Biochars from pyrolysis and gasification for the removal of Cr(VI) and Pb(II) from aqueous solutions

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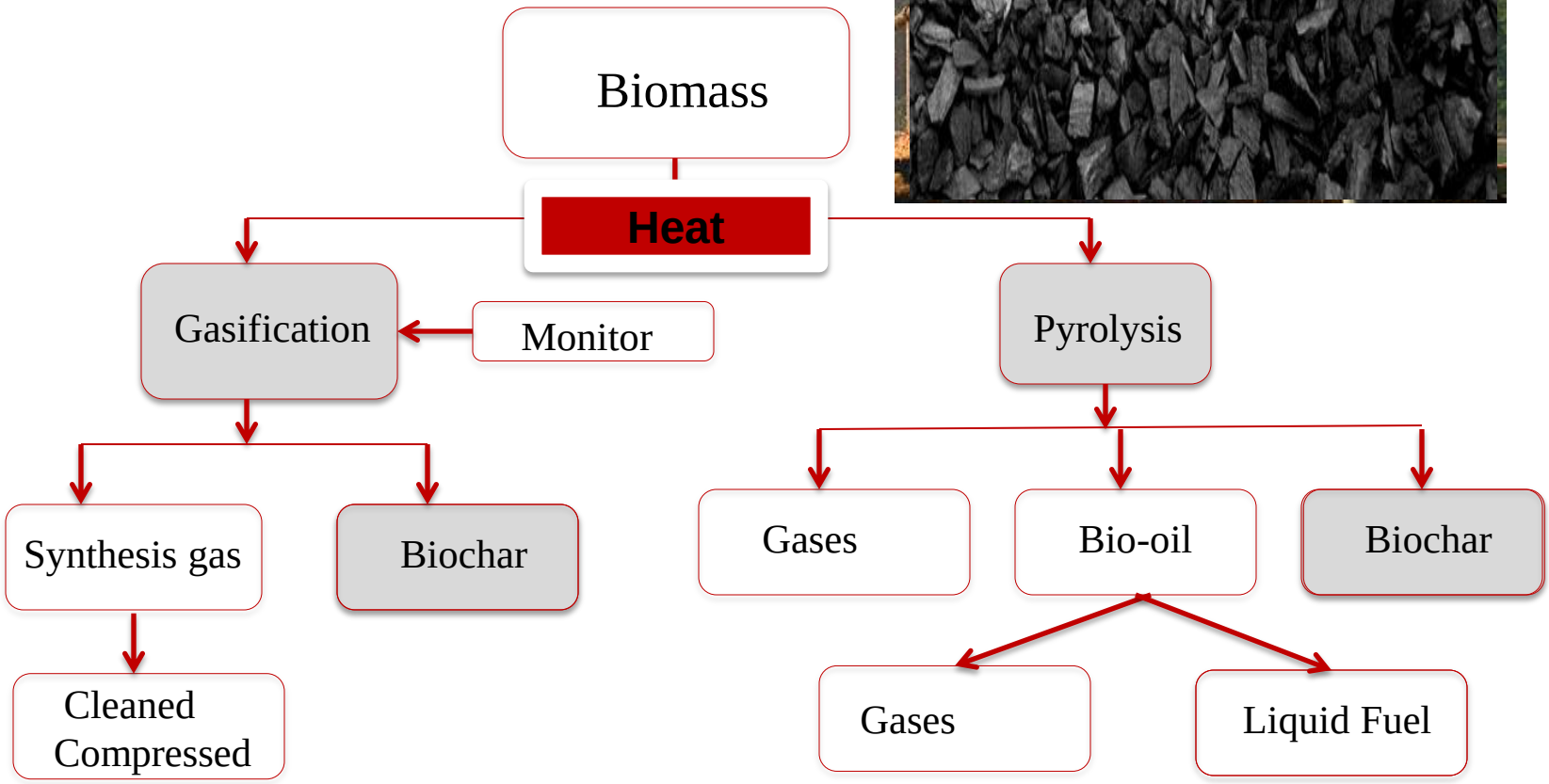
Introduction

