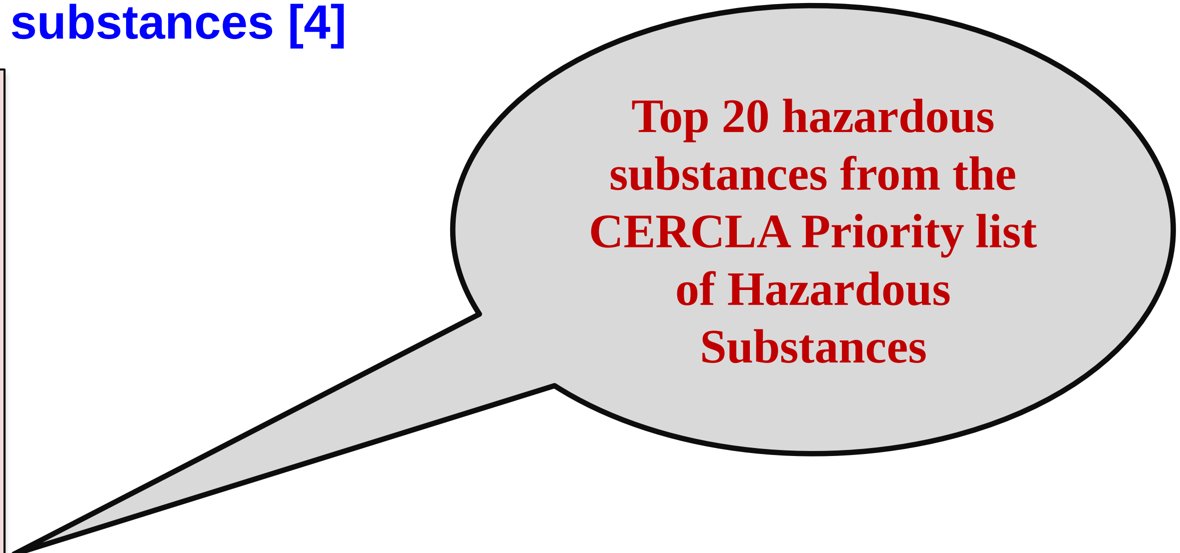
PROBLEM STATEMENT

- Chromium is a highly toxic metal released by anthropogenic activities of mining, metal plating, glass and ceramics, dyes, pigments and tanning are the source for pollution. Mostly chromium exists in the aquatic environment as Cr(III) and Cr(VI).
- Hexavalent form of chromium is more toxic than trivalent.
- Cr(VI) affects human physiology, accumulates in the food chain and strong exposure to Cr(VI) may cause severe health hazards like cancer in the digestive tract and lungs and may cause epigastric pain, vomiting, severe diarrhea, nausea and hemorrhage[1-3]

