AI 3010 WASTE AND BY PRODUCT UTILIZATION

UNIT II NOTES

Insecticide,pesticides and fungicides residues

The levels of pesticides in water have increased due to their excessive use in the modern agricultural domain. Choosing a suitable water treatment method for pesticide removal depends on the type of pesticide and the efficacy of the treatment process.

Pesticides, for instance, have been proven in many studies as toxic substances to humans and the environment). For example, chronic exposure to herbicides like atrazine (1-chloro-3-ethylamino-5-isopropylamino-2,4,6- triazine) which acts as a selective herbicide that inhibits photosynthesis in susceptible plants, causes cardiovascular problems, retinal degenerations, some muscles degeneration and cancer in human. Among herbicides, oxyfluorfen inhibits protoporphyrinogen oxidase, leading to irreversible cell membrane damage. Human exposure to oxyfluorfen can cause problems in the liver and the blood count (anemia) .Besides, among the environmentally concerning pesticides, azoxystrobin, a broad-spectrum fungicide that inhibits fungal spore germination, is known to be highly toxic to freshwater fish and estuarine

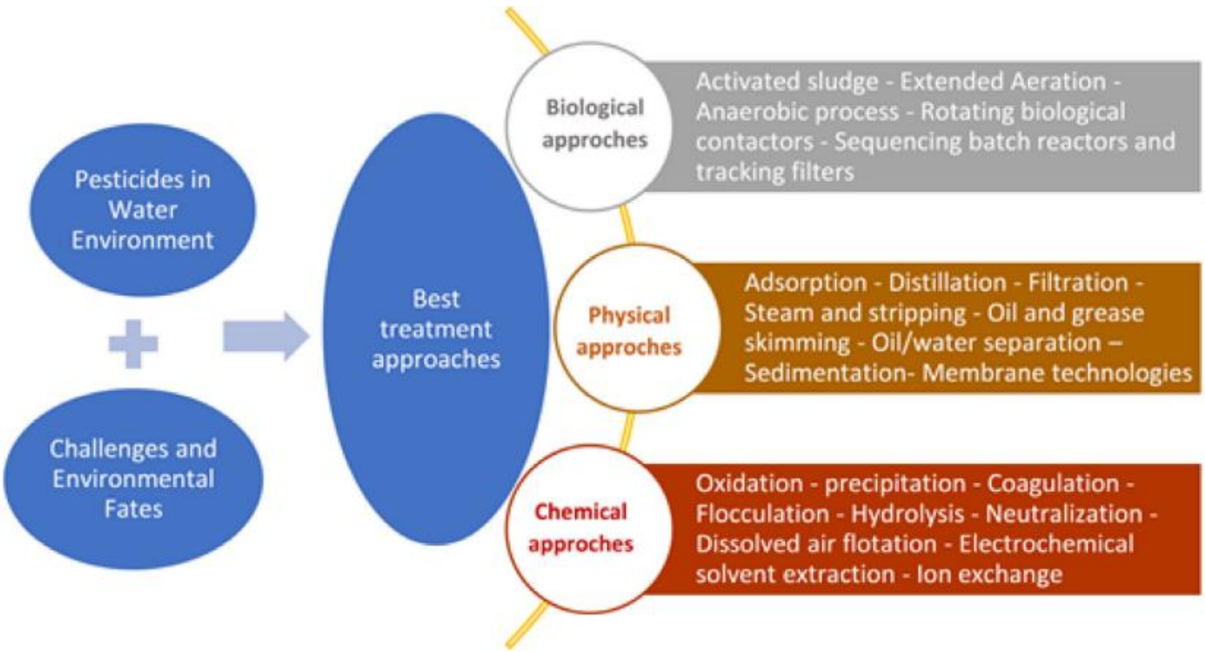


Figure:Pesticide removal method

Among the various challenges that face pesticide treatment from water is the influent composition, the variability of the pesticides' physical structures, and the pH of pesticides-contaminated water, which ranges from very acidic (0.5) to very alkaline (14). Moreover, the chemical oxygen demand

(COD) of pesticides-production wastewater ranges according to the literature between 150 and 33750 mg/L while the biological oxygen demand (BOD) ranges between 30 and 11590 mg/L. The amounts of pesticides in various sources of water vary between 0.1 and 107 mg/L.

