CHAPTER 1

INTRODUCTION

Sustainability starts with you"… Anonymous

Phosphorus is a vital nutrient that is required for healthy crop development and overall plant growth [1,2]. It plays a key role in numerous cellular functions within living organisms. Plants rely on phosphorus for the synthesis of nucleotides, which form the structural components of DNA and RNA, as well as for the production of adenosine triphosphate (ATP), the primary molecule responsible for storing and transferring energy in cells. In addition, phosphorus is also essential in animal and human nutrition [3]. It supports cellular growth and maintenance, aids in energy metabolism via ATP and nucleotides, and contributes to the structural integrity of bones and teeth in form of calcium phosphate [4]. For adults aged 19 and over, the daily recommended intake of phosphorus is around 700 mg. The kidneys help regulate phosphorus levels in the body, excreting excess through urine and faeces [5,6].

In fertilisers, phosphorus serves as a nutrient-rich agricultural input that provides one of the three key macronutrients (nitrogen, potassium and phosphorous) important for healthy crop development in modern farming practices [7]. Globally, agriculture accounts for the majority of phosphorus consumption, using approximately 85% of the total demand [8]. The remaining portion is utilized in the production of animal feed supplements, food and beverages, and detergents. According to International Fertilizer Association, phosphate production capacity is projected to increase to 55.3 million tonnes of P_2O_5 by 2025, representing a 2 % increase compared to 2023. This growth will primarily be fuelled by new capacity developments in North Africa, along with the launch of several small-scale facilities in Brazil, India, and China, collectively contributing approximately 0.9 million tonnes between 2023 and 2025 [9]. The Food and Agricultural Organization of the United Nations reported that phosphate supply is strained, with expected increase in potential price. On the supply side, China may boost MAP/DAP exports due to a reduced customs and export permit period while on the demand side, India is increasing support for DAP importers with an additional USD 41/tonne subsidy, supplementing its USD 5.9 billion nutrient-based subsidy for the kharif season [10].

Phosphorus is a non-renewable resource derived from igneous rocks and marine sedimentary deposits, primarily extracted through mining for industrial use [11]. The availability of phosphate rock reserves is geographically limited, leaving many regions, such as Europe heavily reliant on imports. The largest sedimentary phosphate deposits are located in Northern Africa, China, and the United States. Notably, Morocco holds around 70% of the world's phosphate rock reserves, while China possesses approximately 4.5% [12]. This uneven global distribution poses significant challenges for ensuring a stable supply of phosphate rocks, making the supply chain vulnerable to geopolitical tensions and economic instability, along with the gradual depletion of global reserves. Figure 1.1 shows the global active phosphate reserves country-wise (billion tonnes).

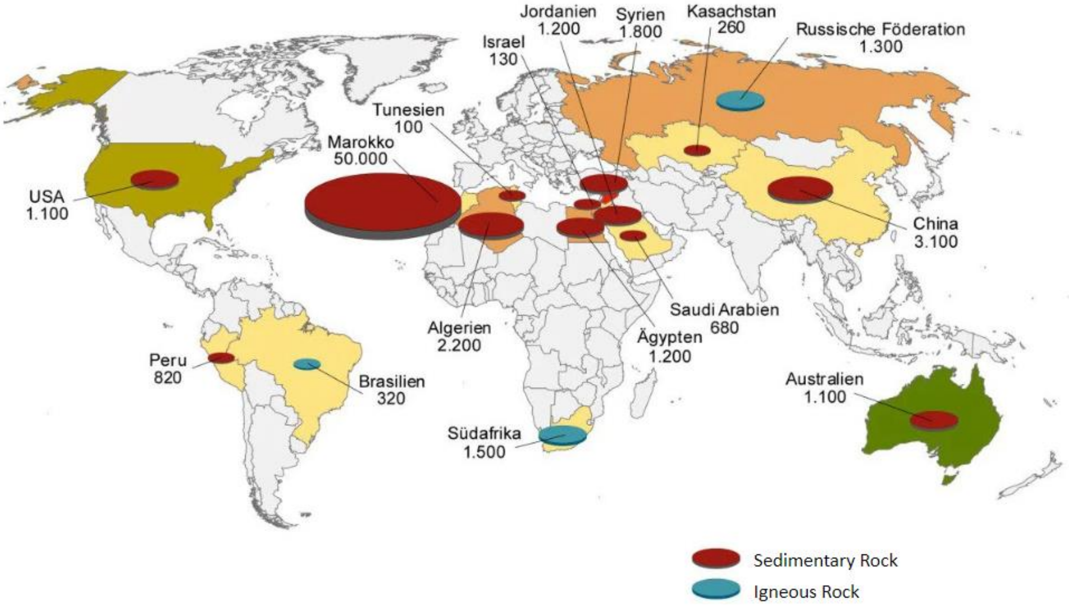

Figure 1.1 Global active phosphate reserves country-wise in billion tonnes.