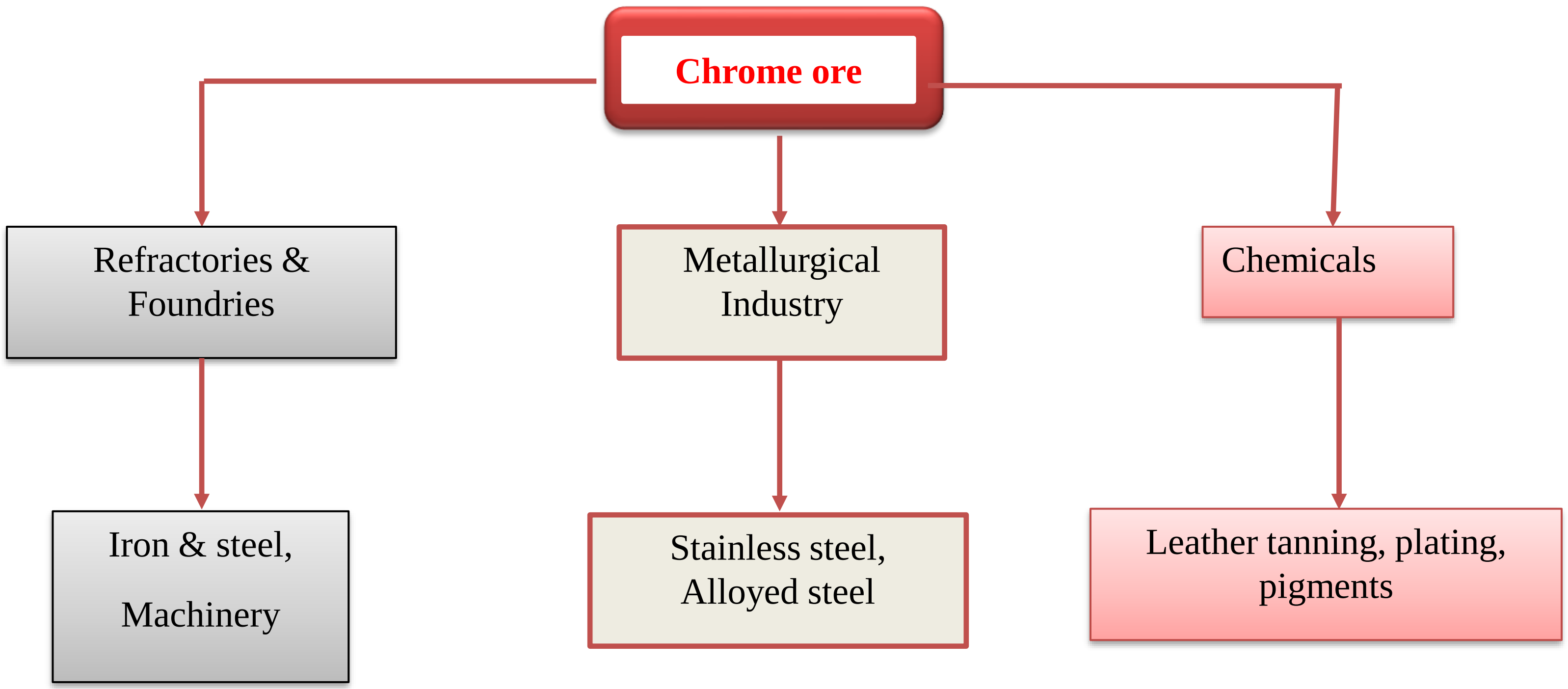
PROBLEM STATEMENT

➢ Chromium is considered as one of the top 20 contaminants listed under the category of hazardous substances [4]

1. Arsenic
2. Lead
3. Mercury
4. Vinyl chloride
5.Polychlorinated biphenyls
6. Benzene
7. Cadmium
8. Benzo(a)pyrene
9. Polycyclic aromatic hydrocarbons
10. Benzo(b)fluoranthene
11. Chloroform
12.Arclor 1260
13. DDT
14. Arclor 1254
15. Dibenzo (a, h) anthracene
16. Ticholoethylene
17. Chromium, hexavalent
18. Dieldrin
19. Phosphorus, white
20. Chlordane



