
[b] Total flow rate in the system (Q_a) = 500 cm^3/min
[c] Mass (g) shown in average± standard deviation

After each batch experiment, glassware and tube system were cleaned following these procedures. Firstly, DBR system was cleaned with in house air for 15 minutes. Glassware and tubes were then rinsed with DI water. Glassware must be thoroughly soaked in acid bath with 10 % HNO_3 and 20 % HCl (by volume) for 4-8 hours or overnight, rinsed triple with DI water, then rinsed triple again with ultrapure water (Milli-Q, Milipore Corp., resistivity >18.6 Ωm*cm) and dried at room temperature overnight or 100 °C for 20 minutes.

However, there is a possibility of mercury loss onto the reactor walls, which is commonly occurred in mercury experiment. Carryover contamination was checked by measuring the contaminant in the compressed air passed through the DBR system and it was found to be negligible.

3.1.3 Mercury measurement from ICP-MS

ICP-MS was used to measure mercury (ppb) in the impinger samples and was calculated to the mercury concentration in gas phase (µg/m^3).

Calibration solutions were prepared with various concentrations of mercury solution in each impinger solution matrix. Two internal standards, ^{185}Re and ^{193}Ir, were added to the calibration solutions and sample solutions to correct for signal drift. The instrument recorded the counts for all 7 naturally occurring isotopes of mercury (^{196}Hg, ^{198}Hg, ^{199}Hg, ^{200}Hg, ^{201}Hg, ^{202}Hg, ^{204}Hg). The isotope used to calculate concentrations was ^{202}Hg because this isotope is most naturally abundant, and there are no isobaric or polyatomic ion interferences with it. The matrix problem with the highest signal suppression, this was the matrix used to optimize and tune the instrument for each use. A tuning solution was prepared for the best sensitivity and the instrument was tuned to get the maximum ^{202}Hg and internal standard signals.

Three sets of mercury concentrationscalibration curves made from the three different impinger solution matrices were generated the day of sample analysis. One set of calibration solutions would be made with the Tris+EDTA matrix, the second set of calibration solutions would be made with the 10% H_2O_2 and 2% HNO_3 matrix, and the third set of calibration solutions would be made with the 0.05 M KI and 2% HCl matrix. All solutions would have the two internal standards added such that their concentrations would be 1 ppb ^{185}Re and 10 ppb ^{193}Ir. Method detection limits were determined by observing the raw counts with respect to concentration. A 200 ppb gold chloride solution in 2% HNO_3, only 2% HNO_3 and ultrapure water were used to rinse the ICP-MS between samples to reduce mercury carryover when running a series of samples.

3.1.4 Sequential Extraction

A three-step sequential extraction was used to investigate the binding mechanisms and the mobility of mercury in the sorbent samples. The sequential extraction process provides leachability information under several different conditions. The toxicity characteristic leaching procedure (TCLP) used to simulate the leaching of metals from solids within the moderately acidic environmental of a municipal landfill (US EPA, 1992). In the first step, a 1.0 M ammonium nitrate (NH_4NO_3) solution was used to remove surface bound metals by ion exchange at 20

°C for 8 hours. Theoretically, one Hg^{2+} ion exchanges with two NH_4^+ ions. However, the formation of soluble Hg-NH_3 complexes have been shown to mobilize mercury bound to the surface by other mechanisms (Noel *et al.*, 2007). The additional benefit provided by the complexation of mercury increases the removal efficiency in this step. In the second step, a weak acid extractant of 0.11 M acetic acid (pH = 2.8) was used to mobilize mercury species that are acid soluble (e.g. mercury oxide (HgO) and some adsorbed Hg(II) species) at 20 °C for 8 hours. The acetic acid solution is similar to the acetic acid solution (pH=2.88) used in the TCLP in EPA Method 1311 (US EPA, 1992). Finally, an acid solution consisting of 5 ml of concentrated nitric acid, 1 mL of concentrated hydrochloric acid, and 1 ml of hydrofluoric acid heated in a digestion bomb at 200 °C for 4 hours was used to completely dissolve the remaining residual material. The sequential extraction process was applied to 10-53 mg of each material. In each step, the solid phase was mixed with 1.0 ml of the extract solution and shaken for 8 hours. The suspension was then centrifuged and the supernatant was sampled and prepared for analysis. The remaining extract solution was decanted and the remaining solids were used in the next step of the three-step sequential extraction procedure.

3.2 Photocatalytic Degradation of Methyl Orange Dye

The photocatalytic degradation of methyl orange dye ($C_{14}H_{14}N_3NaO_3S$, 4-[(4-dimethylamino phenyl)azo]benzene-sulfonic acid sodium salt, Fluka) was tested using synthesized products including TiO_2, SiO_2-TiO_2 nanocomposite and SUZ-4 zeolite and compared to commercial samples (TiO_2 (P25), Degussa) and titania-clay composite (TiO_2-PILC, Triton System Inc.).

The reaction was performed using a batch reactor consisting 150 ml Pyrex glass beaker and a stirrer (Corning Magnetic Stirrer) as shown in Figure 6. For all the experiments 12.5 mg of each material sample was used. The initial volume of methyl orange solution was 100 ml with the 5 mg/l initial concentration ($2x10^{-5}$ mol/l). The solution was sonicated for 20 minutes and continuously stirred at 500 rpm using a magnetic stirrer for all the experiments. Initially the reactor was kept in dark for 20 minutes to establish an adsorption-desorption equilibrium. Oxygen was aerated in the reactor continuously with the 0.5 lpm volumetric flow rate controlled by a mass flow controller. UV light was then irradiated using a high power mercury lamp (365 nm UV light, Blak-Ray Longwave ultraviolet LAMP, 100 W). The reacted methyl orange solution with 6.5 ml was taken at 15 min time intervals for 6 hours. All the samples were centrifuged (Centrifuge 5417C, Eppendorf, Germany) at 17000 rcf (12650 rpm) for 20 minutes to obtain supernatant and residue. The supernatant for each sample was transferred to another vessel and carried out using UV spectrophotometer at 460 nm wavelength to determine the absorbance of methyl orange.

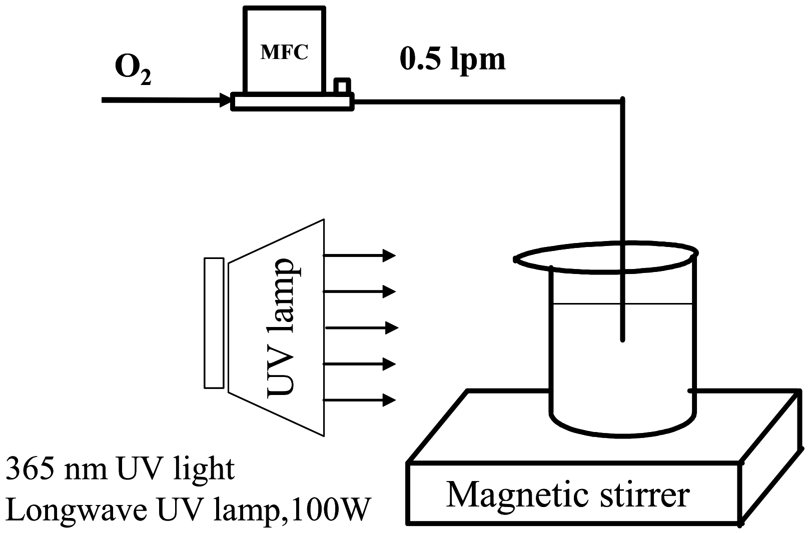

Figure 6 Experimental setup for photocatalytic degradation of methyl orange dye studies.