In context to Indian scenario, India possesses moderate phosphate rock resources, with total reserves estimated at around 310 - 312 million tonnes [13]. Out of these, the reserves constitute only 30.87 million tonnes while 280.37 million tonnes are under Remaining Resources category. These deposits are primarily located in Rajasthan, Jharkhand, Madhya Pradesh, Uttar Pradesh, and Uttarakhand, with Jharkhand and Rajasthan being the leading producers, contributing nearly more than half of the country’s production. Despite these domestic resources, India’s annual phosphate rock production is only about 1.5 million tonnes, falling significantly short of the national demand of around 10 million tonnes. As a result, the country remains heavily dependent on imports, sourcing 85 – 90% of its phosphate rock requirements from nations such as Morocco, Jordan, and Egypt [14]. Table 1.1 shows the total reserves/resources of rock phosphate in India as per NMI data, according to UNFC system as of April 1, 2020. To address this dependency, the Indian government has launched an action plan under the “Aatmanirbhar Bharat” initiative, aiming to enhance self-sufficiency by accelerating the development of existing deposits and encouraging recovery and recycling strategies to secure raw material supplies [15]. In alignment with the national objective, this thesis explores an innovative method for phosphate recovery from wastewater, utilizing bio-based materials as a sustainable solution.

Table 1.1 Total reserves/resources of rock phosphate in India in million tonnes.

STATES	RESERVES TOTAL (A)	REMAINING RESOURCES TOTAL (B)	TOTAL RESOURCES (A+B)
Gujarat	0	314820	314820
Jharkhand	0	107370000	107370000
Madhya Pradesh	9031093	49425938	58457031
Meghalaya	0	1311035	1311035
Rajasthan	21845000	72003769	93848769
Uttar Pradesh	0	25773444	25773444
Uttarakhand	0	24178386	24178386

1.1 Properties of Phosphorous

Phosphorus constitutes 0.1 percent of the Earth's crust. However, it does not occur in its elemental form in nature due to its high reactivity with air and oxygen-containing compounds and is mostly found in the oxidized state in variety of minerals. Phosphorus-bearing rocks typically contain phosphate anions (PO_4^{3-}) that form tetrahedral structures bonded with various cations. The most prevalent phosphate minerals belong to the apatite group, with the general formula $Ca_5(PO_4)_3(OH, F, Cl)$. These include hydroxyapatite ($Ca_5(PO_4)_3OH$), fluorapatite ($Ca_5(PO_4)_3F$), and chlorapatite ($Ca_5(PO_4)_3Cl$), which are composed of calcium and phosphate ions combined with hydroxide, fluoride, or chloride ions [16,17].

Phosphorus found in soils exists in both dissolved and solid forms and can be classified based on its solubility and chemical bonding. Dissolved P mainly includes orthophosphate ions ($H_2PO_4^-$ and HPO_4^{2-}), inorganic polyphosphates, and organic P compounds, with plants primarily absorbing P as HPO_4^{2-} [16,18]. Solid P occurs as inorganic forms, typically bound to aluminium, iron, or calcium, and organic forms associated with decomposed plant material, soil organisms, and organic matter. Organic P is largely composed of phosphate esters (mono, di-, and triesters), although around 50% remains unidentified. Based on bonding, P compounds are categorized into bio- (P–O), carbo- (P–C), aza- (P–N), and metallo-P (P–metal) types, with P–O linkages being the most prevalent[19].