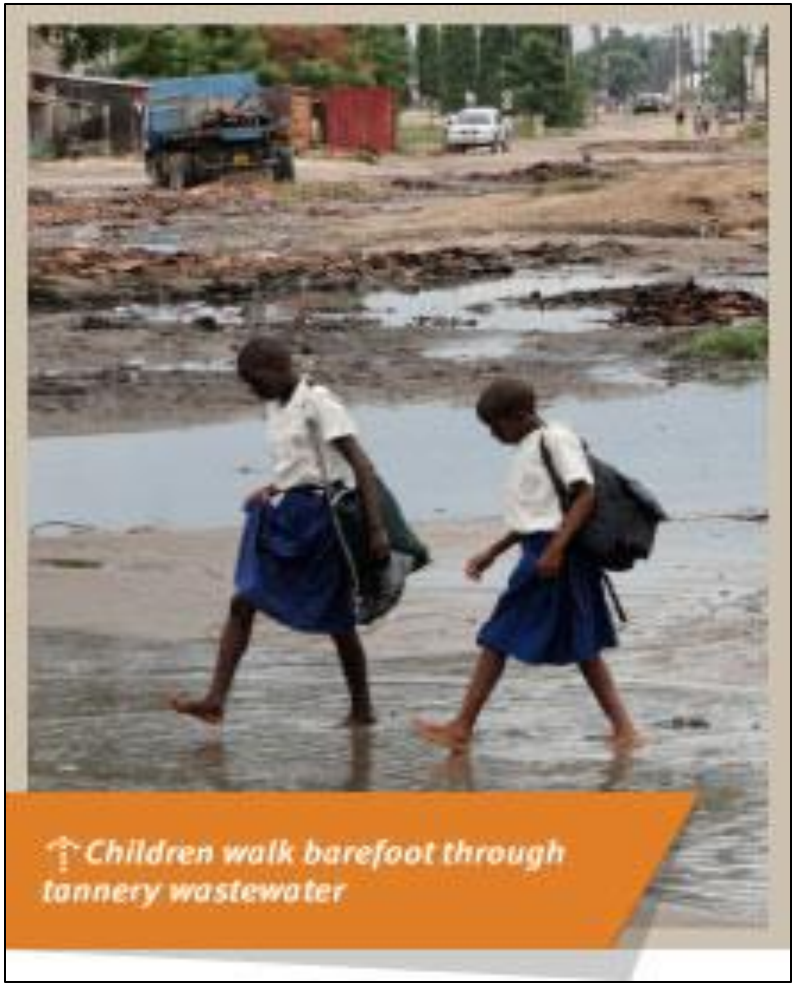
The application of the chrome ore in the different industrial sector[5]

