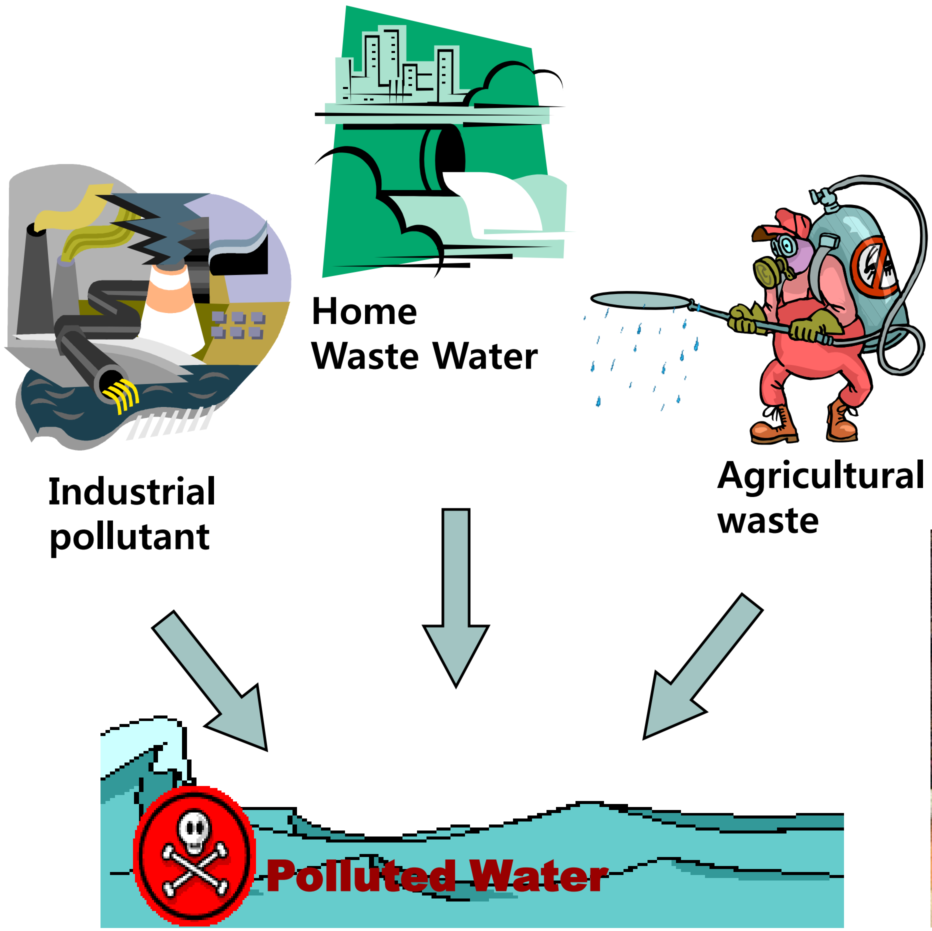
Part 2. The Hydrosphere

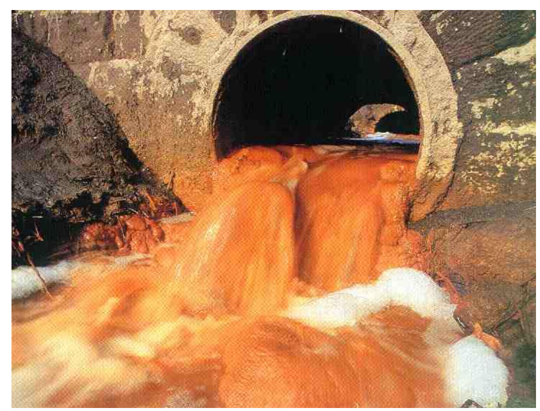
Additional Chapter 2.
The Water Pollution Solutions
(Carbon adsorbent)

Additional Chapter 2. The Water Pollution Solutions

2.1 The Water Pollution

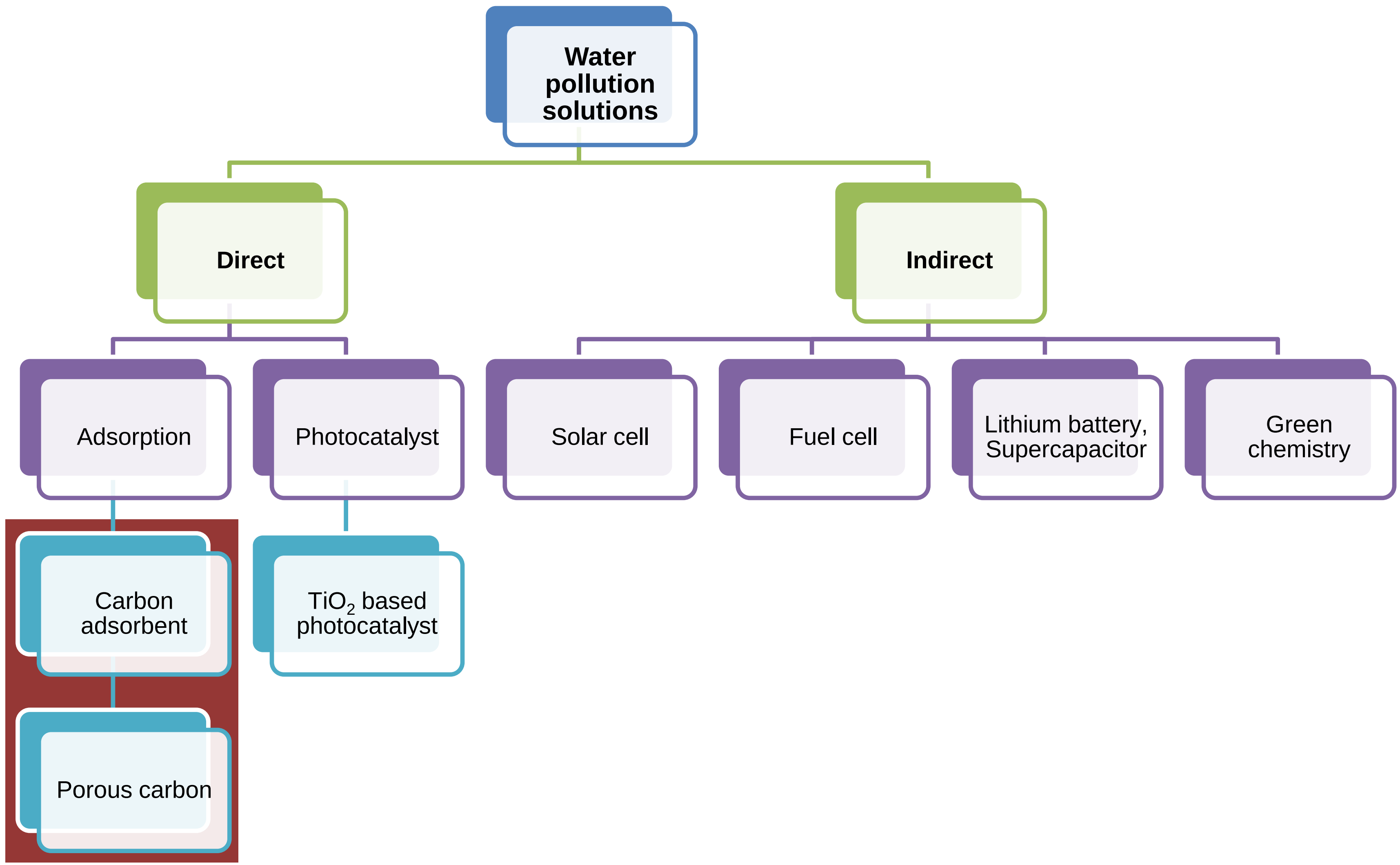
Elimination of Pollutants by !!!!





Additional Chapter 2. The Water Pollution Solutions

2.2 The Water Pollution Solutions



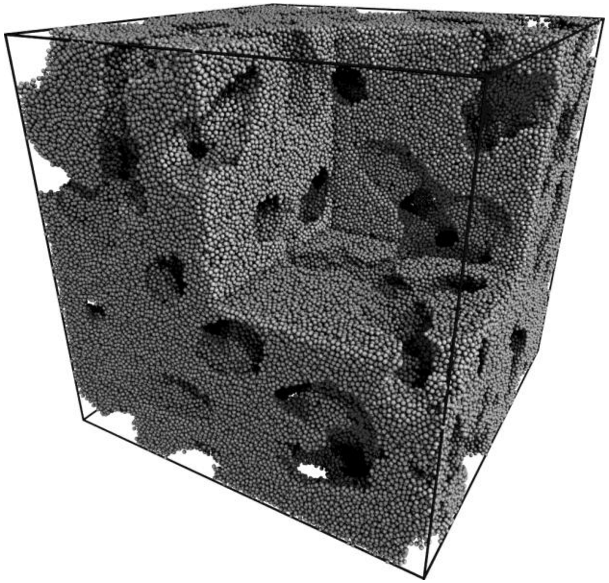
Additional Chapter 2. The Water Pollution Solutions

2.2 The Water Pollution Solutions

Contents

Porous carbon

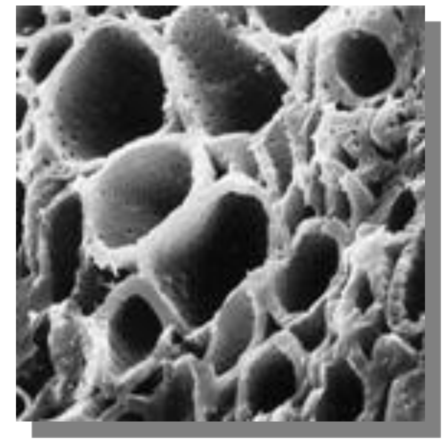
2.3 Porous carbon adsorbent

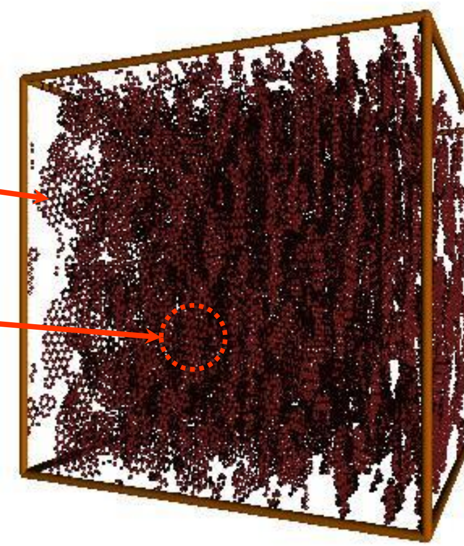


- Carbonaceous adsorbents with highly and extensively developed pore structure
- Non graphite carbon having a random imperfect structure such as cracks and crevices
- A broad range of pore size distribution on carbon surface
- Internal surface area : 500~3000 m^2 g

2.3 Porous carbon adsorbent : what is porous carbon?

What is Porous Carbon ?