Phosphorus is predominantly found in form of phosphates (PO_4^{3-}), which are categorized into three main types: orthophosphates, condensed phosphates, and organic phosphates [20]. Orthophosphates, also known as reactive phosphates, are the primary form used in agricultural and residential fertilizers. They are commonly present in natural waters and represent the most bioavailable form of phosphorus for algae and plant uptake, often entering aquatic systems through surface runoff. Condensed phosphates, including pyrophosphates, metaphosphates, and polyphosphates, are inorganic compounds containing metal ions such as sodium, potassium, or calcium. Due to their widespread use in the food and beverage industry, both domestic and industrial wastewater serve as significant sources of these phosphate species. Organic phosphates, on the other hand, are produced through biological processes, such as the formation of ATP, a molecule essential for energy transfer in living organisms. These compounds typically enter sewage systems through human waste and food residues and can also originate from orthophosphates during biological treatment or natural processes in receiving waters.

Orthophosphate is the simplest and most fundamental form of phosphate, consisting of a single PO_4^{3-} unit. In solid orthophosphates, all four oxygen atoms typically coordinate with cations, forming stable and strongly bonded extended structures. Derived from phosphoric acid, orthophosphate undergoes hydrolysis in water, resulting in alkaline solution and acquiring a negative charge. During biological oxidation processes in wastewater treatment plants, both organically bound phosphates and condensed phosphates are converted into orthophosphates, making it the most prevalent form of phosphorus in wastewater streams. Orthophosphate can exist in different ionic forms; H_3PO_4, $H_2PO_4^-$ and HPO_4^{2-} or PO_4^{3-}, depending on the pH of the solution and its corresponding dissociation constants. The equations are as follows:

$$H_3PO_{4(aq)} + H_2O \leftrightharpoons H_2PO_4^-{}_{(aq)} + H_3O^+{}_{(aq)} \qquad pK_1 = 2.12 \qquad (1.1)$$

$$H_2PO_4^-{}_{(aq)} + H_2O \leftrightharpoons HPO4_2^-{}_{(aq)} + H_3O^+{}_{(aq)} \qquad pK_2 = 7.2 \qquad (1.2)$$

$$HPO_4^{2-}{}_{(aq)} + H_2O \leftrightharpoons PO_4^{3-}{}_{(aq)} + H_3O^+{}_{(aq)} \qquad pK_3 = 12.36 \qquad (1.3)$$

Figure 1.2 illustrates the dominant phosphate species across varying pH levels. In highly acidic environments, H_3PO_4 is the predominant form, while under strongly alkaline conditions, PO_4^{3-} dominates. For pH values below 7, $H_2PO_4^-$ is more prevalent than HPO_4^{2-}, whereas HPO_4^{2-} becomes the dominant species between pH 7 and 12.

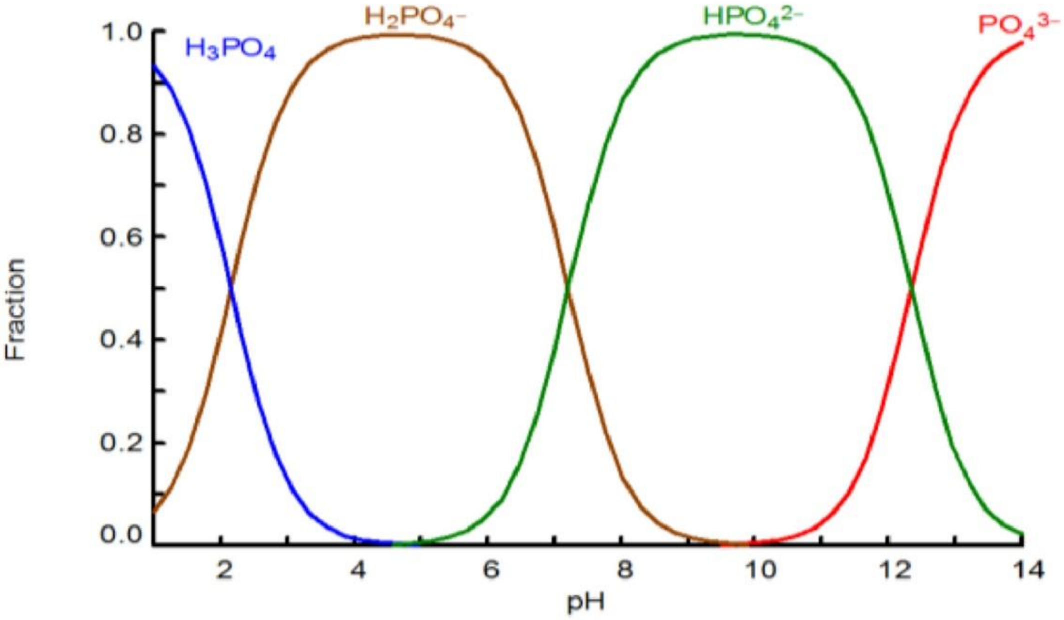

Figure 1.2 Change of phosphate speciation as a function of pH [21].

