Adsorption of BPS by Clay Minerals

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BPS Properties

Table 1. U.S. EPA's EPI Suite- Predicted BPS Properties

Properties	value
Boiling point (*Stein & Brown method*)	422.52°C
Melting point (*Mean or Weighted MP*)	176.41°C
Log Kow	1.65
Water Solubility at 25°C	3518 mg/L
Soil Adsorption coefficient, Log Koc	3.882
pKa	8.2
Biodegradability	Less than BPA

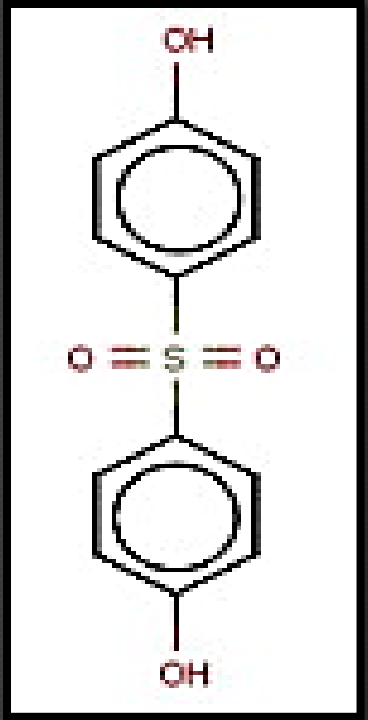

Figure 1. BPS chemical Structure

***Reference**: Royal Society of Chemistry-ChemSpider-BPS http://www.chemspider.com/Chemical-Structure.6374.html*

BPS Applications

- Bisphenol -S (BPS), 4,4'-sulphonyl diphenol is an analog of BPA
- BPS is extensively used as a:
  - monomer in the plastic production,
  - electroplating solvent,
  - dental sealant,
  - chemical additive in plastics,
  - coating and plasticizer in canned foods and baby bottles
- Global BPA production is expected to rise to 8.4 million tons by 2018

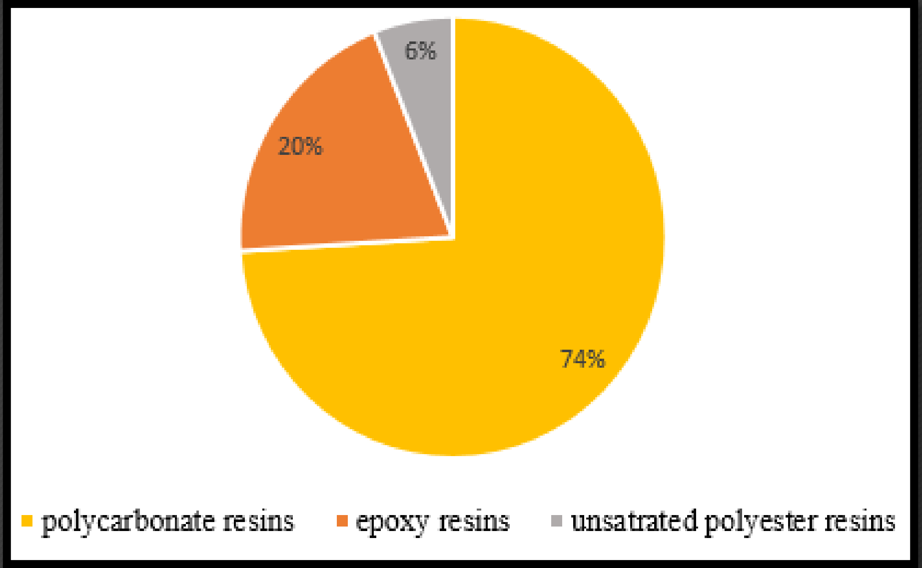

Figure 2. Percent BPA U.S. consumption in 2007 by U.S.EPA

Reference: *EPA BPS action plan – CASRN 80-05-7https://www.epa.gov/sites/production/files/2015-09/documents/bpa_action_plan.pdf*