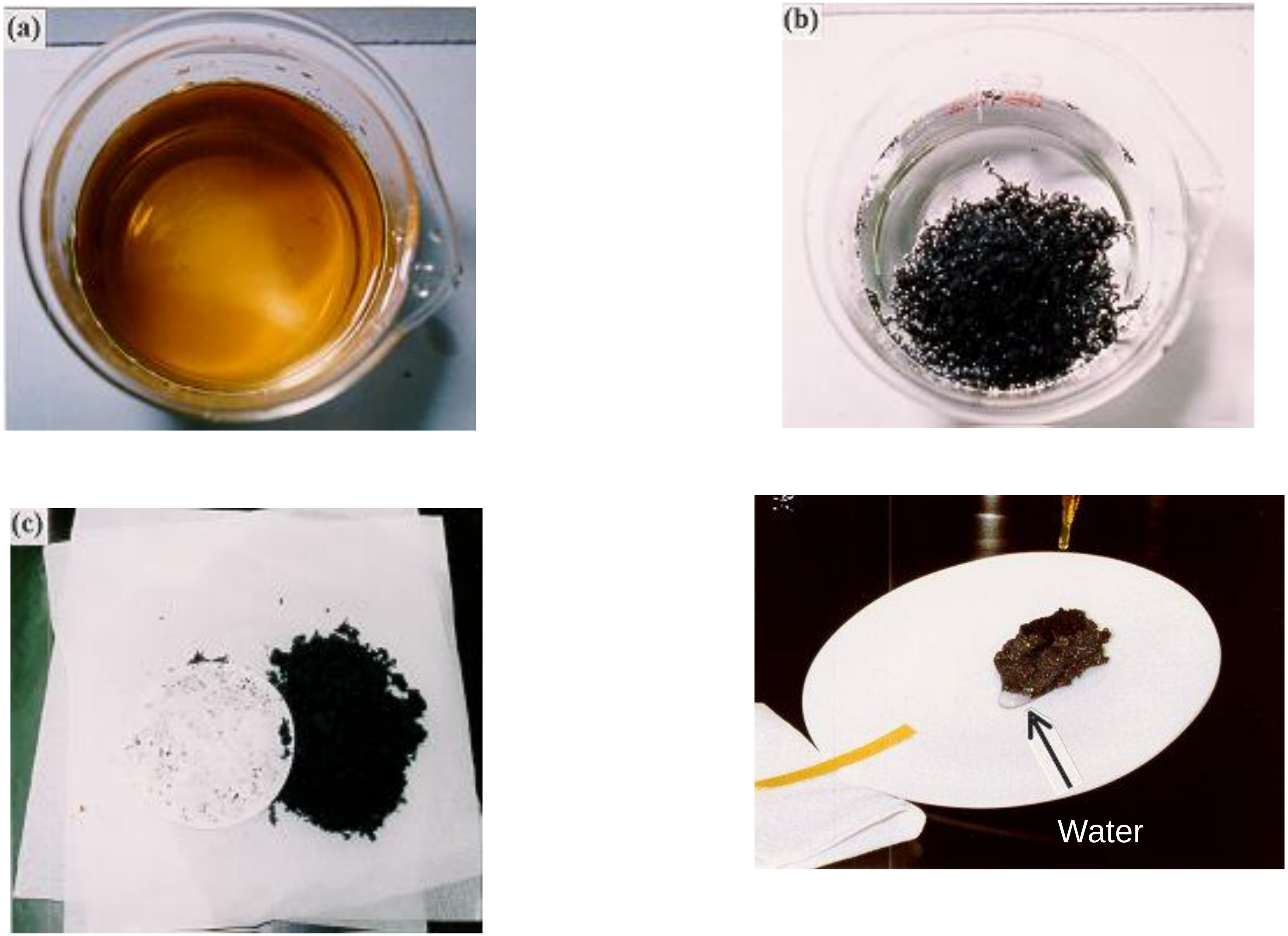




A non-graphitic form of carbon with surface areas ranging from 500 to 3000 m^2/g.

Additional Chapter 2. The Water Pollution Solutions

2.3 Porous carbon adsorbent : what is porous carbon? (spilled heavy oil recovery)



Inagaki et al., Carbon Science 2001, 1, 1-8.

Additional Chapter 2. The Water Pollution Solutions

2.3 Porous carbon adsorbent : what is porous carbon?

Air purification

Filters

Masks

Cartridge

Water purification

Additional Chapter 2. The Water Pollution Solutions

2.3 Porous carbon adsorbent : what is porous carbon?

States	Purpose	Applications	Examples
Gas phase	Recovery	Gasoline Vapor Recovery	Gasoline Fuel recovery,ELCD
		Solvent Recovery	MEK, Cyclohexanone, CS2, Furon, Trichloroethane
	Odor Removal	Room Odor Removal	Tobacco, CO, Room filters, Toilet Odor, Pet Odor
		Refrigerator	Deodorizer
		Automobile	Cabin air filters
		Tobacco	Cigarette Filter
		Hospital	Anesthetic gas removal
		Ozone Removal	Copiers, Laser Printers
	Harmful Gas	Closed Environment	Dioxin removal,Space Ships, Underground CO2
	Gas Separation	Nitrogen PSA	Nitrogen Gas Separation
		Other PSA	Radio Active Gas
Liquid Phase	Water Treatment	Factory Waste Water	Cleaning Waste Water
		Drinking Water Treatment	Trihalomethane, Chlorine, VOCs, Lead, Arsenate removal
	Decolorization of Indusrial Chemicals	Industrial Use	Sugar refinement, Pharmaceutical use, Whisky distilment
	Medical Applications	Medical and Nursing	Kidney machine, Nursing supplies, Respirators
	Electronics	Eletrorodes	Double Layer Capacitors, Hardisks
	Mineral Recovery	Gold Recovery	Gold Recovery

Additional Chapter 2. The Water Pollution Solutions

2.3 Porous carbon adsorbent : brief history

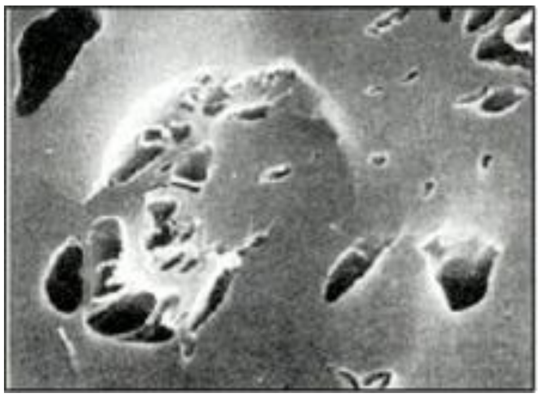
Charcoal, 2000 BC
Ancient Egyptian
; in water purification

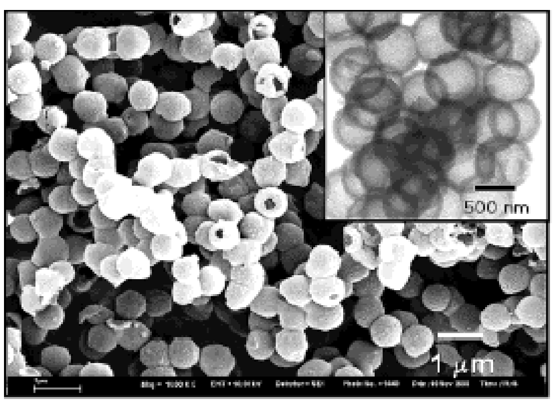
Granular Activated
Carbon (GAC)
During World WAR II
; in gas mask

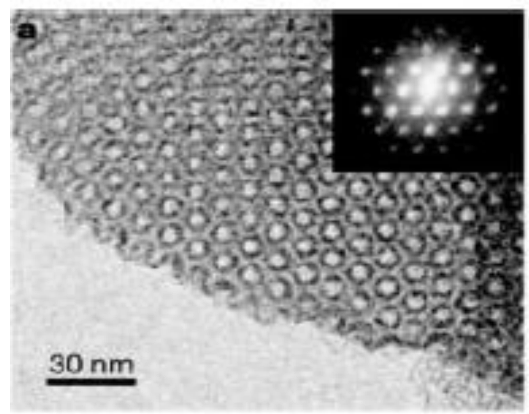
Powdered Activated
Carbon (PAC)
; Larger pore diameter
than GAC