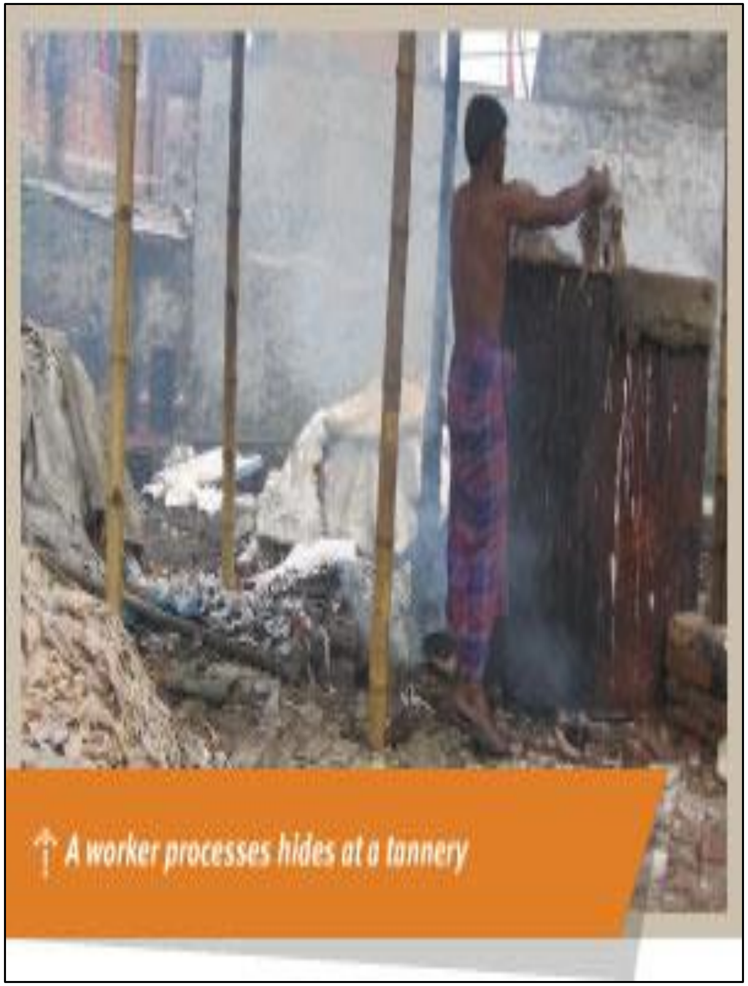


The permissible concentration limit of Cr(VI) for discharge into inland surface waters is 0.1 mgL^{-1} and for potable water is 0.05 mgL^{-1} [6]

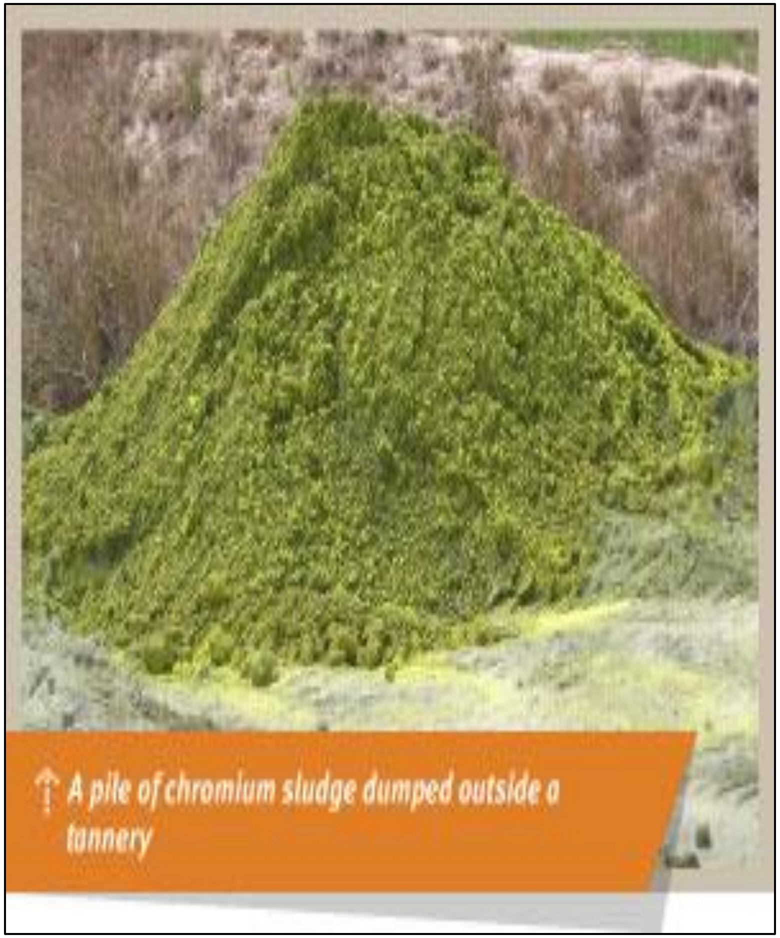
Chromium pollution from tanneries distributed worldwide