BPS- Health Impacts

- BPS is a serious endocrine disrupting chemical
- U.S. human urine samples contain BPS average concentration of 0.299 ng/L
- BPS-human health impacts:
    - respiratory issues and mental aggression,
    - kidney and Cardiovascular diseases, and
    - breast cancer.
- BPS effects animal lymphocyte proliferation and is linked to reproductive disorders

Fate and Transport of BPS in the Environment

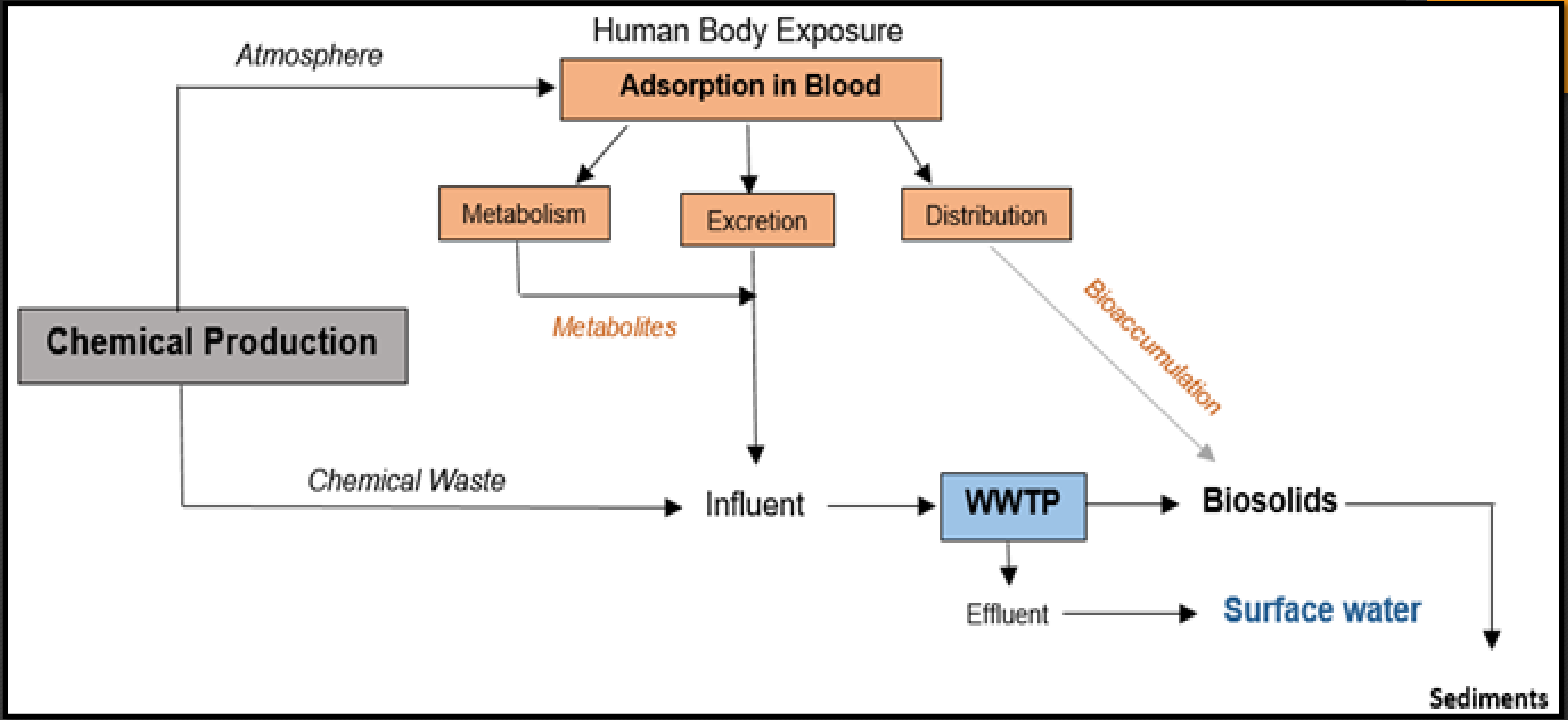

Figure 3. Flow Chart of BPS Fate in the Environment

Environmental Concentrations of BPA in U.S.