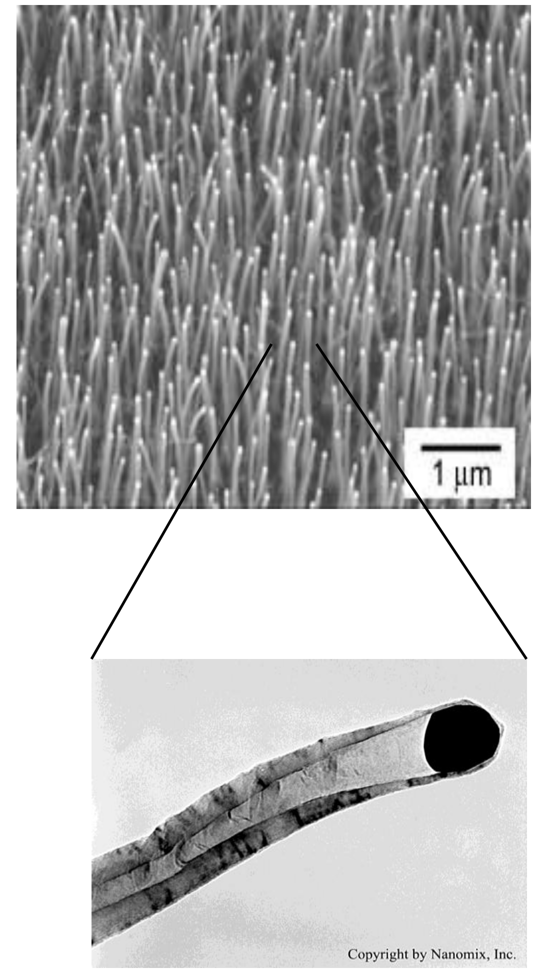
Additional Chapter 2. The Water Pollution Solutions

2.3 Porous carbon adsorbent : structure of porous carbon









- IUPAC classification

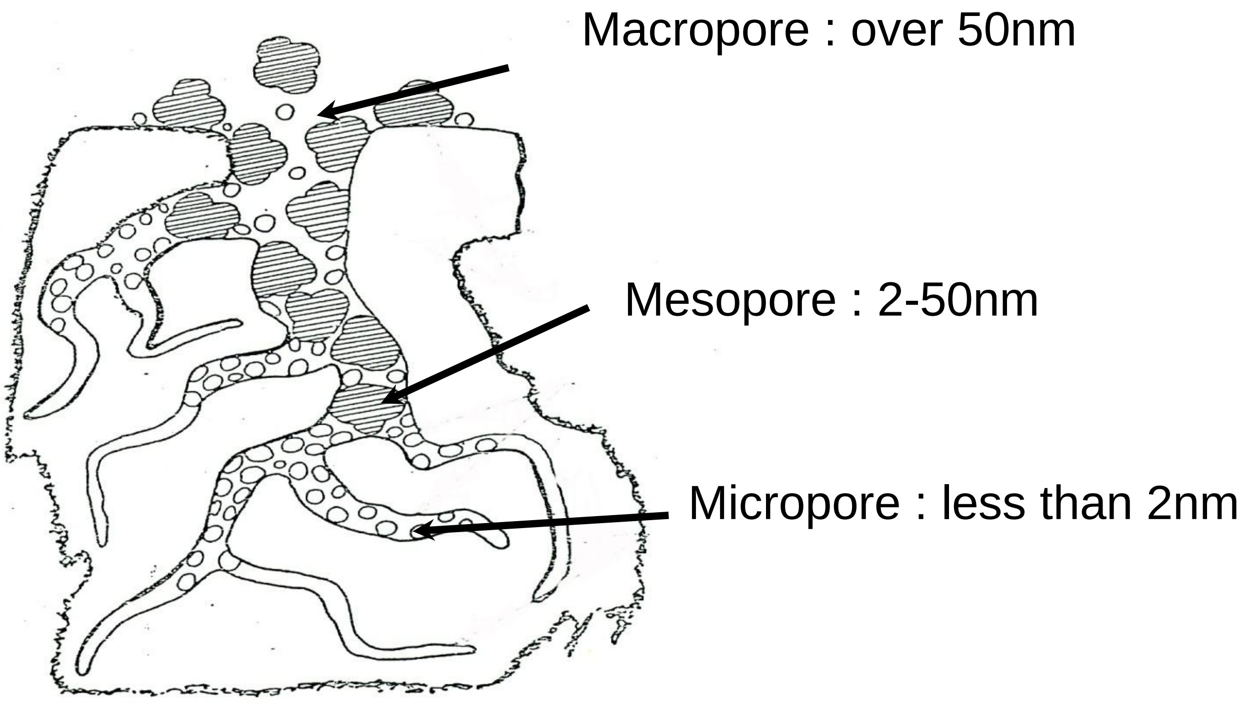
  Ultra-micropore : < 0.5 nm diameter

  Micropore : 0.5 to 2.0 nm diameter

  Mesopore : 2.0 to 50 nm diameter

  Macropore : > 50 nm diameter

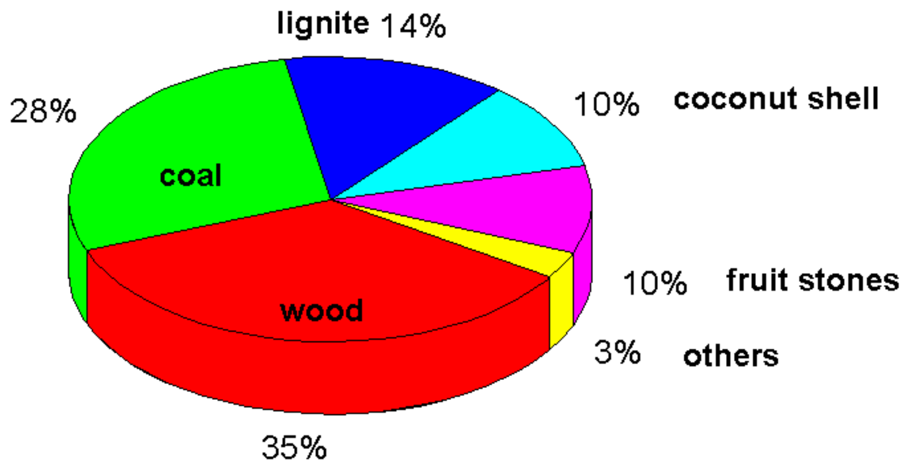
2.3 Porous carbon adsorbent : surface chemistry on porous carbon



Additional Chapter 2. The Water Pollution Solutions

2.3 Porous carbon adsorbent : preparation (precursor)

Table. Commercial carbon precursor



- The selection of the precursor essentially determines the range of adsorptive and physical properties that can be attained in the activated carbon products
- Important consideration of selecting a source
  ; cost, availability, consistency of quality
- Particularly for coal, peat, and lignite
  ; the mineral matter and sulfur contents

Additional Chapter 2. The Water Pollution Solutions

2.3 Porous carbon adsorbent : preparation (precursor)

Raw materials	Carbon (%)	Volatile (%)	Density (Kg/M^3)	Ash (%)	Texture of activated carbon	Application of activated carbon
Softwood	40–45	55–60	0·4–0·5	0·3–1·1	Soft, large pore volume	Aq. phase adsorption
Hardwood	40–42	55–60	0·55–0·8	0·3–1·2	Soft, large pore volume	Aq. phase adsorption
Lignin	35–40	58–60	0·3–0·4	–	Soft, large pore volume	Aq. phase adsorption
Nut shells	40–45	55–60	1·4	0·5–·6	Hard, large multi pore volume	Vapour phase adsorption
Lignite	55–70	25–40	1·0–1·35	5–6	Hard small pore volume	Waste water treatment
Soft coal	65–80	25–30	1·25–1·50	2·12	Medium hard, medium micropore volume	Liquid & vapour phase adsorption
Petroleum coke	70–85	15–20	1·35	0·5–0·7	Medium hard, medium micropore volume	Gas–vapour adsorption
Semi hard coal	70–75	1–15	1·45	5–15	Hard large pore volume	Gas–vapour adsorption
Hard coal	85–95	5–10	1·5–2·0	2·15	Hard large volume	Gas–vapour adsorption

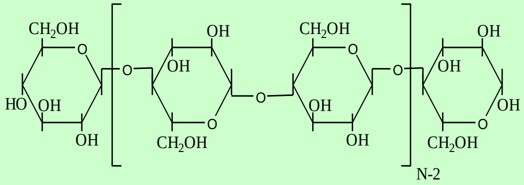
Additional Chapter 2. The Water Pollution Solutions

2.3 Porous carbon adsorbent : preparation (methods)

Precursor

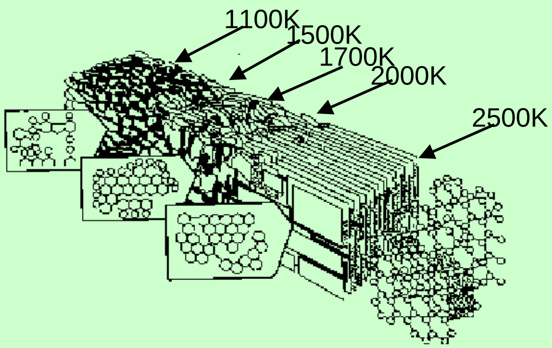
Coal, Biomasses,

Polymers, Pitch, etc.