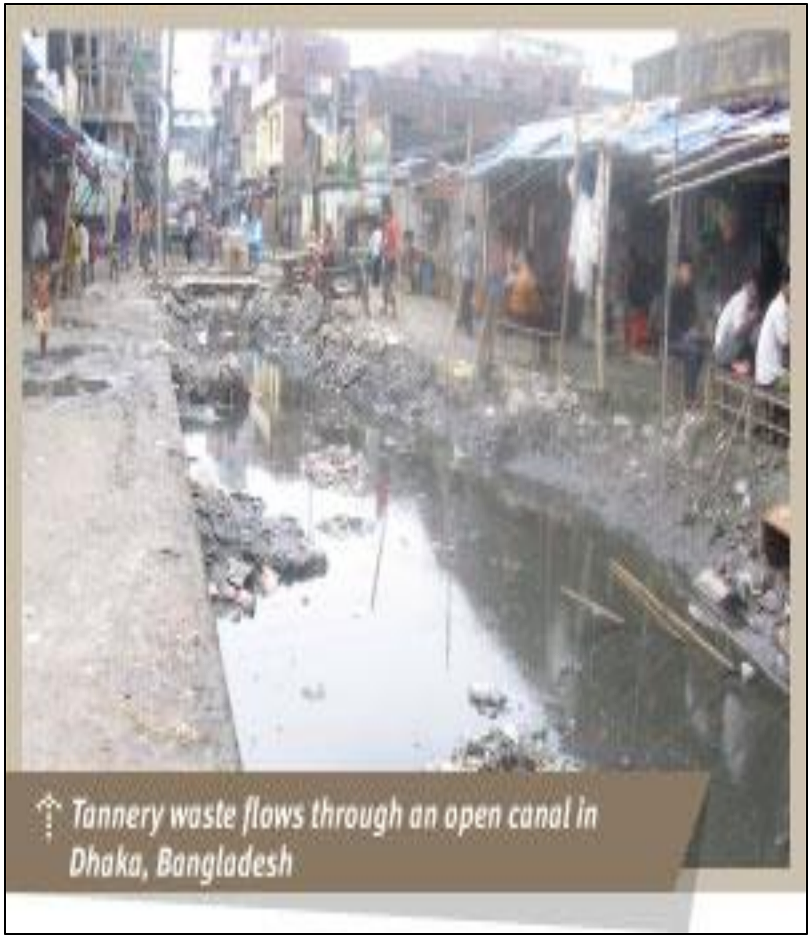
- **According to the information collected in Blacksmith's inventory of sites, South Asia, and in particular India and Pakistan, has the highest number of tanning industries, with South America also at risk of large populations being exposed to chromium contamination [7,8].**
- **The populations are mostly affected in the underdeveloped and in the developing country due to chromium contamination.**
- **In case of Indian population, the north east and south part is mostly affected due to chromium compounds release from the leather tanning industry.**





Hexavalent chromium and health risk [7,8]





Chromium and environmental contamination [7,8]

METHODS TO REMOVE METAL IONS FROM WASTEWATERS[9].

METHOD	ADVANTAGES	DISADVANTAGES
Chemical Precipitation	• Simple •Inexpensive •Most of metals can be removed	•Large amounts of sludge produced • Disposal problems
Ion-exchange	• High regeneration of materials • Metal selective	•High cost •Less number of metal ions removed
Electrochemical methods	• Metal selective • No consumption of chemicals • Pure metals can be achieved	• High capital cost • High running cost • Initial solution pH and Current density
Adsorption Using activated carbon	• Most of metals can be removed • High efficiency (>99%)	• Cost of activated carbon • No regeneration • Performance depends upon adsorbent

Biosorption

- **Biosorption is the potential alternative to conventional technologies for the recovery of heavy metals. Lignocellulosic agricultural wastes materials are abundant source for significant metal biosorption.**

- **The functional groups distributed in agricultural waste biomass viz. acetamido, alcoholic, carbonyl, phenolic, amido, amino, sulphydryl groups etc. have affinity for heavy metal ions in such a way to form metal complexes [10-12].**