The current treatment techniques involve a combination of physical, chemical, and biological methods have been utilized to instigate and elucidate the problem of the removal of pesticides from water. Each treatment technique has its own advantages and limitations not only in terms of capital and operational costs, but also in terms of efficiency, operability, reliability, environmental impact, pre-treatment requirements, and the production of sludge and toxic byproducts. For instance, advanced oxidation process (AOPs) produces less sludge, rapid reaction rates, less retention time, but it has a high capital, operational, and maintenance cost). Fenton’s reaction can degrade soluble and insoluble dyes in the industrial effluents, does not form any bromated byproducts, has a wide application range, and simple operation. It has some drawbacks that it requires low pH (2.5–4) which leads to increased operating costs. However, it forms anions in high concentrations in the treated wastewater, as well as forming a large amount of ferrous iron sludge .Another chemical treatment technique is photochemical degradation which has no potential for the formation of bromated byproducts. However, it needs a separation step when adding the catalyst as a slurry. Chlorination is a cheap and easy to implement chemical treatment technique, but the pre-chlorination can cause the oxidation of micro-contaminants into more toxic and less removable by-product.

Water treatment techniques for pesticides removal

Chemical treatment techniques

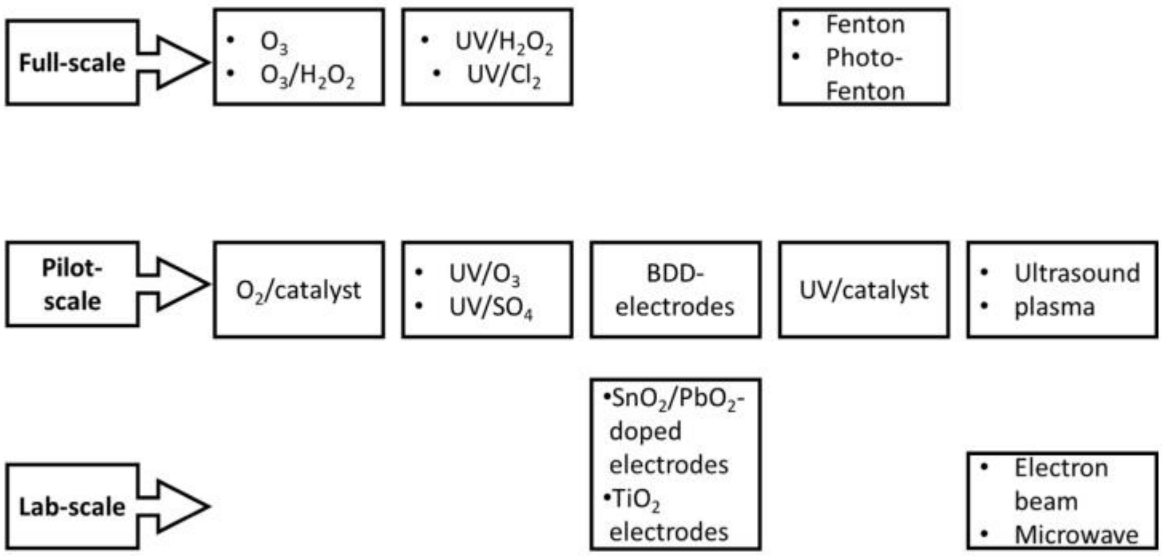
Chemical wastewater treatment consists of a variety of chemical reactions that help in hydrolyzing contaminants into safer chemicals. The main chemical methods are coagulation and advanced oxidation process (AOPs), including ozonation and Fenton treatment.

Iron-enhanced sand filters (IESFs)

Upon filtration of the stormwater samples with IESFs, which consist of conventional sand filters with around 5% iron filings, the removal rate of the contaminants was between 26% and 100%. However, when it comes to pesticides, some of the moderately hydrophobic types had a removal rate of only 10 to 30%. Moreover, the study showed negative removal of some contaminants, including some pesticides. This indicates the back-transformation of some derivatives into their toxic formula in the IESFs. Another study on stormwater has shown high levels of different kinds of pesticides in water, especially atrazine and 2,4-dichlorophenoxyacetic acid (2,4- D) that were detected in all tested samples. IESFs did not show a significant decrease in the levels of many contaminants, including the two tested pesticides. The large-scale study implies that IESFs is not a promising method when it comes to pesticides.