Carbonization

Under inert atmospheres

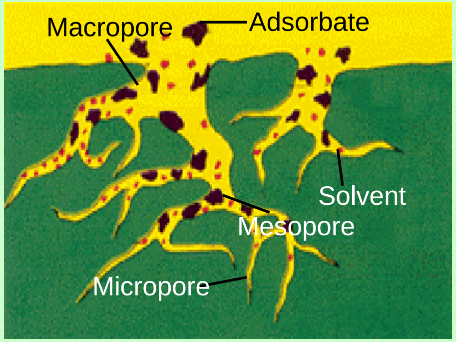


-. Elimination of non-carbon atoms.

-. Well-ordered structure like graphite

Activation

- Physical (H_2O, CO_2)
- Chemical (KOH, $ZnCl_2$, H_3PO_4)



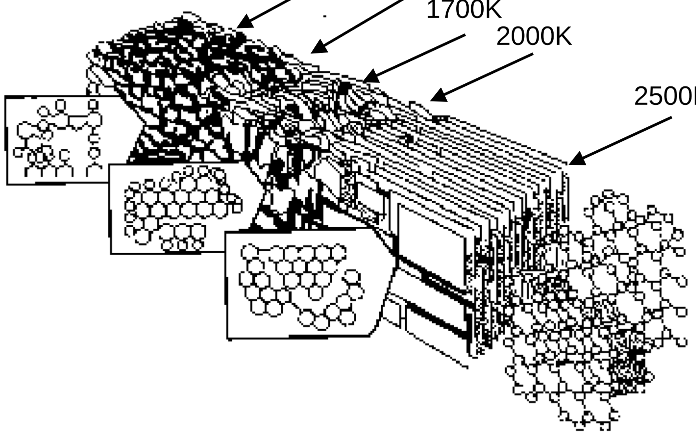
-. Porous Carbons with higher surface area

-. Different pore structure under various conditions

2.3 Porous carbon adsorbent : preparation (carbonization)

Carbonization

Under inert atmospheres



-. Liberation of non-carbon atoms

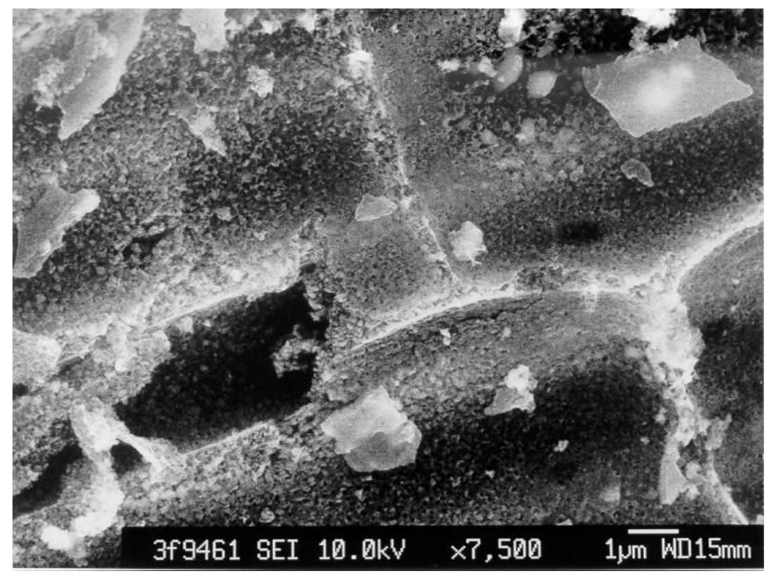
-. Rigid carbon skeleton formed by aromatic sheets and strips.

-. Pores are filled or blocked by disorganized carbon.

Gasification with

H_2O, CO_2

-. Disorganized material is removed with subsequent increase in pore volume



Porous carbon from rice straws

Rodriguez-Reinoso F, Molina-Sabio M., Carbon 1992, 30, 111-8.

2.3 Porous carbon adsorbent : preparation (carbonization)

Variables of carbonization

- Rates of heating
- Final heat treatment temperature
- Soak time
- Ambient gases
- Reaction temperature
- Reacting gases

2.3 Porous carbon adsorbent : preparation (carbonization)

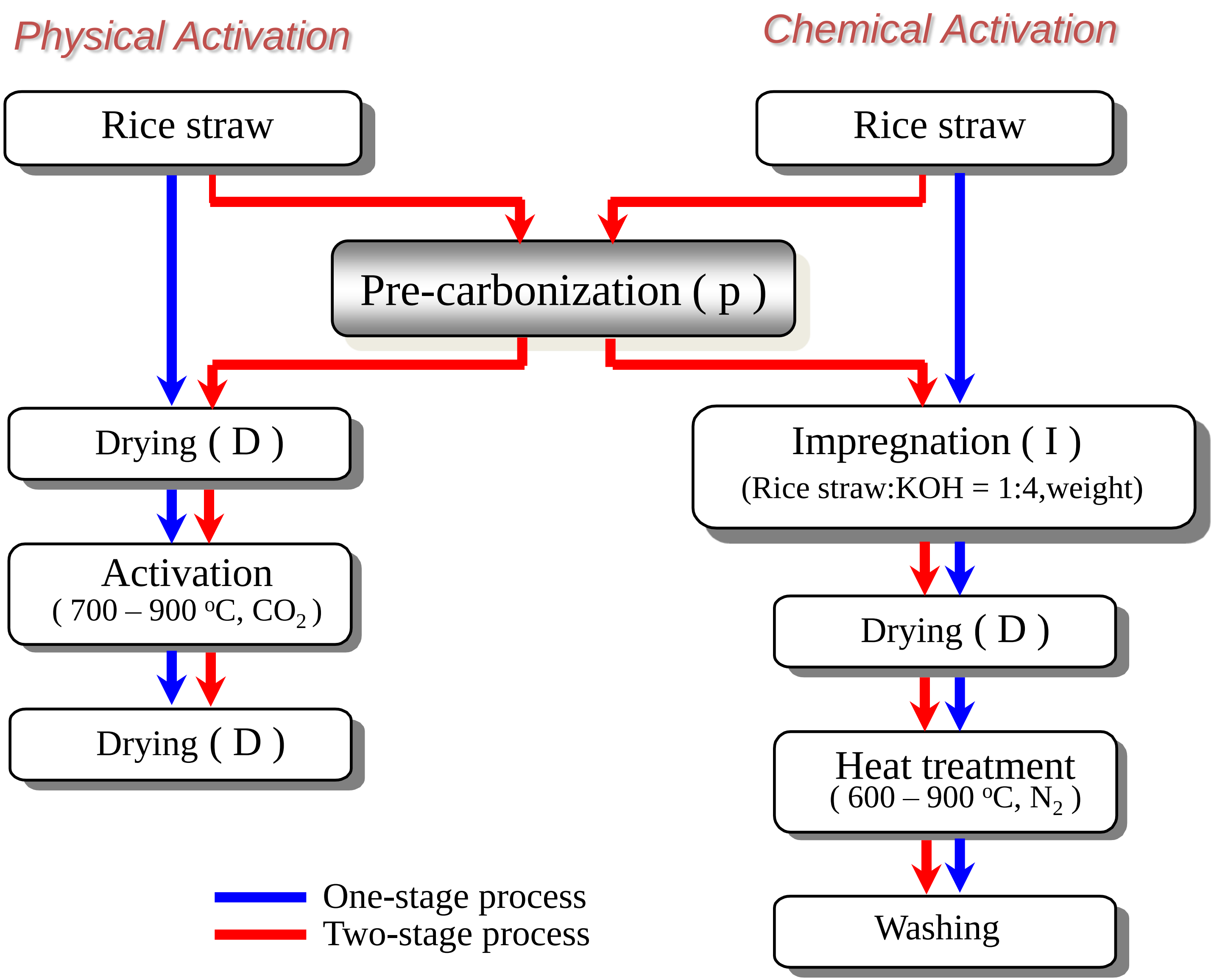
Effect of carbonization temperature on yield and composition of charcoal

Carbonization Temperature	Chemical analysis of charcoal		Charcoal yield based on oven dry wood
°C	% of fixed charcoal	% volatile material	(0% moisture)
300	68	31	42
500	86	13	33
700	92	7	30

Low carbonization temperatures give a higher yield, but low grade

Additional Chapter 2. The Water Pollution Solutions

2.3 Porous carbon adsorbent : preparation (activation)



2.3 Porous carbon adsorbent : preparation (physical activation)

Gasification with Oxidizing Gases

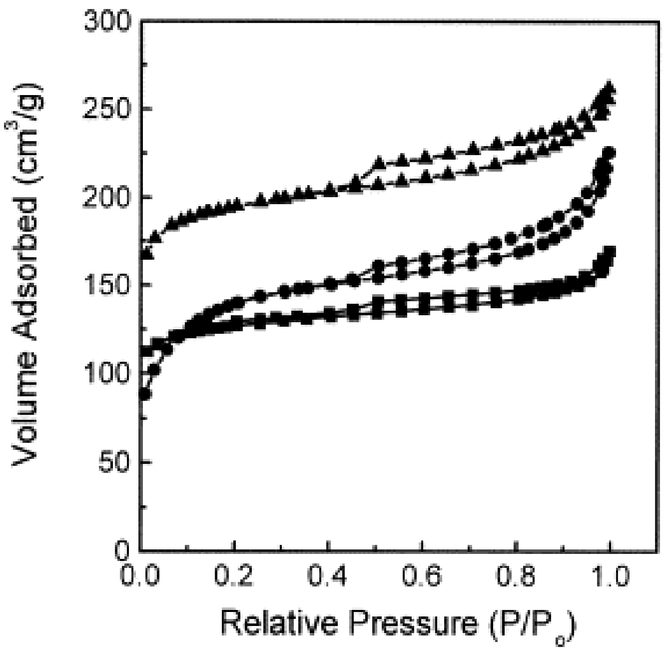


Fig. 1 Adsorption/desorption isotherms of porous carbon from rice straws.
(■: 700℃, ▲: 800℃, ●:900℃)