1.2 Phosphorous cycle

Unlike the carbon and nitrogen cycles, the phosphorus cycle lacks an atmospheric component [22]. Phosphorus originates exclusively from rocks, making it a sedimentary cycle [23]. Through weathering, phosphorus is released into the soil, where plants absorb it via their roots and transport it to their tissues. Once integrated into biological molecules, it enters the food chain and is consumed by animals. However, not all phosphorus from weathered rock is absorbed by plants; a portion binds to metals such as aluminium, iron, and calcium, limiting its availability [24]. When plants and animals die, decomposers convert the organic phosphorus in their remains back into inorganic forms that can be reused by plants. Due to the natural limitation of phosphorus in soils, synthetic fertilizers are often applied to maintain productivity. Additionally, natural phosphate sources like guano-accumulated seabird droppings found on Peru islands off the west coast of South America, are mined for fertilizer production [25]. Another long-term source includes phosphate-rich marine deposits formed from the skeletal remains of ancient sea life. While phosphorus cycles through ecosystems, a portion is lost through leaching and soil erosion into water bodies [26]. Agricultural activities and mining significantly accelerate these losses. Once phosphorus reaches oceans, it often reacts with other elements to form insoluble compounds that settle on the seafloor, becoming effectively unavailable for biological use. Over long geological timescales, this "lost" phosphorus can be replenished through rock weathering. Figure 1.3 represents the phosphorus cycle and the anthropogenic phosphorus cycle. However, human activities have significantly altered the natural phosphorus cycle, giving rise to an anthropogenic phosphorus cycle [27]. Practices such as deforestation lead to soil erosion and the conversion of plant-bound phosphorus into ash, which is then transported into water bodies, increasing dissolved phosphorus levels in streams. More critically, large-scale mining of phosphate rock for fertilizer production is necessary to meet the demands of high agricultural yields [28]. The widespread use of these fertilizers contributes substantially to the accumulation of dissolved phosphorus in soils and aquatic systems. Additionally, phosphorus-containing products like detergents and animal feed supplements further elevate phosphate levels in wastewater and environmental discharges. The anthropogenic loads to freshwater results in ecological disbalance and reduced water quality, and also disrupting the natural phosphorus cycle [22,23]. This leads to an imbalance in the human-influenced phosphorus cycle, where supply and demand are no longer aligned. However, this gap can potentially be closed through effective phosphorus removal and recovery from waste streams, offering a sustainable alternative to the reliance on mined phosphate rock [29,30].

Phosphate-laden waste streams arise from a variety of sources (see Table 1.2). Animal manure and slurry from swine, poultry, and cattle operations introduce substantial phosphorus loads in urban environments, sewage and water treatment plants contribute significant loads of phosphate, primarily through domestic wastewater containing excreta, detergents, and food residues [31]. Industrial discharges such as those from food processing and chemical manufacturing, industries can release significant amounts of phosphate into wastewater [32]. Furthermore, converting phosphate rock into phosphorus-based fertilizers yields phosphogypsum, a by-product of phosphoric acid and P-fertilizer production [33].