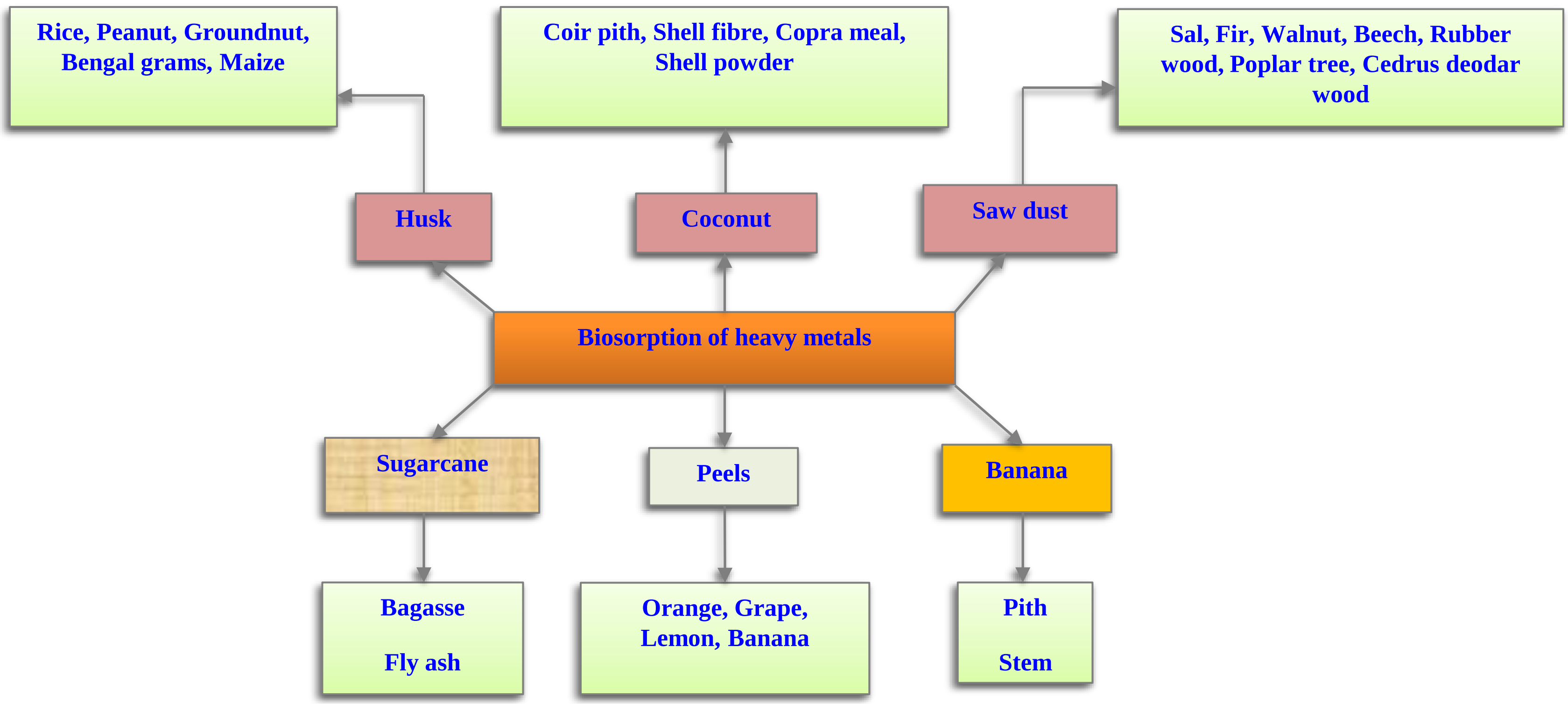
Research in biosorption suggests the following advantages over other techniques [13]

1. **The materials are usually wastes or byproducts and at almost no cost.**
2. **There is no need of costly growth media and aseptic conditions.**
3. **The process is independent of physiological constraints of living cells.**
4. **Reversible process, after pollutant desorption the material can be subjected for the further recycle.**
5. **The formation of chemical or biological sludge is minimized.**

Agricultural production (ton/year) in some countries[14]

Products/ Country	Malaysia	Indonesia	India	Mexico	Nigeria	Philippines
Coconut	459640	21565700	10148000	1004710	236700	15667600
Oil palm	84842000	86000000	–	292499	8500000	516115
Coir	23400	–	507400	–	–	–
Rice paddy	2510000	64398900	133700000	263028	3402590	16266400
Sugar cane	700000	26500000	285029000	49492700	1412070	22932800