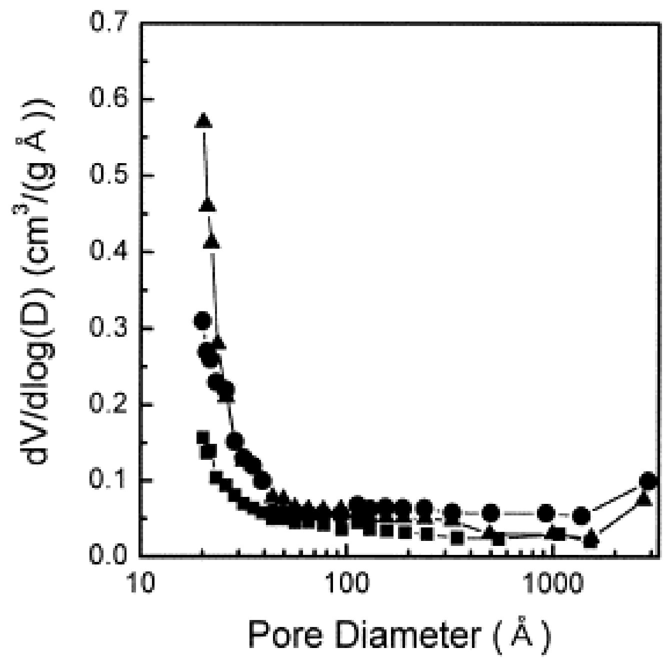


Fig. 2 Pore size distribution of porous carbon from rice straws.
(■: 700℃, ▲: 800℃, ●:900℃)

Yun CH et al., Carbon 2001, 39, 559-67.

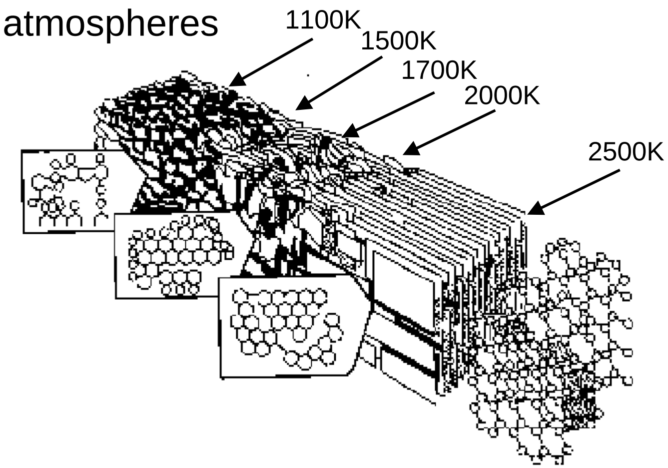
Additional Chapter 2. The Water Pollution Solutions

2.3 Porous carbon adsorbent : preparation (chemical activation)

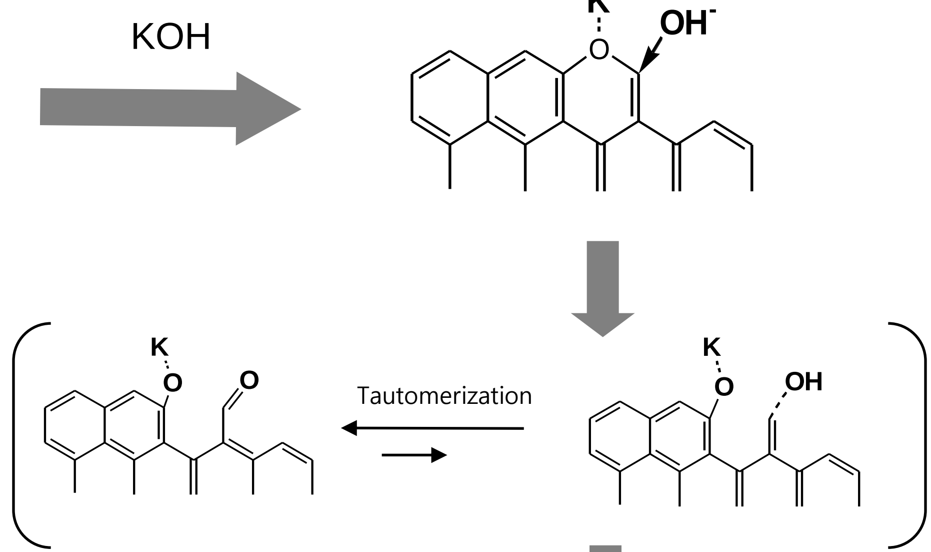
Gasification with Oxidizing Chemicals

*Carbonization

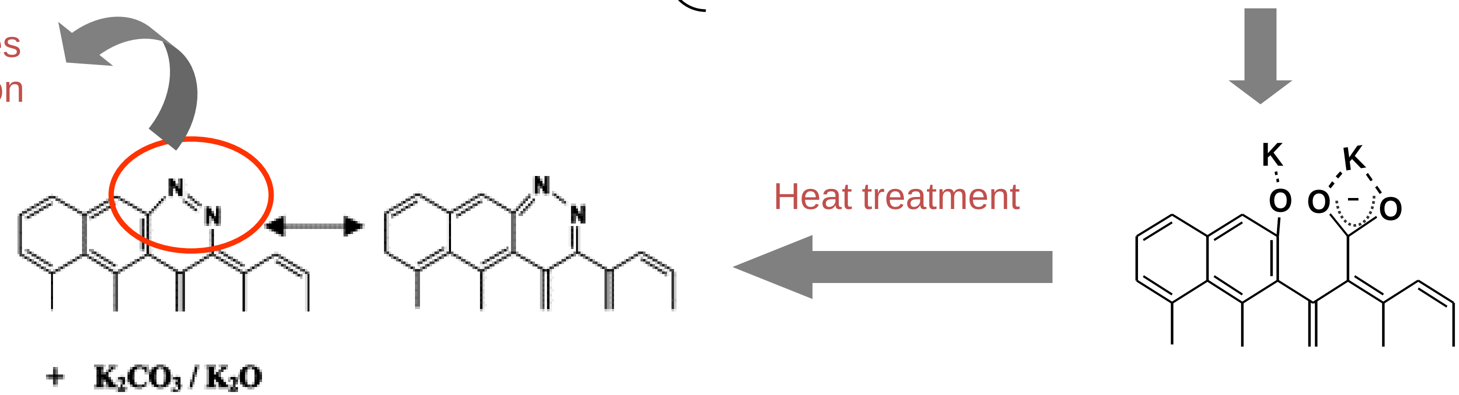
Under inert atmospheres



**Gasification with



Creation of pores
by decomposition



*Marsh H, Carbon 1991, 29, 703.

**Oh GH, Park CR, Fuel 2002, 81, 327-36.

Additional Chapter 2. The Water Pollution Solutions

2.3 Porous carbon adsorbent : preparation (chemical activation)

Gasification with Oxidizing Chemicals

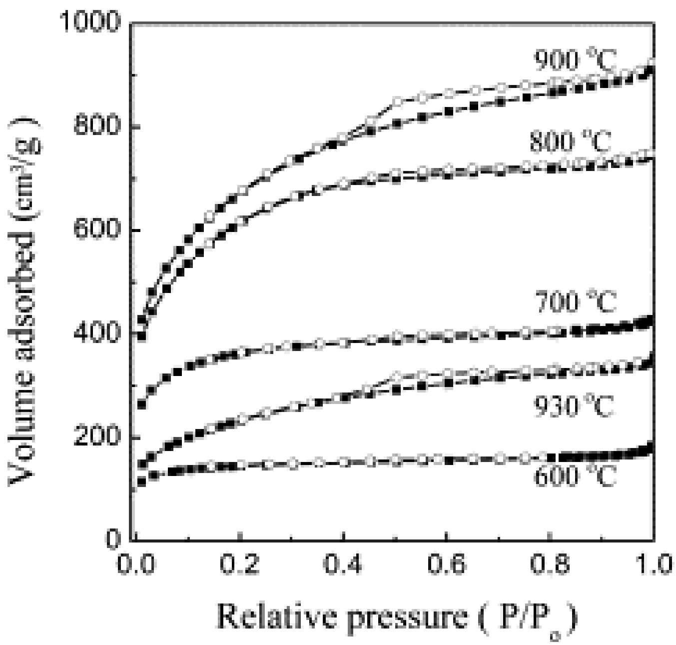


Fig. 3 Adsorption/desorption isotherms of porous carbon from rice straws.