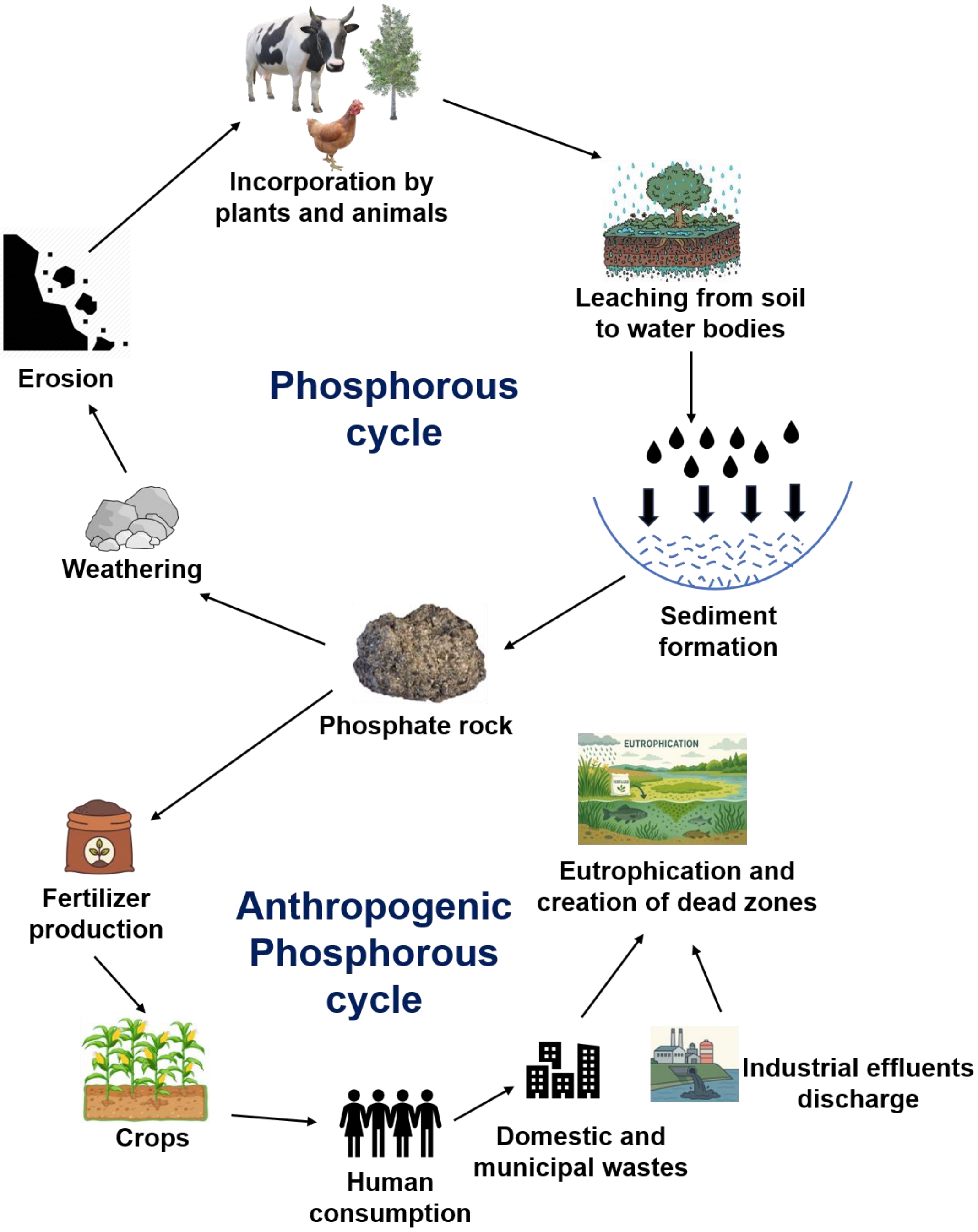

Figure 1.3 Schematic illustration of phosphorous cycle and anthropogenic phosphorous cycle.

Table 1.2 Various sources of phosphate pollution and its concentration range found in wastewater.

Source	Example Activities	Phosphate Concentration Range (mg/L)	References
Agricultural Wastewater	Animal manure, swine lagoons, runoff from fields	10 – 300	[34]
Food & Beverage Industry	Dairy, fish canning, winemaking, olive oil processing	10 – 50	[35]
Phosphate Fertilizer Industry	Phosphate rock processing, phosphoric acid production	100 – 1,000+ (in sludge/by-products)	[36]
Municipal Wastewater	Domestic sewage, toilets, dishwashing, greywater	4 – 20	[37]
Laundry & Detergents (Domestic/Industrial)	Laundry wastewater, detergent discharge	5 – 50	[2,38]
Stormwater Runoff	Urban drainage, garden and lawn fertilizer wash-off	1 – 10	[39]
Landfill Leachate	Organic waste decomposition	5 – 30	[40]

1.3 Adverse effect of phosphate pollution

Phosphorus-induced environmental pollution, especially in aquatic ecosystems, has drawn increasing attention over the past several decades. This element is widely recognized as a primary contributor to the eutrophication process [41,42]. Etymologically, the term *eutrophication* means "well nourished." It describes the outcome of excessive nutrient enrichment, primarily phosphorus and nitrogen, in water bodies, ultimately leading to *dystrophication*, an ecological imbalance [43,44]. While nitrogen can be often mitigated through biogeochemical pathways such as denitrification, P removal is quite complex due to its limited mobility and strong binding affinity to sediments [45].