Table 2. U.S. Reported Environmental Concentrations of BPA

Location	Mean (ppb)	Range (ppb)
Surface Water	0.012 to 0.14	0.0009 to 12
Ground Water	0.0041 to 1.9	0.006 to 2.55
Drinking Water	0..005 to <0.1	<0.1 to 0.42
Waste Water	<0.1	0.0036 to 50
Soils	6 to 7	4 to 14
Fresh Sediment	0.6 (*Median*)	1.4 to 140
Marine Sediment	3.5 (*Median*)	1.5 to 5

Reference: Klecka GM, Staples CA, Clark KE, van der Hoeven N, Thomas DE, Hentges SG. 2009. Exposure Analysis of Bisphenol A in Surface Water Systems in North America and Europe. Environ Sci Technol 43(16):6145-6150

Bisphenol A-Clay Sorption Studies

- Previously, batch sorption studies with different soil (g) vs volume (mL) of BPA were conducted to study the adsorption phenomenon

- Literature review on sorption of BPA onto sediments concludes:
  - BPA sorption onto sediments is an exothermic reaction
  - It is dominated by the dispersive forces and driven by enthalpy
  - Sorption increased with an increase of ionic concentration
  - In acidic environments, as pH increased, the sorption of BPA is reduced

My Research

- Dearth of published research available on sorption behavior of BPS to sediments
- Hence, adapted available BPA soil sorption studies for the research as follows:
  - Sterilized Clays (Kaolinite, Montmorillonite) as the sorbents
  - Clay mass (g)/BPS volume (mL) ratios of 1:2, 1:4, 1:5, 1:10, 1:12 were evaluated in batch sorption studies- influence of clay type and dose

My Research

- Constant 10 ppm BPS concentration in ultrapure water
- For the ionic strength influence on sorption, the below solutions were simulated:
  - $CaCl_2$ solution with an ionic strength of 0.3M and 0.9M
  - KCl solution having an ionic strength of 0.1M, 0.3M

Materials Used

- BPS by Sigma Aldrich Chemistry (St. Louis, MO)
- Clays: Montmorillonite (Swy-2); Kaolinite (Kga-2)
- $CaCl_2$ and KCl solutions (0.1 M and 0.3 M)
- Ultra pure water for the solution preparations
- 50-mL centrifuge tubes, 2000-µL HPLC vials, 40-mL amber vials

Materials Used

- Rotary shaker for 24 hour sample mixing
- Centrifuge to separate the soil and liquid suspensions
- HPLC by Perkin Elmer, to quantify the BPS sorption using:
  - UV-VIS detector,
  - acetonitrile and water as mobile phase liquids,
  - adsorbent material in the column is silica (2-50µm)

Source Clay Mineral Properties

Table 3. Properties of Kaolinite and Montmorillonite clay

Properties	Montmorillonite (Swy-2)	Kaolinite (Kga-2)
Surface Area	31.8 m2/g	23.5 m2/g
Cation Exchange Capacity (CEC)	76.4 meq/100g	3.3 meq/100g
Interlayer Bonding	Weak, van der Waals	Strong, H-bonding
Shring -swell	High; Expansive clay with interlayer swelling	Low; no interlayer Swelling