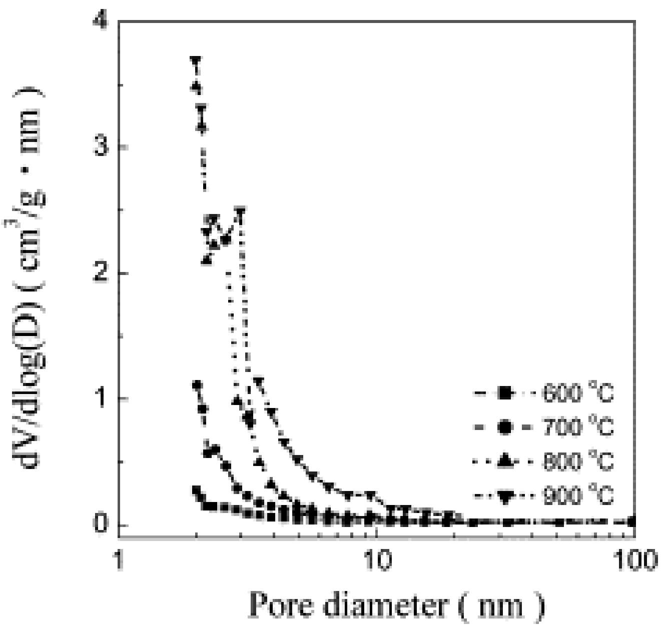


Fig. 4 Pore size distribution of porous carbon from rice straws.

Oh GH, Park CR, Fuel 2002, 81, 327-36.

2.3 Porous carbon adsorbent : Characterization (nitrogen adsorption)

Adsorption Isotherm

To quantify the adsorption process, extents of adsorption ($mmolg^{-1}$) are related to the equilibrium partial pressure p/p^0 at constant temperature to create the *isotherm*

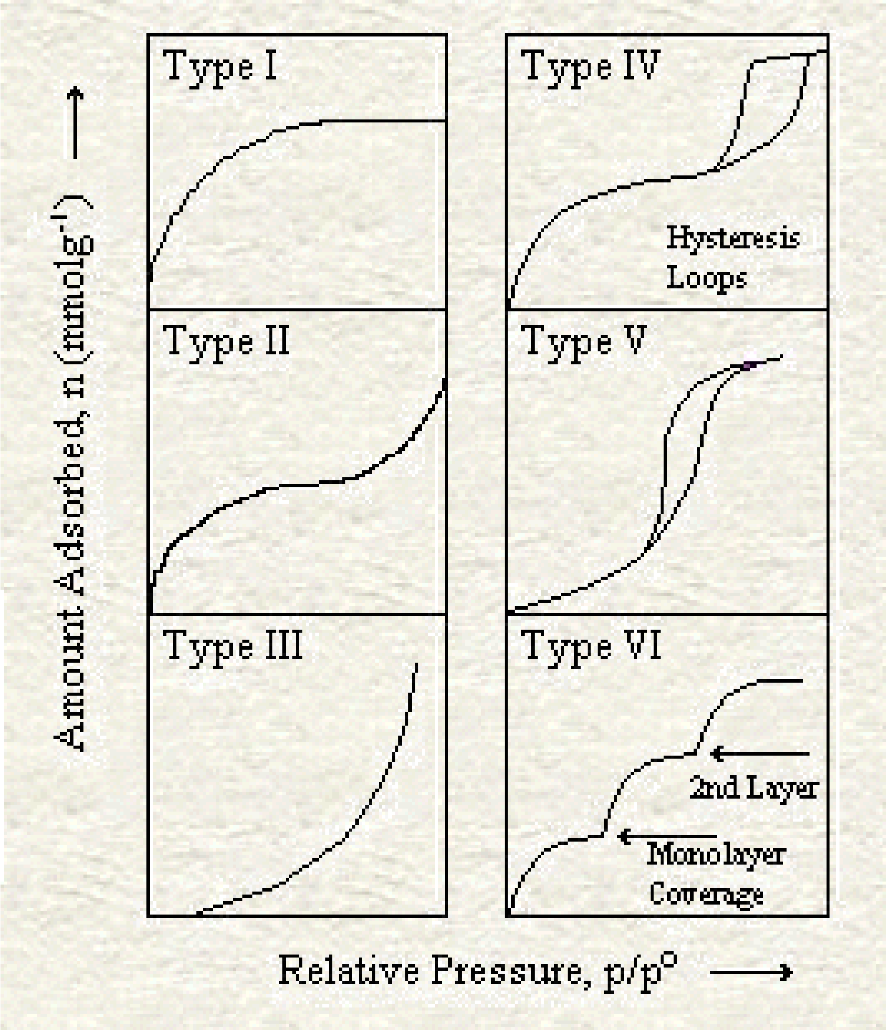
- Estimates of the surface area
- Estimates of pore volumes in the various porosity, i.e. pore-size of potential energy distributions
- Assessments of the surface chemistry of the adsorbent
- The nature of the adsorbed phase
- Assessments of the efficiency of industrial carbons employed in separation/purification techniques

Additional Chapter 2. The Water Pollution Solutions

2.3 Porous carbon adsorbent : Characterization (nitrogen adsorption)

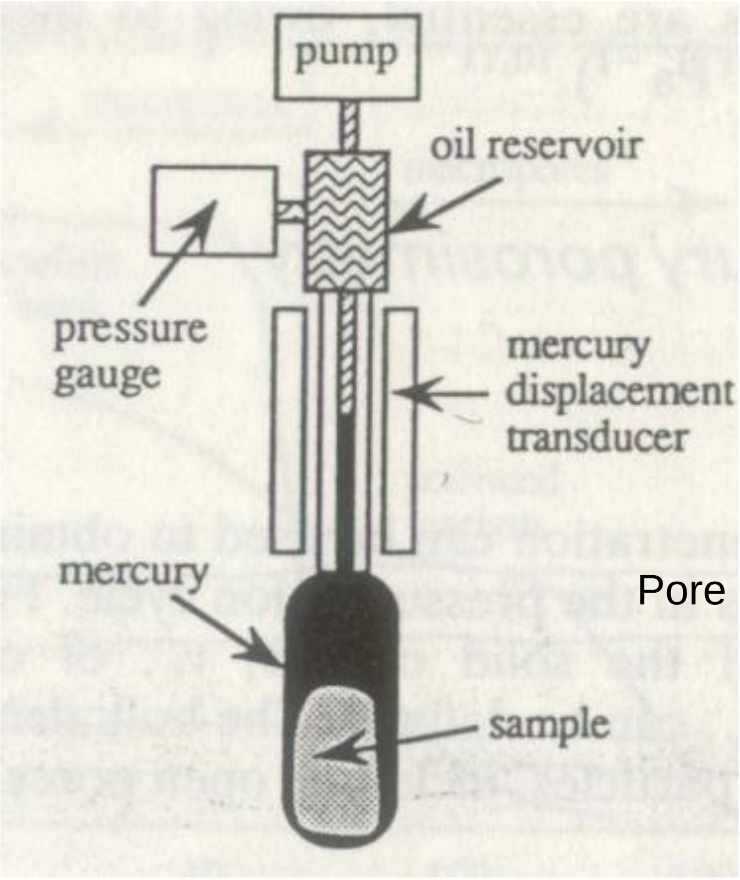
Adsorption Isotherm

6-Major Class of Isotherm Shape



2.3 Porous carbon adsorbent : Characterization (mercury porosimetry)

Mercury Porosimetry



- Applied to a wide range of pore size
- Mesopore and macropore
- 1.8 nm ~ 7000 nm

Washburn equation

Surface tension

Contact angle

Pore radius

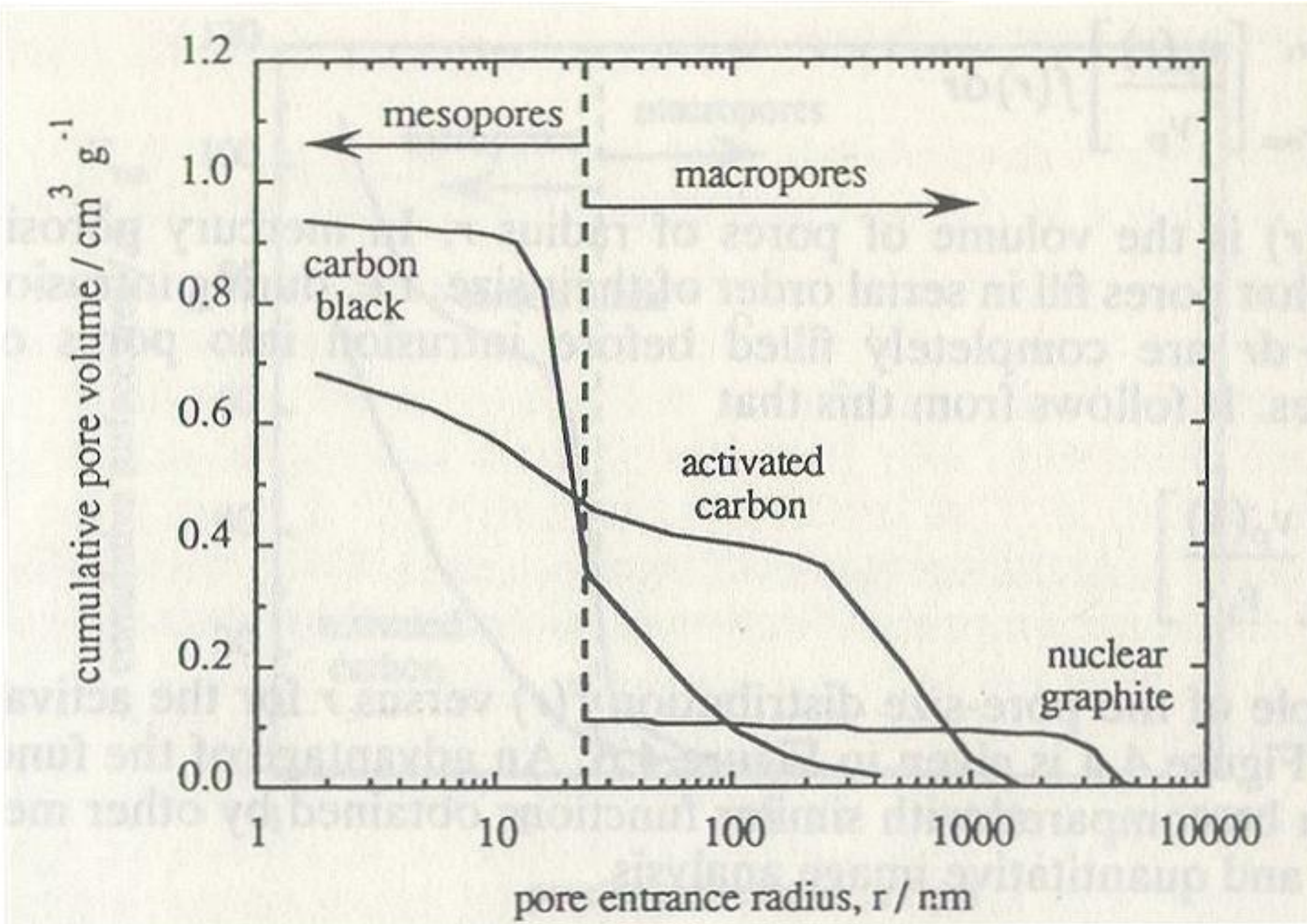
$$r = -\frac{2\gamma\cos\theta}{\Delta p}$$