Block diagram for the different source of agricultural byproducts for metal biosorption [15]



The amount and the percentage removal of Cr(VI) by SMFS are calculated by using the following Equations (1) and (2) respectively.

$$q = \frac{(C_0 - C_e)V}{m} \qquad (1)$$

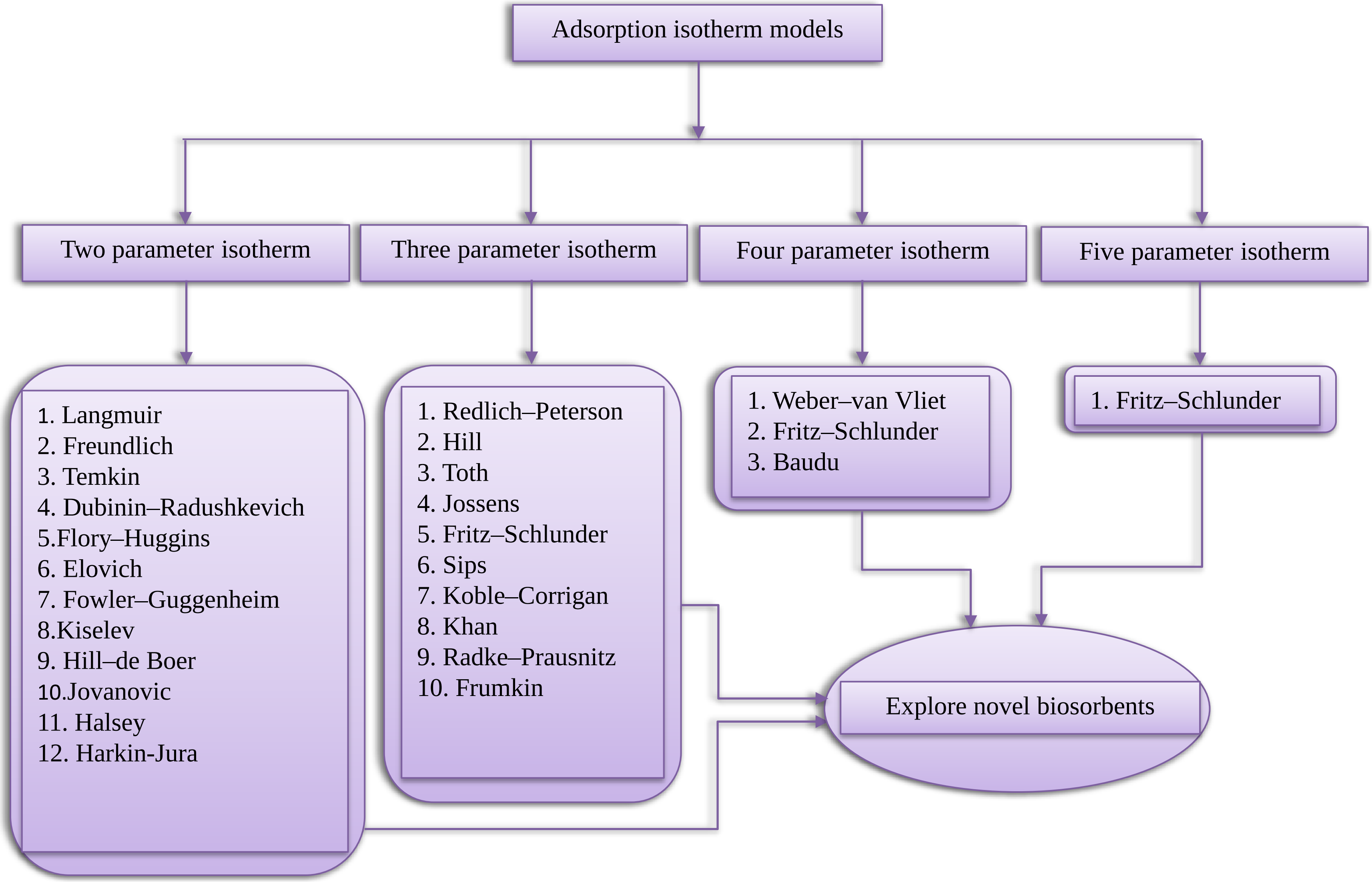
$$\%\ \text{Removal of Cr(VI)} = \left[\frac{C_0 - C_f}{C_0}\right] \times 100 \qquad (2)$$