Method

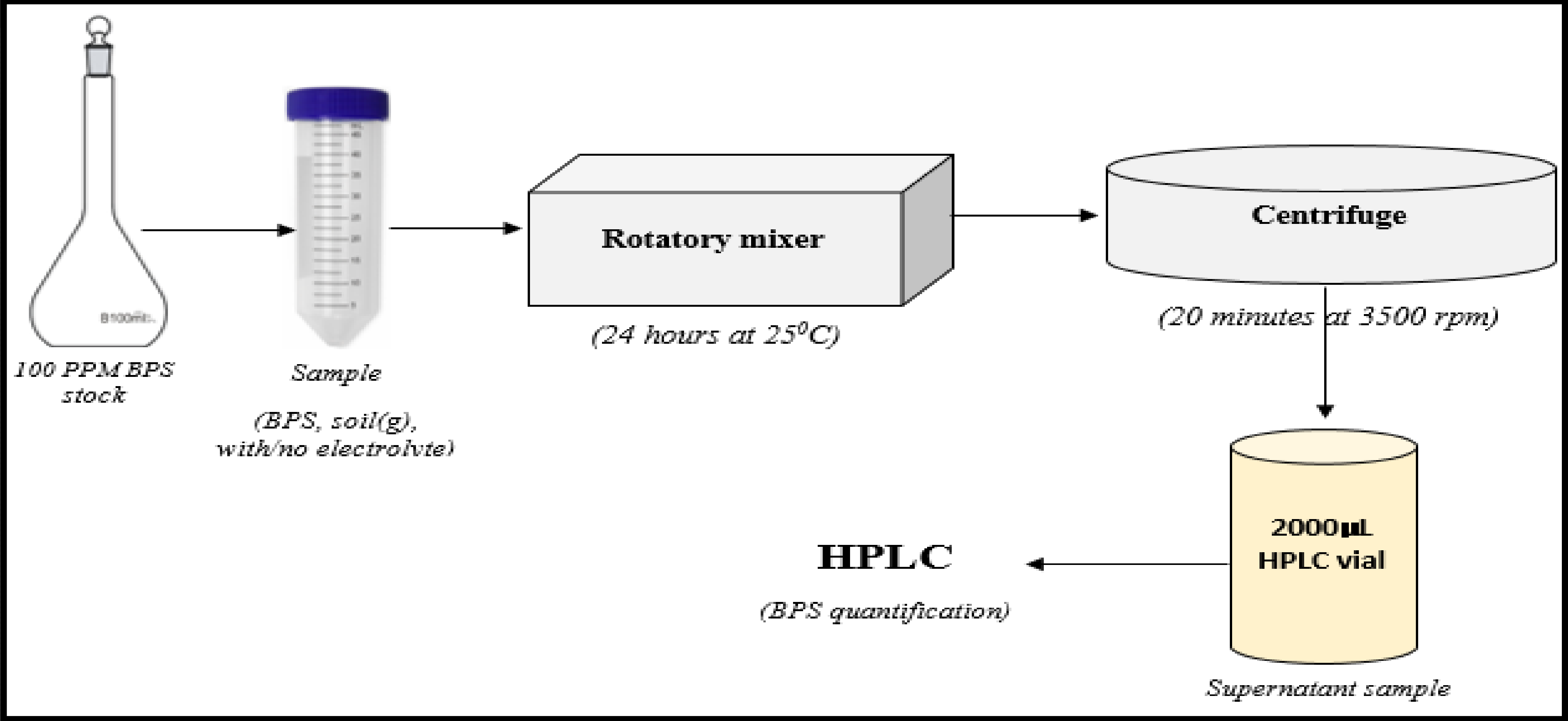

Figure 4. Schematic diagram of the method

Method

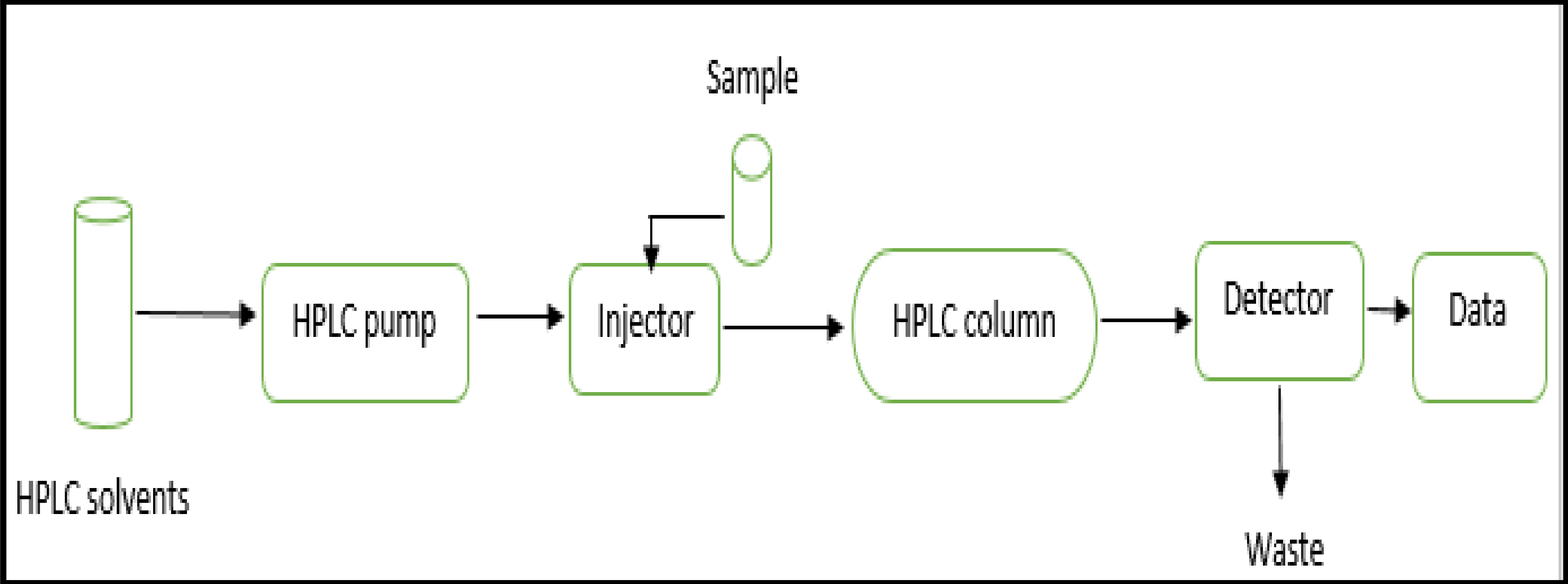

Figure 5. Flow chart of HPLC operation

Results- Kaolinite Clay