- Fossil fuel, coal, oil and natural gas are non renewable source of energy
- US consume one-quarter of the world's oil supply, but have just 1.6% of its oil reserves
- Estimated reserves are expected to last between 40 and 70 years at the current rate of use
- Major source of environmental pollutants, greenhouse gases and ocean acidification.
- Alternative for fossil fuel – Biofuel

Introduction

Total Calories



Char Characterization

Biochars:

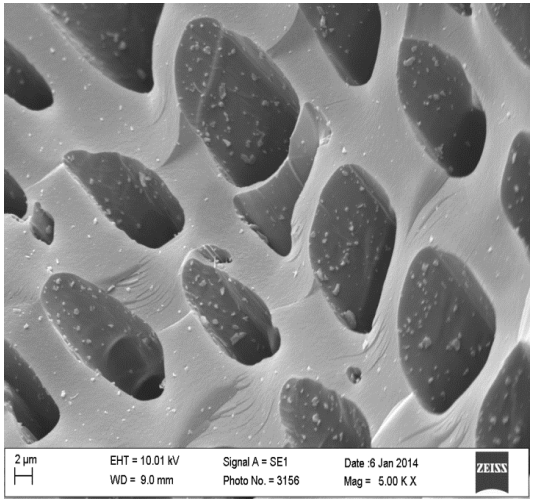
- Pine wood-chips pyrolysis (PP) 425˚C
- Pine wood-chips gasification (GP) 300-350˚C
- Switch grass pyrolysis (PS) 425˚C

BET Surface Area

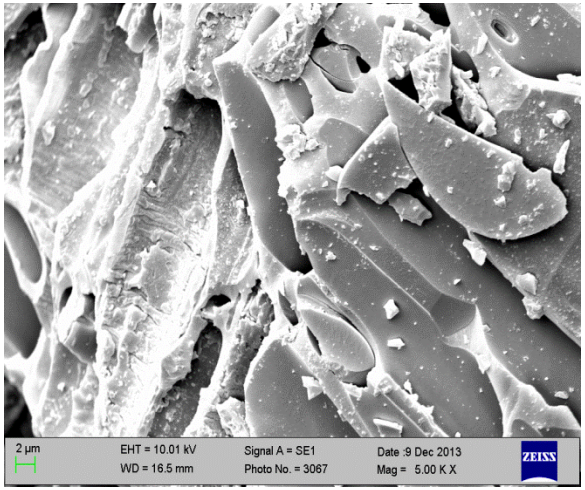
- Pyrolysis char: 1.35 m^2/g
- Switchgrass char: 1.10 m^2/g
- Gasified char: 0.94 m^2/g

Char Characterization

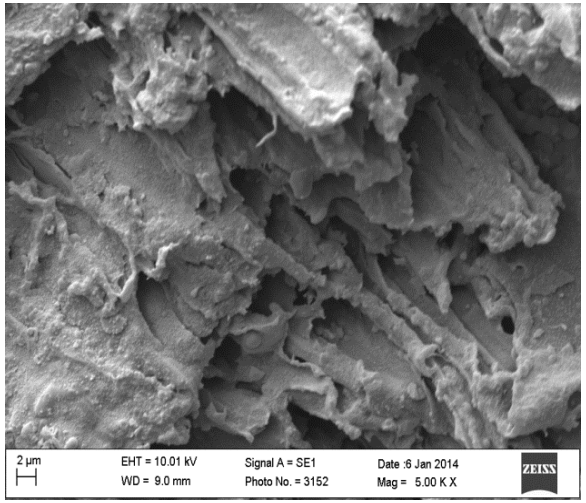
SEM Images



Pyrolysis Pine



Gasification Pine



Pyrolysis Switch Grass

EDS: 80-90 % Carbon, 10-19% oxygen and traces amount of other metals%

Analytes - Metals

Metals:

- Chromium: Liver, kidney damage, internal hemorrhage
- Lead: Nervous system, reproductive system, kidney damage

Concentration in H_2O:

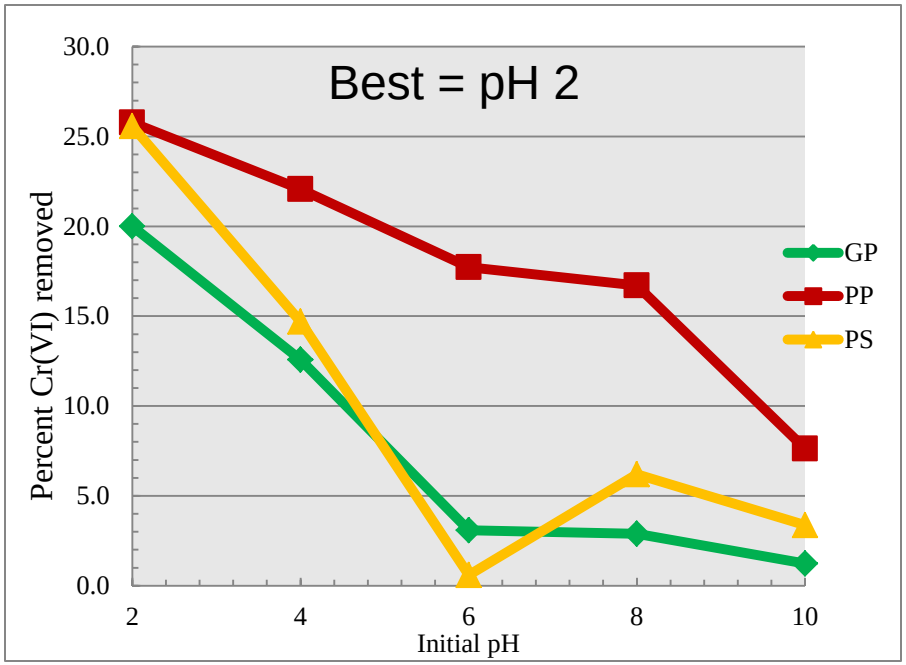
- Lead: 15 ppb (EPA)
- Chromium : 100 ppb (EPA)

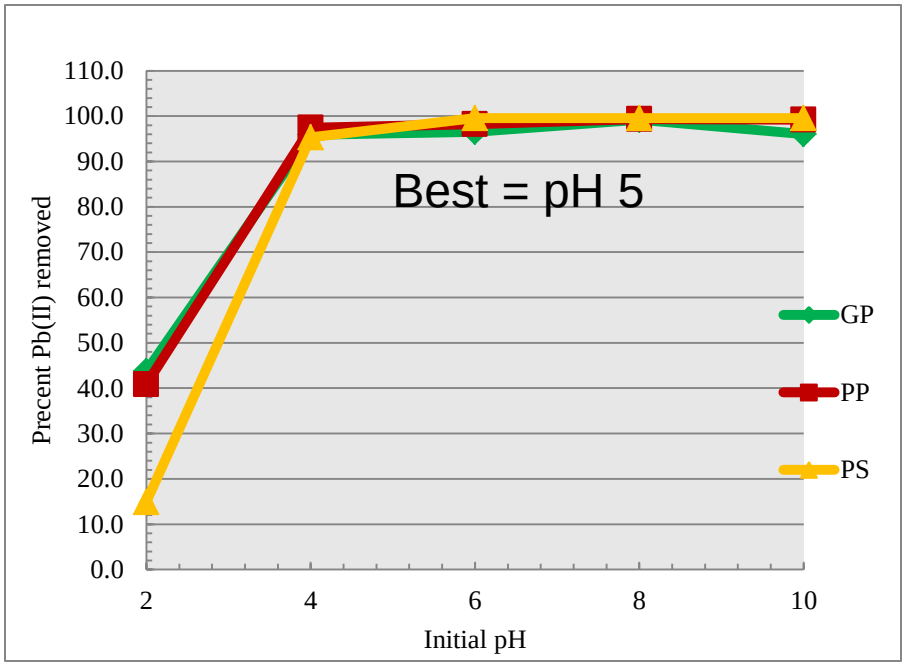
Speciation

Chromium		**Lead**	
pH	Speciation	pH	speciation
1<pH<7	$HCrO_4^-$	<6	$Pb(OH)^+$
>7	CrO_4^{2-}	6-8.5	$Pb(OH)_2$ ppt
8 to 9	$Cr(OH)_3$	>8.5	$Pb(OH)_2$ soluble

Teoh, Y. P.; Khan, M. A.; Choong, T. S. Y. Kinetic and isotherm studies for lead adsorption from aqueous phase on carbon coated monolith. *J Chem Eng.* **2013,** *217* (0), 248-255.