Pressure required to force mercury into the pore [Mpa (MNm^{-2})]

Additional Chapter 2. The Water Pollution Solutions

2.3 Porous carbon adsorbent : Characterization (mercury porosimetry)

Mercury Porosimetry



Additional Chapter 2. The Water Pollution Solutions

2.3 Porous carbon adsorbent : state of the art (Anthropogenic inputs of trace metal into the aquatic ecosysrem)

Critical contaminants (As, Cr)

Table 4 Anthropogenic inputs of trace metals into the aquatic ecosystems (10^6 kg yr^{-1})

Source category	Annual global discharge (10^9 m^3)	As	Cd	Cr	Cu	Hg	Mn	Mo	Ni	Pb	Sb	Se	V	Zn
Domestic wastewater†														
-Central	90	1.8–8.1	0.18–1.8	8.1–36	4.5–18	0–0.18	18–81	0–2.7	9.0–54	0.9–7.2	0–2.7	0–4.5	0–2.7	9.0–45
-Non-central	60	1.2–7.2	0.3–1.2	6.0–42	4.2–30	0–0.42	30–90	0–1.8	12–48	0.6–4.8	0–1.8	0–3.0	0–1.8	6.0–36
Steam electric	6	2.4–14	0.01–0.24	3.0–8.4	3.6–23	0–3.6	4.8–18	0.1–1.2	3.0–18	0.24–1.2	0–0.36	6.0–30	0–0.6	6.0–30
Base metal mining														
and dressing	0.5	0–0.75	0–0.3	0–0.7	0.1–9	0–0.15	0.8–12	0–0.6	0.01–0.5	0.25–2.5	0.04–0.35	0.25–1.0	—	0.02–6
Smelting and refining														
-Iron and steel	7						14–36			1.4–2.8				5.6–24
-Non-ferrous metals	2	1.0–13	0.01–3.6	3–20	2.4–17	0–0.04	2.0–15	0.01–0.4	2.0–24	1.0–6.0	0.08–7.2	3.0–20	0–1.2	2.0–20
Manufacturing processes														
-Metals	25	0.25–1.5	0.5–1.8	15–58	10–38	0–0.75	2.5–20	0.5–5.0	0.2–7.5	2.5–22	2.8–15	0–5.0	0–0.75	25–138
-Chemicals	5	0.6–7.0	0.1–2.5	2.5–24	1.0–18	0.02–1.5	2.0–15	0–3.0	1.0–6.0	0.4–3.0	0.1–0.4	0.02–2.5	0–0.35	0.2–5.0
-Pulp and paper	3	0.36–4.2	—	0.01–1.5	0.03–0.39	—	0.03–1.5	—	0–0.12	0.01–0.9	0.–0.27	0.01–0.9	—	0.09–1.5
-Petroleum products	0.3	0–0.06	—	0–0.21	0–0.06	0–0.02	—	—	0–0.06	0–0.12	0–0.03	0–0.09	—	0–0.24
Atmospheric fallout‡		3.6–7.7	0.9–3.6	2.2–16	6.0–15	0.22–1.8	3.2–20	0.2–1.7	4.6–16	87–113	0.44–1.7	0.54–1.1	1.4–9.1	21–58
Dumping of sewage	[6×10^9 kg]													
sludge§		0.4–6.7	0.08–1.3	5.8–32	2.9–22	0.01–0.31	32–1.06	0.98–4.8	1.3–20	2.9–16	0.18–2.9	0.26–3.8	0.72–4.3	2.6–31
Total input, water		**12–70**	**2.1–17**	**45–239**	**35–90**	**0.3–8.8**	**109–414**	**1.8–21**	**33–194**	**97–180**	**3.9–33**	**10–72**	**2.1–21**	**77–375**
Median value		41	9.4	142	112	4.6	262	11	113	138	18	41	12	226

Nature 1988, 333, 134–139

Additional Chapter 2. The Water Pollution Solutions

2.3 Porous carbon adsorbent : state of the art (Anthropogenic inputs of trace metal into the aquatic ecosysrem)

Critical contaminants (As, Cr)

Exposure to Arsenic

- Skin, lung, bladder, and kidney cancer
- Pigmentation changes
- Skin thickening (hyperkeratosis)
- Muscular weakness
- Loss of appetite
- Nausea

Exposure to Chromium

- nausea, diarrhea, liver and kidney damage
- dermatitis,
- internal hemorrhage,
- respiratory problems(asthma)

Journal of Hazardous Materials 2007, 142, 1–53

2.3 Porous carbon adsorbent : state of the art (Aresenic adsorption)

Iron-containing mesoporous carbon (IMC)

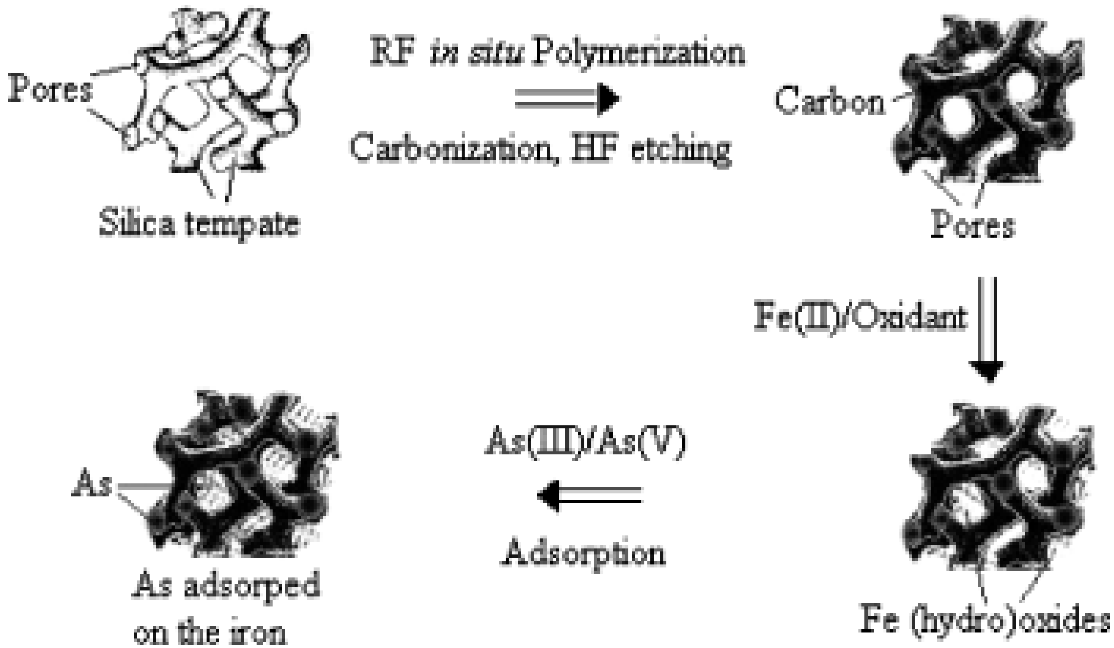


Table 2. Physicochemical properties of mesoporous silica templates and mesoporous carbons prepared in this study.