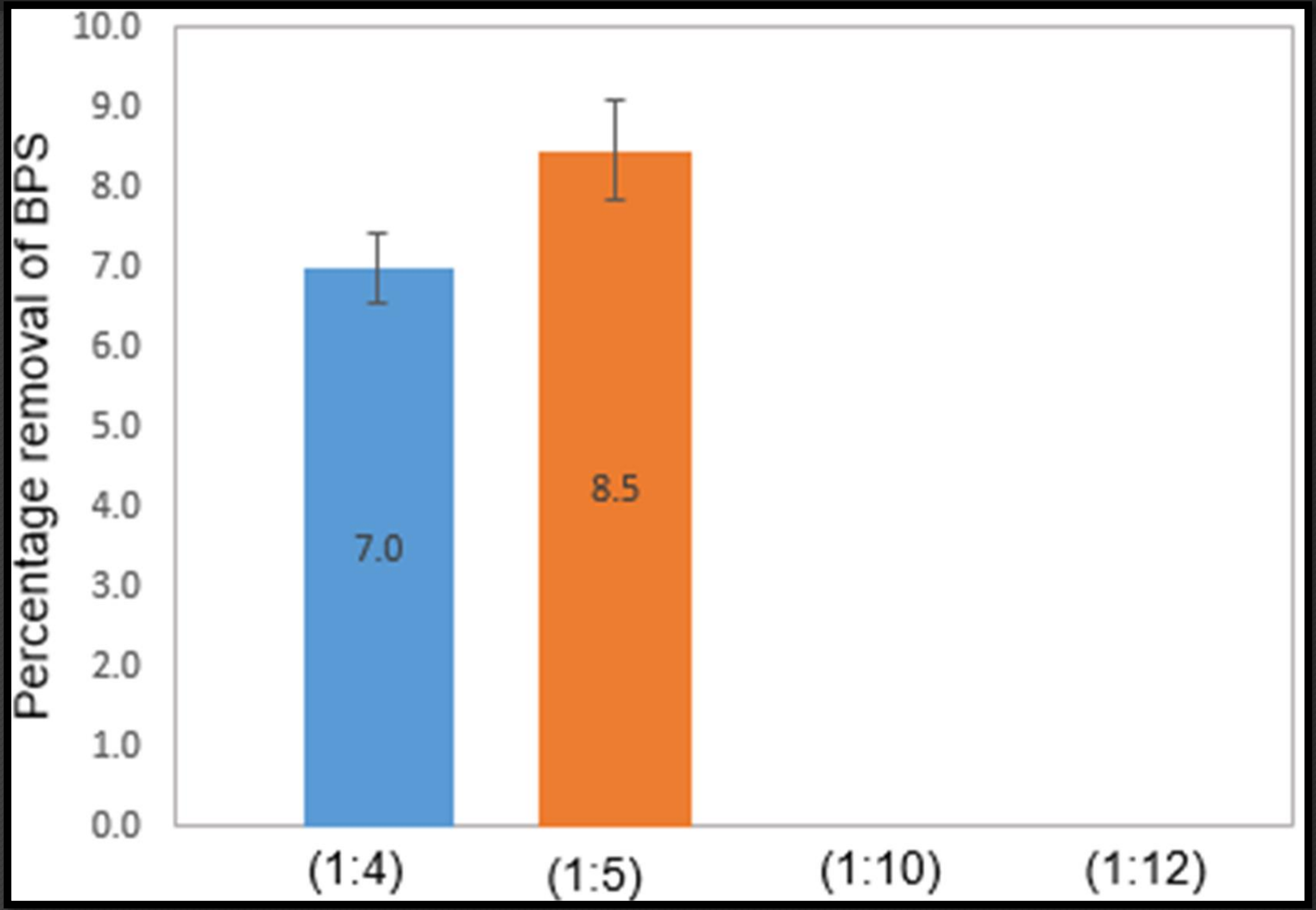

Figure 6. Percent BPS removal by Kaolinite clay using 1:4, 1:5, 1:10, 1:12 soil (g)/BPS (mL) ratios.

- Maximum BPS sorption was 8.5% at the 1:5 ratio
- Ratios of 1:10 and 1:12 showed zero BPS sorption
- Kaolinite's lower effective surface area, strong interlayer hydrogen bonding, and minimal expansion results in limited available BPS sorption sites