Zero point charge and pH





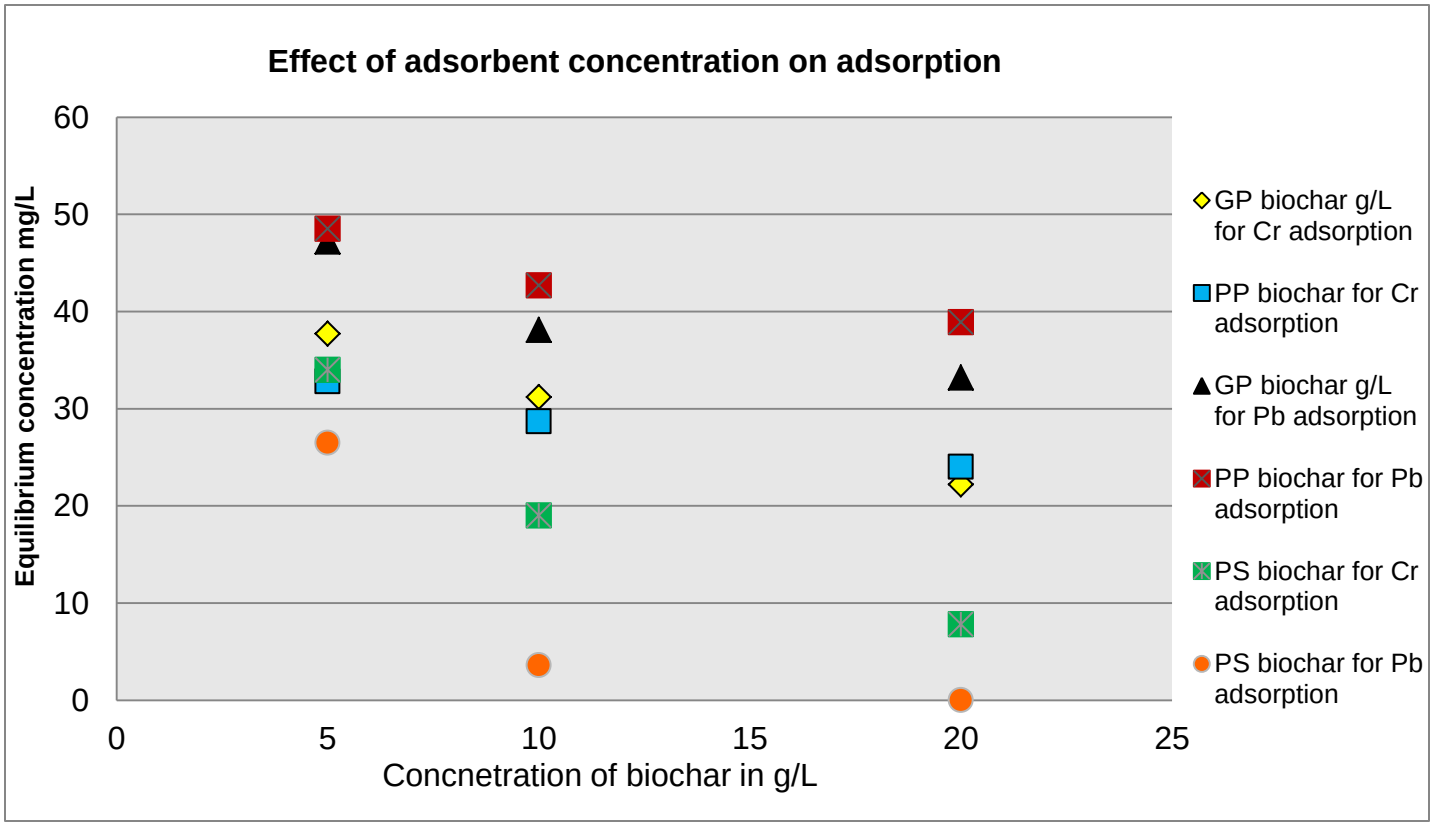
pH_{pzc} = 2

pH_{pzc} > pH of the solution, the surface of the char is positively charge

pH_{pzc} < pH of the solution, the surface of the char is negatively charge.