Eutrophication is commonly marked by a rapid and excessive increase in algal biomass, which blocks sunlight penetration and leads to a decline in oxygen levels throughout the water column [46]. This oxygen depletion is primarily caused by the heterotrophic breakdown of accumulated organic matter, ultimately resulting in the formation of extensive dead zones [47]. This phenomenon affects rivers, lakes, and coastal zones, often disrupting the composition of plankton communities. It can lead to the excessive growth of undesirable algae, such as *Dinophyceae* and *Cyanobacteria*, some of which are capable of producing harmful toxins[48]. The resulting deoxygenation may also trigger the release of pollutants, such as heavy metals and micropollutants from sediments. Beyond ecological consequences, eutrophication poses significant economic challenges, including the degradation of recreational water areas due to toxic algal blooms and complications in drinking water production [49]. These issues may involve clogged pumping filters, the proliferation of parasitic organisms in distribution networks, and the emergence of unpleasant tastes and odours that render the water unsuitable for consumption [7,50].

Dead zones are low-oxygen, or hypoxic, areas in the world's oceans, bays and lakes since they receive excess nutrients from upstream sources [51,52]. It occurs as a result of eutrophication. Hypoxia occurs when the harmful algae die and decomposes, a process that strips off oxygen from surrounding regions, leading to difficulty in survival of aquatic plants and animals. To date, dead zones have been documented in over 400 coastal systems worldwide, covering more than 245,000 square kilometres [47,53]. It is quite alarming to know that this number is doubling every decade since 1960 [54].

These hypoxic areas are now considered a major stressor on marine ecosystems. The Gulf of Mexico experiences a seasonal hypoxic zone each late summer, ranging in size from under 5,000 km² to around 22,000 km² roughly the size of Massachusetts [55]. Growing concerns over its expansion led to the creation of the Mississippi River/Gulf of Mexico Watershed Nutrient Task Force in 1997, aiming to reduce the five-year average size of the dead zone to below 5,000 km². The Baltic Sea contains seven of the world's ten largest marine dead zones, primarily caused by agricultural runoff, sewage, and overfishing [56]. The decline in cod populations has disrupted the food chain, leading to algal overgrowth and further oxygen depletion [57]. These harmful environmental effects are alarming and demand urgent attention. Effective management of nutrient leakage into water systems is essential, and any excess should be strategically removed and recovered to protect aquatic life and ensure the health of underwater ecosystems. Figure 1.4 shows a global snapshot of ocean dead zones: tracking the spread and severity of hypoxic zones across the world's coastal waters.

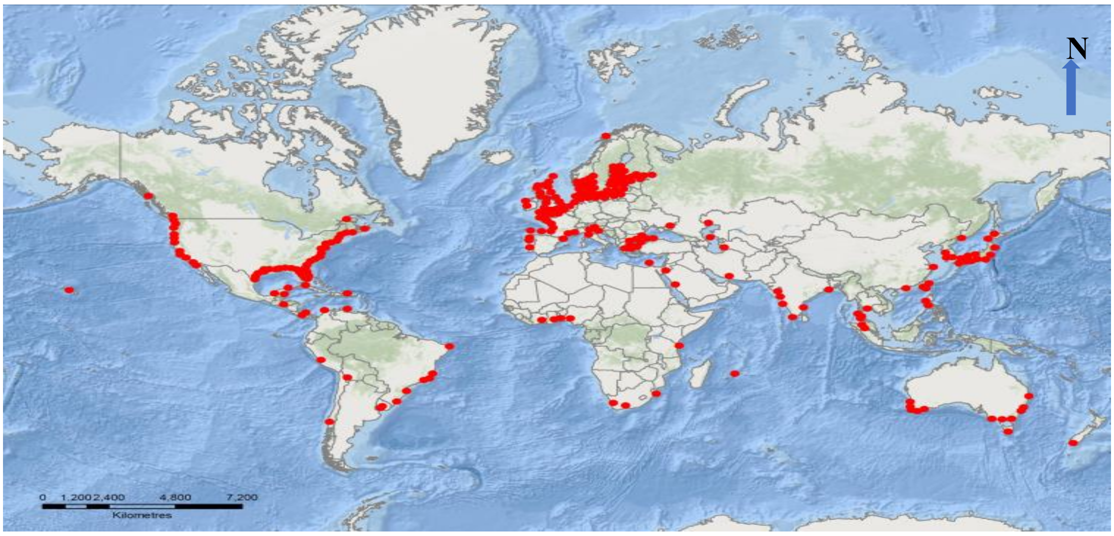

Figure 1.4 A global snapshot of ocean dead zones: tracking the spread and severity of low-oxygen areas across the world's coastal waters.