	BET surface area (m^2/g)	*Average pore diameter (nm)*	*Median pore diameter (nm)*	*Porosity*	*Volume of pore (cm^3/g)*
MCM-48	1167	2.64	2.70	0.48	0.77
Porous C	513	4.07	5.83	0.34	0.52
IMC	401	4.41	7.87	0.31	0.44

Environ. Eng. Sci. 2007, 24, 113–121

Additional Chapter 2. The Water Pollution Solutions

2.3 Porous carbon adsorbent : state of the art (Aresenic adsorption)

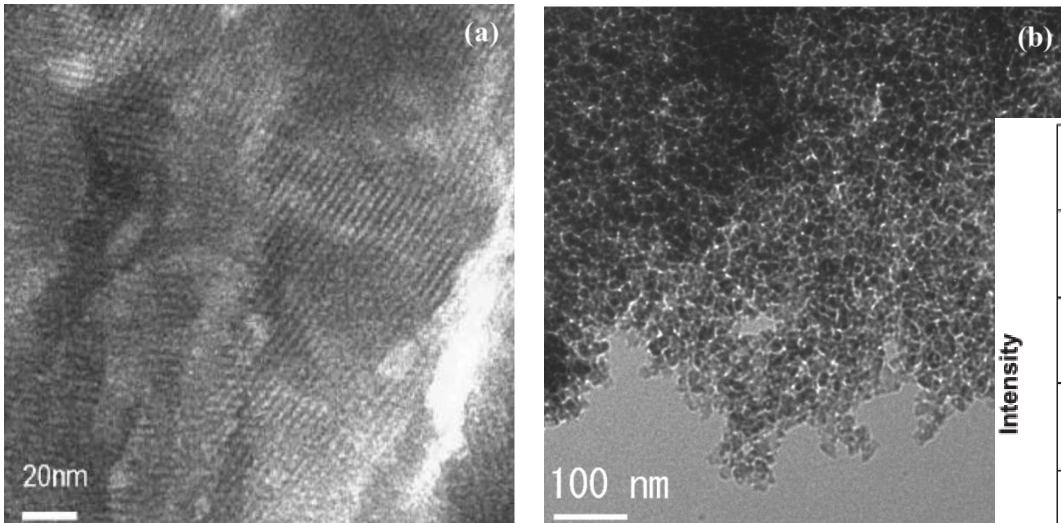


Fig. HR-TEM images of a) MCM-48, b) IMC

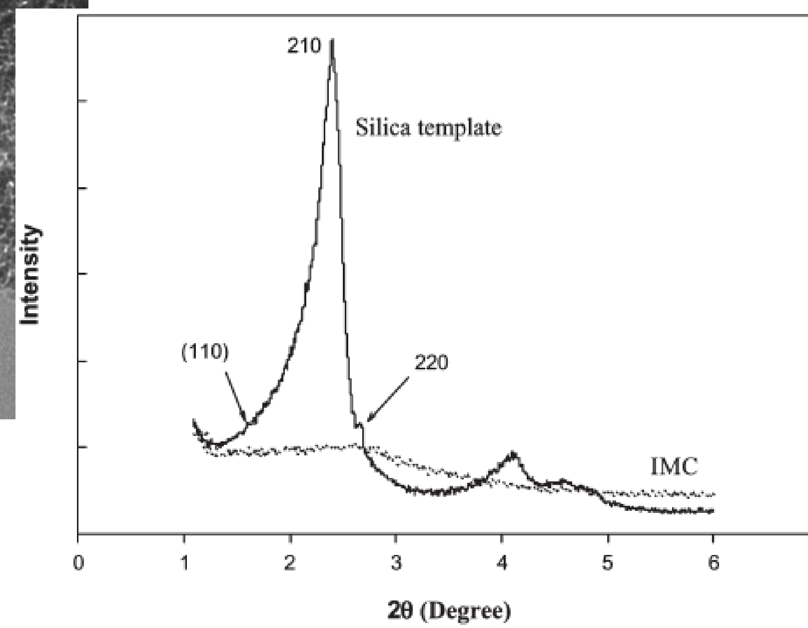


Figure. Low-angle X-ray diffraction (XRD) patterns of silica template and IMC.

Environ. Eng. Sci. 2007, 24, 113–121

2.3 Porous carbon adsorbent : state of the art (Aresenic adsorption)

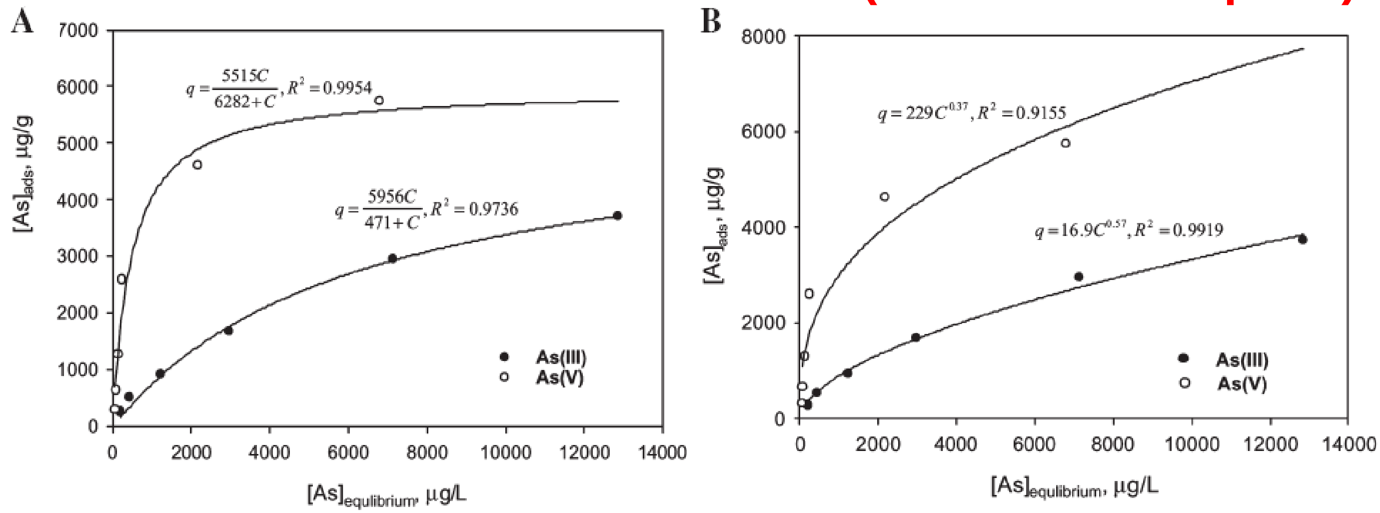


Figure. Arsenic adsorption isotherm regressed by different model (**A) Langmuir adsorption isotherm, (B) Freundlich adsorption** isotherm.

Table 4. Regressed parameters of isotherm adsorption modeled by different equations.

Arsenic speciation	*Langmuir equation* q_m (µg/g)	b (l/µg)	R^2 (%)	*Freundlich equation* K_F (µg/g)	l/n	R^2 (%)
As(III)	5956	471	97.36	16.9	0.57	99.19
As(V)	5515	6282	99.54	229	0.37	91.55

Table 5. Arsenic adsorption kinetics fit by a pseudosecond-order kinetic model.

Arsenic speciation	k ($g \cdot \mu g^{-1}\ min^{-1}$)	q_e $\mu g_{As}/g$	q_e $mmol_{As}/g$	*Determination coefficient* (R^2)
As(III), 4,925 µg/L	2.21×10^{-4}	1,250	0.017	0.988
As(V), 4,910 µg/L	1.80×10^{-4}	1,667	0.022	0.997

Highest arsenic adsorption capacity and adsorption kinetic rate

Environ. Eng. Sci. 2007, 24, 113–121

2.3 Porous carbon adsorbent : state of the art (Chromium adsorption)

Adsorbents	pH	Temperature (°C)	Model used to calculate adsorption capacities	Adsorption capacity (mg/g)	
				Cr(VI)	Cr(III)
Untreated *R. nigricans*	2.0	30	Langmuir	123.5	–
CTAB-treated R. nigricans	2.0	30	Langmuir	140.8	–
PET-treated *R. nigricans*	2.0	30	Langmuir	161.3	
APTS-treated *R. nigricans*	2.0	30	Langmuir	200.0	
Biomass of filamentous algae *Spirogyra* species	2.0	18	Langmuir	14.7	–
	2.0	22	Langmuir	48.1	–
Carbonaceous adsorbent from waste tires (TAC)	2.0	30	Langmuir	55.3	–
	2.0	38	Langmuir	58.5	–
	2.0	22	Langmuir	1.9	–
Carbonaceous adsorbent from sawdust (SPC)	2.0	30	Langmuir	2.2	–
	2.0	38	Langmuir	2.3	–
	2.0	22	Langmuir	44.4	–
Carbon, F-400	2.0	30	Langmuir	48.5	–
	2.0	38	Langmuir	53.2	–
IRN77 resin	3.5	25	Freundlich	–	35.4
SKN1 resin	3.5	25	Freundlich	–	46.3
Dried anaerobic activated sludge	1.0	25	Langmuir	577.0	–
	2.0	30	Langmuir	22.7	–
Red mud	2.0	40	Langmuir	21.6	–
	2.0	50	Langmuir	21.1	–
Tannin gel (66% water content)	2.0	30	–	192.0	20.0
Tannin gel (72% water content)	2.0	30	–	224.0	28.0
Tannin gel (75% water content)	2.0	30	–	235.0	38.0
Tannin gel (77% water content)	2.0	30	–	287.0	50.0
Cow dung carbon	3.4	30	Langmuir	10.0	–
Carbon C3	3.0	25	Langmuir	35.0	–
Carbon C4	3.0	25	Langmuir	15.0	–
Algae, *Chlorella vulgaris*	2.0	25	Langmuir	27.3	–
Insoluble straw xanthate (ISX)	3.6–3.9	25	Langmuir	–	1.9
Alkali-treated straw (ATS)	3.6–3.9	25	Langmuir	–	3.9
Algae, *C. vulgaris*	2.0	25	Langmuir	79.3	–
Algae, *S. obliquus*	2.0	25	Langmuir	58.8	–
Algae, *Synechocystis* sp.	2.0	25	Langmuir	153.6	–
Algae, *C. vulgaris*	2.0	25	Freundlich	6.0	–
Peat	2.0	25	–	30.7	–

Various activated carbon have shown the high chromium adsorption capacity

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