* PP Pine woodchips biochar obtained from pyrolysis, GP: Pine woodchips biochar obtained from gasification, PS: Switchgrass biochar obtained from pyrolysis

Affect of adsorbent concentration on adsorption



Cr(VI) 40 ppm , Pb(II) 200 ppm, adsorbant concentration: 10 g/L
Operation temperature: 25 ºC, equilibration time: 48 h

Effect of adsorbate concentration and temperature

Cr(VI) and Pb(II) adsorption in 10 g/L Switchgrass biochar (PS) at 25˚C, 35˚C and 45˚C

Cr(VI)	At 25 ˚C		At 35 ˚C		At 45 ˚C		Pb(II)	At 25 ˚C		At 35 ˚C		At 45 ˚C	
C_o (mg/L)	C_e	q_e (mg/g)	C_e	q_e	C_e	q_e	C_o (mg/L)	C_e	q_e (mg/g)	C_e	q_e	C_e	q_e
20	16.5	0.35	14.5	0.55	11.5	0.85	100	5.1	9.49	5.4	9.46	2.6	9.74
40	19.0	2.10	18.2	2.18	15.8	2.42	200	3.6	19.68	3.4	19.66	2.0	19.8
60	28.5	3.15	23.0	3.70	17.0	4.30	300	8.5	29.15	8.2	29.18	3.9	29.6
80	35.2	4.48	33.5	4.65	24.0	5.60	400	50.2	38.98	17.2	38.28	11.5	38.9

Ce: concentration of metal in solution after reaction. qe: mg of metal adsorbed per g of biochar

Switchgrass
Endothermic process for Cr , Pb- adsorption increase with temperature.
qe (mg/g) increased with increase in adsorbate concentration.

Pine Chars
Pb(II) adsorption - exothermic
Cr(VI) adosrption-endothermic

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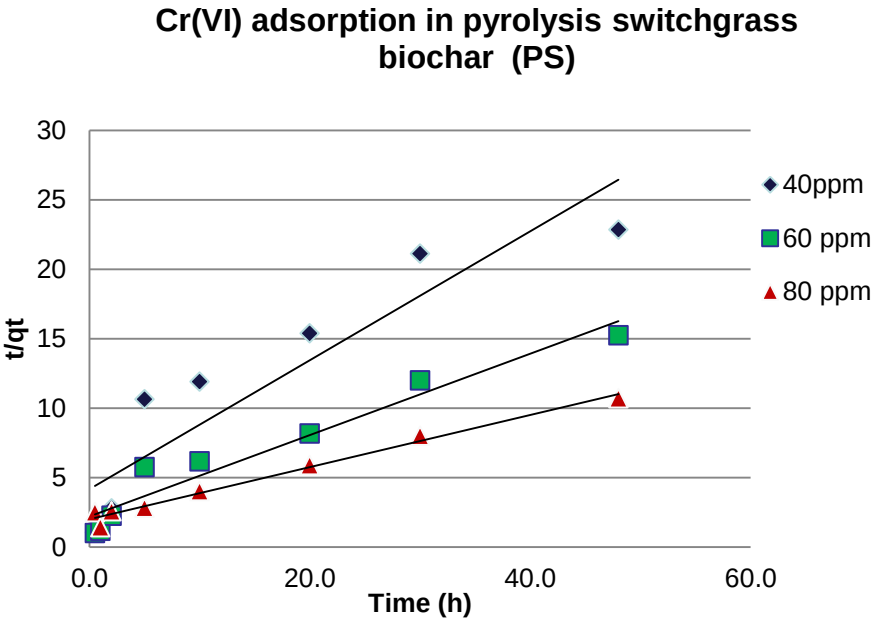
Kinetic studies