Advanced oxidation processes (AOPs)

Advanced oxidation processes consist (AOPs) of the usage of oxidizing agents to oxidize contaminants Among the strongest oxidizing radicals used is the hydroxyl radical (•OH). Sulfate radical (SO4•-) has also been widely studied for the removal of organic contaminants from water). AOPs are environmentally friendly chemical techniques that can degrade organic contaminants into harmless products that neither transfer contaminants from one phase to another and nor produce massive amounts of sludge. Furthermore, this technique has various advantages, including rapid reaction rates leading to less retention time compared to other conventional treatment techniques, and it does not require a large area for processing the needed flow rate for the system. However, various drawbacks can also be highlighted, including its high operating, and maintenance costs. It also has a complex chemistry tailored to specific contaminants which requires skilled personnel to design the system Figure shows the various AOPs methods applied in water treatment systems. The AOPs are divided, in general, into ozone-based treatment, ultraviolet (UV)-based treatment, electrochemical advanced oxidation processes (eAOP), catalytic advanced oxidation processes (cAOP), and photo advanced oxidation processes.



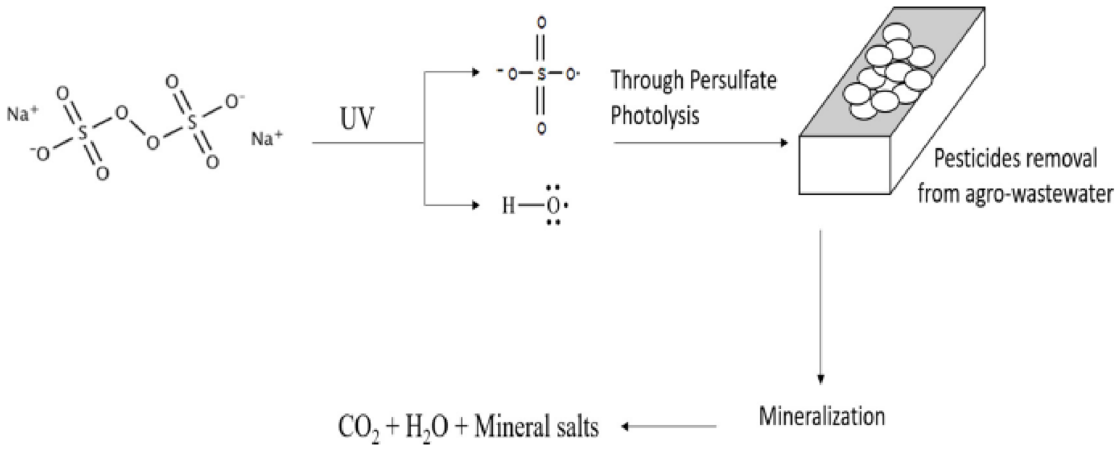
Various advanced oxidation processes (AOPs) methods applied for water treatment

Ozonation.

Ozonation is the process of using ozone for contaminant removal either by direct effects of the ozone molecules on the contaminants or indirectly by the oxidation effect of the free radicals resulting from the decomposition of ozone in water. Produced free radicals are highly reactive and less selective than chemical oxidants. Ozone has a very short lifetime, so it should be generated on-site, which increases the cost of the treatment. Among the studies conducted on ozonation, .It has been tested the removal rate of 23 pesticides using this method. The results showed efficient removal for six pesticides, namely dimethoate, chlortoluron, diuron, isoproturon, metoxuron, and vinclozolin. However, when ozonation was accompanied by H_2O_2 oxidation, the results showed a good removal rate for all the tested 8 I.A. The removal of 40 different pesticides using ozonation was studied by Ormad et al. (2008). The results showed 70% removal of isoproturon, 75% of diuron, and parathion methyl while only 50% of the atrazine level were removed. However, when ozonation treatment was combined with activated carbon and 20 mg Al/L, atrazine removal rate has reached 90%, while 100% of the remaining three pesticides were removed.