Results- Montmorillonite Clay

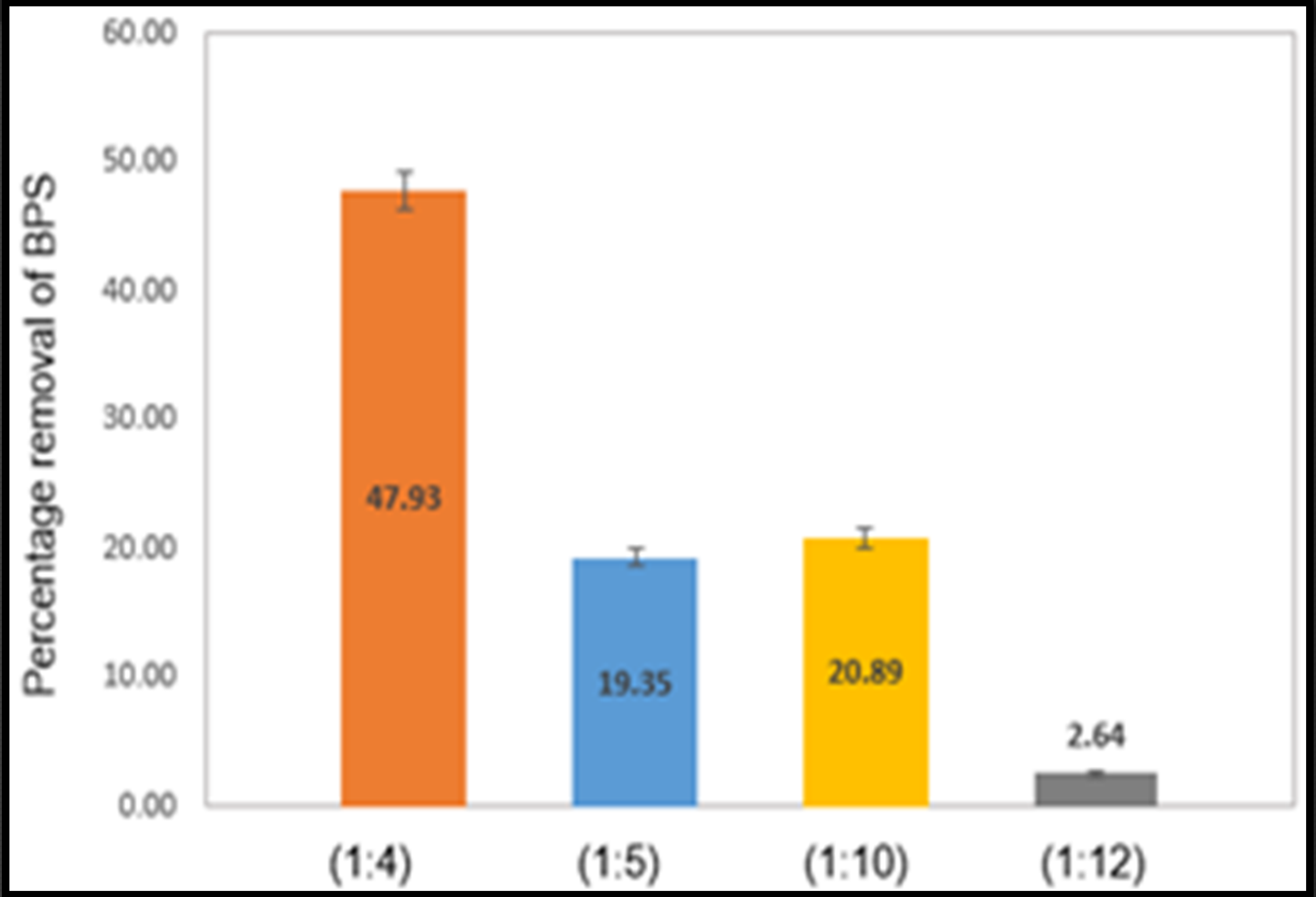

Figure 7. Percent BPS removal by Montmorillonite clay using (1:4, 1:5, 1:10, 1:12) soil (g)/BPS (mL) ratios

- Maximum percentage (48%) of BPS was sorbed at 1:4 ratio
- Least adsorption of BPS (2.6%) at 1:12 ratio
- Higher clay amounts yielded better BPS sorption
- The clay’s high surface area, weak interlayer bonds, and expansion likely result in more sorption

Results- KCl and $CaCl_2$

- For ionic strengths lower than 0.3M and 0.1M for $CaCl_2$ and KCl respectively, the 1:2 ratio remained in suspension even after vigorous centrifugation
- 1:2 and 1:10 ratios were examined in experiments
- No BPS sorption was observed for the tested ratios
- The background electrolyte destabilized montmorillonite clay minerals, causing them to agglomerate, and the limited access to sorption sites likely resulted in no BPS adsorption

Findings

- Ionic strength limits BPS adsorption for both clay minerals, by destabilizing and aggregating the clay minerals and limiting accessibility and availability of sorption sites
- In the absence of background electrolyte (no ionic strength), higher clay minerals masses (1:4 and 1:5 ratios) favored sorption for both clay minerals
- Montmorillonite clay sorbed more BPS than kaolinite, because it is a more reactive clay, with more accessible internal and external surface area due to weaker interlayer van der Waals bonding

Future Work

Future experimental work includes:

- Ionic strength influence studies using $MgCl_2$ to test whether the ion size impacts the sorption
- Variable pH studies for optimum clay:BPS ratios
- Similar adsorption studies using biochar

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Thank You!
Questions?
Comments?
Suggestions?