Kinetic study of Cr(VI) removal with Pine woodchips and switchgrass (PP, GP and PS)

Adsorbent/ Regression coefficient	q_e Experimental (mg/g)			q_e calculated (using pseudo second-order kinetic model) (mg/g)		
	40 mg/L	60 mg/L	80 mg/L	40 mg/L	60 mg/L	80 mg/L
GP	0.9	1.5	2.1	1.0	1.6	2.9
R^2				0.91	0.97	0.99
PP	1.2	2.0	2.5	1.1	1.9	2.4
R^2				0.97	0.96	0.98
PS	2.1	3.2	4.5	2.2	3.4	5.3
R^2				0.85	0.94	0.99

Experimental calculation: $$q_e = \frac{(C_o - C_e)V}{W}$$

Pseudo second order: $$\left(\frac{t}{q_t}\right) = \left(\frac{1}{K_2 q_e^2}\right) + \left(\frac{t}{q_e}\right)$$

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Isotherm modeling

- **Langmuir:**

$$\left(\frac{1}{q_e}\right) = \left(\frac{1}{Q^o b}\right)\left(\frac{1}{C_e}\right) + \left(\frac{1}{Q^o}\right)$$

Assumption: The surface is homogeneous.

Monolayer adsorption

- **Freundlich:**

$$\log q_e = \log K_F + \left(\frac{1}{n}\right)\log C_e$$

Assumption: The surface is heterogeneous.

Isotherm parameters	Gasification (GP) Cr(VI)			Gasification (GP) Pb(II)		
	25˚C	35˚C	45˚C	25˚C	35˚C	45˚C
Freundlich						
K_F(mg/g)	0.17	0.26	0.27	2.40	1.94	1.44
1/n	0.44	0.34	0.40	0.46	0.49	0.50
R^2	0.80	0.85	0.80	0.88	0.91	0.92
Langmuir						
Q_0(mg/g)	1.42	1.00	1.20	19.7	19.3	13.8
b ($x10^{-2}$)	6.00	21.0	20.0	8.00	6.00	7.00
R^2	0.95	0.95	0.93	0.81	0.93	0.88

Cr(VI) data fits Langmuir isotherm for GP, PP and PS
Pb(II) data fits Freundlich isotherm for GP, PP and PS

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Conclusion

- Biochar from GP, PP and PS were successfully used for Cr(VI) and Pb(II) adsorption.
- Adsorption was better in switchgrass.
- Removal was achieved upto 95% for Pb(II) and upto 25% for Cr(VI).
- Follow pseudo-second order kinetics.
- Langmuir model fits better for Cr(VI) adsorption and Freundlich model fits better for Pb(II).

Future work: Study other isotherms.

Acknowledgements

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- Dr. C. Pittman
- MSU-Department of Forest Products
- MSU- Department of Biological and Agricultural Engineering
- MSU-Department of Chemistry

Thank you

Kinetic studies

Adsorbent	q_e Experimental			q_e calculated (using second-order kinetic model)		
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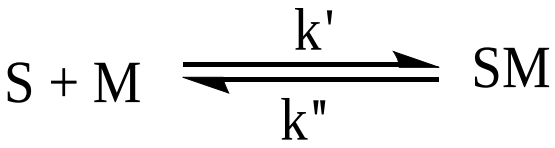
GP	0.9	1.5	2.1	1.0	1.6	2.9
R^2				0.91	0.97	0.99
PP	1.2	2.0	2.5	1.1	1.9	2.4
R^2				0.97	0.96	0.98
PS	2.1	3.2	4.5	2.2	3.4	5.3
R^2				0.85	0.94	0.99