Free radicals.

sodium persulfate ($Na_2S_2O_8$) is efficient as oxidizing species to remove 17 different pesticides (pymetrozine, flonicamid, imidacloprid, acetamiprid, cymoxanil, thiacloprid, spinosad, chlorantraniliprole, triadimenol, tebuconazole, fluopyram, difenoconazole, cyflufenamid, hexythiazox, spiromesifen, folpet and acrinathrin) of initial concentration in water between 0.02 and 1.17 mg/L. Persulfate should be activated to form sulfate radicals, knowing that sulfate radicals have a longer lifetime than •OH which allows them to stay in contact with the organic contaminants for a longer period. The ideal activation of persulfate is by UV light (245 nm) However, due to feasibility and cost reduction reasons, sunlight was used instead. As shown in persulfate photolysis was used to produce ($SO_4^{\bullet-}$) free radicals that have the ability to oxidize pesticides into less harmful substances, which will ultimately lead to the mineralization of the parent pesticide into CO_2 and water. The results showed that the initial dissolved organic carbon (DOC) was reduced by 87%. Four of the seventeen tested pesticides showed a level above their limit of detection in water. Therefore, it is believed that oxidation by sulfate radicals would be a promising method that deserves further investigation.



Schematic illustration of the removal pathway of pesticides by sodium persulfate, modified from

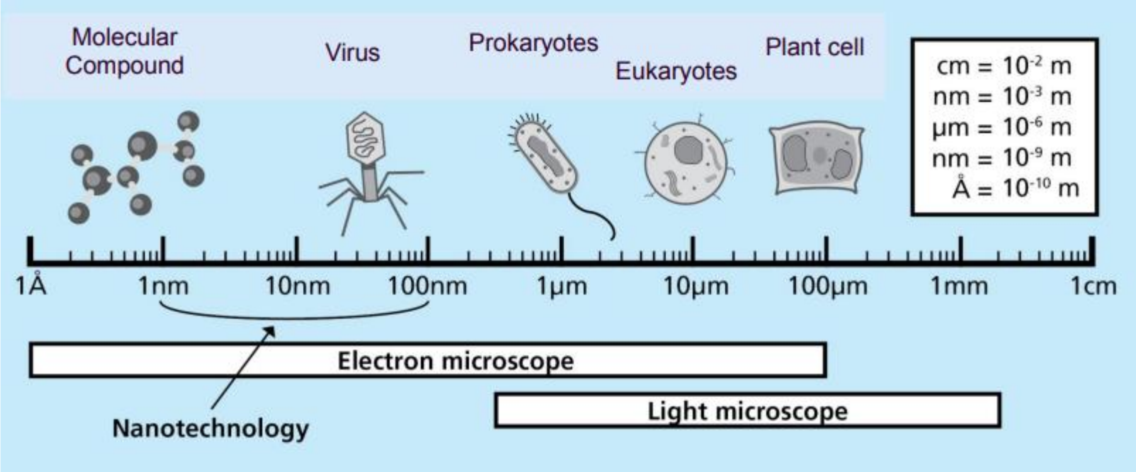
Chlorination

Treatment of water containing alachlor by chlorination as a secondary treatment following oxidation helped in further oxidizing the pesticide (100 µg/L) by the remaining persulfate from the primary treatment and the free chlorine. Alachlor is an herbicide that belongs to the chloroacetanilide family and that inhibits weed growth by elongase inhibition. It is used to control grass and broadleaf weeds in crops. Although the hybrid technique discussed in the study showed a reduction in the disinfection byproducts (DBPs), yet further investigations were needed to reduce DBPs to an acceptable level.

Microbiology of water

The goal of biological wastewater treatment is to produce an environment in which microorganisms consume the maximum amount of organic substrate and produce clear effluent water. To do this microorganisms must convert soluble organic pollutants (BOD) into insoluble biomass (microorganisms) which can be separated.

Size of Microorganism – Typically 0.01 µm to 1 mm



Why is wastewater microscopy important?

Critical for monitoring and troubleshooting Make observations and detect changes P/M & filament ID to troubleshoot settling and plant performance issues.

Filamentous Bacteria String or threadlike bacteria Chains of cells which can extend from the floc, grow within the floc, or even free in the bulk water. Prevent effective settling by interfering with floc formation (bulking). Can be helpful in small quantities, acting as a backbone for floc to form.