where q is the biosorption capacity (mg g^{-1}). C_o, C_f and C_e are the initial, final and equilibrium concentrations (mg L^{-1}) of Cr(VI) in the samples respectively. m and V are weight of SMFS (mg) and the volume of solution (L).

BIOSORPTION ISOTHERMS

- Equilibrium studies are described by a biosorption isotherm, characterized by certain constants which state the surface properties and affinity of the biosorbent.
- Large numbers of expressions that describe the sorption isotherms are available. In the present investigation the equilibrium data were analyzed using the two parameters isotherm models like Langmuir, Freundlich, and Elovich were used to fit the experimental data.
- The linear regression was used to determine the most fitted model among all the three above written isotherms.

The significance of adsorption isotherm models in exploring novel biosorbents



The Langmuir Isotherm model

According to the Langmuir model, adsorption process takes place uniformly on the active sites of the adsorbent and further adsorption cannot take place at the adsorbate occupied site [17]. The Langmuir equation is given as follows:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \qquad (3)$$

Where Q_0 is the saturated monolayer adsorption capacity (mg g^{-1}) and b is the adsorption equilibrium constant (L mg^{-1}). q_e is the amount of Cr(VI) adsorbed at the equilibrium (mg g^{-1}).

The essential features of the Langmuir isotherm expressed in terms of equilibrium parameter R_L, a dimensionless constant, referred to as equilibrium parameter also called as separation factor.

$$R_L = 1/\ (1 + bC_o) \tag{4}$$

R_L **value indicates the adsorption nature of unfavourable if** ***R_L*****>1, linear if** ***R_L*** **=1, favourable if 0<** ***R_L*****<1 and irreversible if R_L=0.**

The Freundlich isotherm model

The Freundlich isotherm [18] is an empirical model that is based on adsorption on heterogonous surface and is given by the following equation:

$$\log\ q_e = \log\ k + \frac{1}{n}\ \log\ C_e \tag{5}$$

where ***q_e*** **is the adsorption capacity (mg g^{-1}),** ***C_e*** **is the equilibrium concentration of the Cr(VI) solution (mg L^{-1}),** ***k*** **(mg$^{1-1/n}$ L$^{1/n}$ g^{-1})and** ***n*** **represents the adsorption capacity and adsorption intensity, respectively.**

The Elovich isotherm model

The equation defining the Elovich model is based on the assumption of adsorption sites increase exponentially with adsorption, which implies a multilayer adsorption [19]. The model is given as follows

$$\ln \frac{q_e}{C_e} = \ln K_E q_m - \frac{q_e}{q_m} \quad (6)$$

Where K_E represents the Elovich equilibrium constant (L mg^{-1}), q_m is the Elovich maximum adsorption capacity (mg g^{-1})

Kinetic modeling

Several kinetic models were used to explain the biosorption mechanisms. A simple pseudo-first order equation is given by Lagergren equation [20].

$$\log(q_e - q) = \log q_e - \frac{k_1}{2.303} t \qquad (7)$$

Where q and q_e are the amounts of ion adsorbed at time t and at equilibrium (mg g^{-1}), respectively, and k_1 is the rate constant of pseudo-first-order adsorption process (min^{-1}).

Pseudo - second order rate kinetics [21] can be expressed by the following equation:

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (8)$$

Where k_2 (g mg^{-1} min^{-1}) is the second order rate constant.