Adsorbent	q_e Experimental			q_e calculated (using second-order kinetic model)		
	200 mg/L	300 mg/L	400 mg/L	200 mg/L	300 mg/L	400 mg/L
GP	12.8	19.1	26.3	12.8	19.2	17.2
R^2				0.99	0.98	0.99
PP	10.5	17.2	25.0	10.5	17.3	24.9
R^2				0.99	0.99	1
PS	19.7	29.2	35	20.5	31.7	38.3
R^2				0.99	0.99	0.96

Experimental calculation: $q_e = \frac{(C_o - C_e)V}{W}$

Pseudo second order: $\left(\frac{t}{q_t}\right) = \left(\frac{1}{K_2 q_e^2}\right) + \left(\frac{t}{q_e}\right)$

Kinetic studies

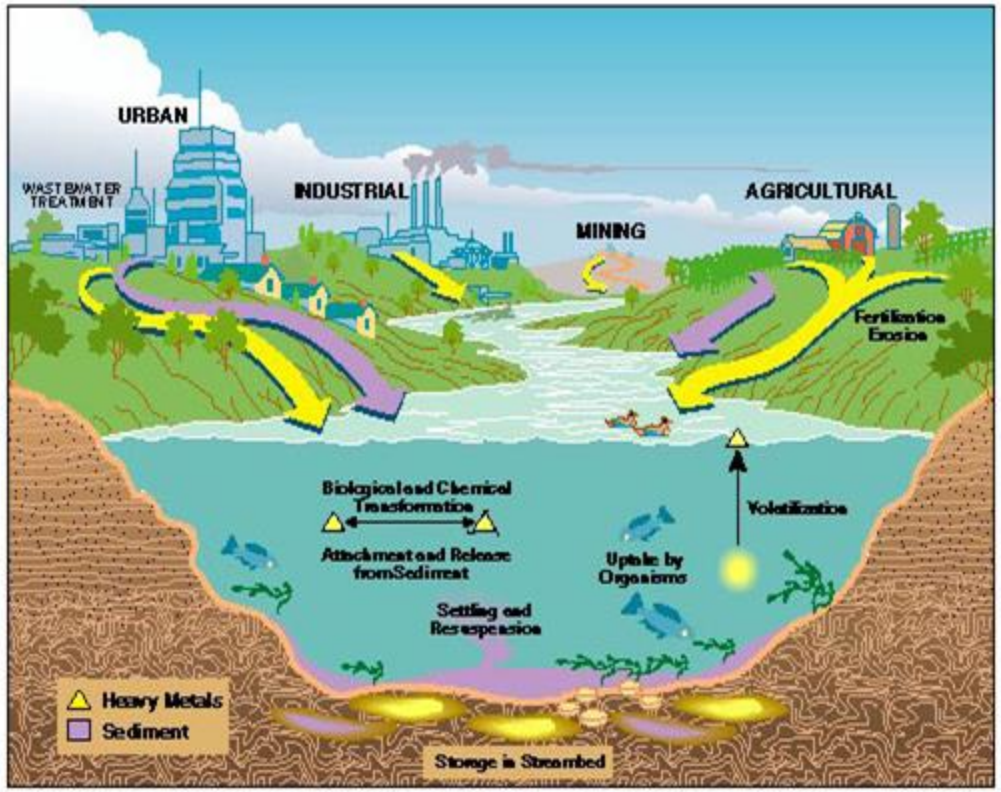


Assumptions

- Metal adsorption energy is independent of surface coverage
- No interaction occurs between adsorb ions
- Maximum adsorption is a saturated monolayer of adsorbates on adsorbents surface
- Rate of backward reaction is negligible compare to forward reaction.

Mohan, D.; Pittman Jr, C. U.; Bricka, M.; Smith, F.; Yancey, B.; Mohammad, J.; Steele, P. H.; Alexandre-Franco, M. F.; Gomez-Serrano, V.; Gong, H. *Journal of Colloid and Interface Science* **2007,** 310, 57-73.

Importance of metal removal



Metals:

Chromium : Liver , kidney damage, internal hemorrhage

Lead: Nervous system, reproductive system, kidney damage

Concentration in H_2O:

Lead: 15 ppb (EPA)
Chromium : 100 ppb (EPA)

Industrial waste:
Lead concentration >15 ppm