1.4 Phosphate removal methods

Various techniques have been developed for phosphate removal and recovery from wastewater to mitigate eutrophication and address the depletion of non-renewable phosphate rock. These include chemical, physical, and biological methods such as chemical precipitation, adsorption, membrane filtration, ion exchange, constructed wetlands, struvite crystallization, and enhanced biological phosphorus removal (EBPR) etc. The advantages and disadvantages of these methods have been discussed in Table 1.3.

Table 1.3 Advantages and disadvantages of phosphate removal techniques.

Method	Advantages	Disadvantages	References
Adsorption	- High efficiency at low P concentrations - Low sludge production - Reusable adsorbents - Flexible for small-scale use - Simple and easy operation	- Competing ions may interfere - Adsorbent regeneration may require chemicals	[58]
Membrane Filtration	- No chemical addition needed	- High cost - Membrane fouling - Reject stream requires management	[59]
Ion Exchange	- No sludge production	- Expensive resin regeneration - Limited resin life	[60]
Constructed Wetlands	- Eco-friendly - Low energy requirements	- Large land area required - High operational costs - Limited P recovery	[61]
Struvite Crystallization	- Recovers reusable fertilizer (struvite) - Reduces sludge volume	- High initial setup cost	[62]

		- Requires precise pH and Mg/NH_4/P balance	
Enhanced Biological Phosphate Removal (EBPR)	- No chemicals required - Efficient removal in integrated systems	- Sensitive to environmental conditions - Sludge handling issues - Slow process	[63]

Conventional methods for phosphate removal often come with significant drawbacks, including being time-consuming, labour-intensive, and environmentally burdensome. In contrast, adsorption offers a balanced, high-performance technique for phosphate removal with fewer drawbacks than other methods. Its advantages in removal efficiency, sludge minimization, regeneration, and applicability at low concentrations make it the most versatile and practical method currently available, particularly for decentralized or resource-limited settings [44,58,64].

Adsorption is a surface phenomenon in which molecules of a gas, liquid, or dissolved substance accumulate on the surface of a solid or liquid, rather than diffusing into its bulk [65,66]. The substance on which adsorption takes place is called the adsorbent, and the substance that gets deposited is known as the adsorbate. Depending on the forces involved, adsorption can be of two types: physical adsorption (physisorption), which is caused by weak van der Waals forces and is usually reversible, and chemical adsorption (chemisorption), which involves stronger chemical bonds and is often irreversible [67].

Adsorption has many advantages that make it valuable in different fields. It is widely used in water purification, where materials like activated carbon remove dyes, heavy metals, and organic pollutants. In air purification, it helps capture toxic gases, foul odours, and volatile organic compounds, improving environmental quality [68]. In industries, adsorption plays a key role in gas separation and storage, such as in the production of pure oxygen, nitrogen, or hydrogen [69]. It also enhances chemical processes through catalysis, as reactions occur more effectively when molecules adsorb onto catalyst surfaces. In medicine, adsorption is important for detoxification treatments, where activated charcoal is used to adsorb antibiotics, toxins, and in controlled drug delivery systems [70]. Overall, adsorption is a simple, efficient, and versatile process that offers significant benefits in environmental protection, healthcare, and industrial applications [71].

1.5 Adsorbents used in removal of phosphate from wastewaters

Various adsorbents have been developed for phosphate removal from wastewater, each with distinct advantages and limitations. Figure 1.5 shows the examples of common adsorbents used in phosphate removal processes. Natural materials like zeolites and clay minerals are abundant and low-cost but often require modification to enhance performance [7,62,72]. Metal oxides and metal organic frameworks (MOFs) offer high phosphate affinity and efficiency, especially at low concentrations, though some may be sensitive to pH or competing ions [73]. Modified biochar and industrial byproducts present sustainable and economical options, while polymeric nanomaterials and composite adsorbents provide exceptional adsorption capacities but at higher costs and synthesis complexity [50]. To tackle this, scientists have developed interest in sustainable bio-based adsorbents which are low cost, easy to produce and can be modified easily to improve its selectivity towards phosphate anions.

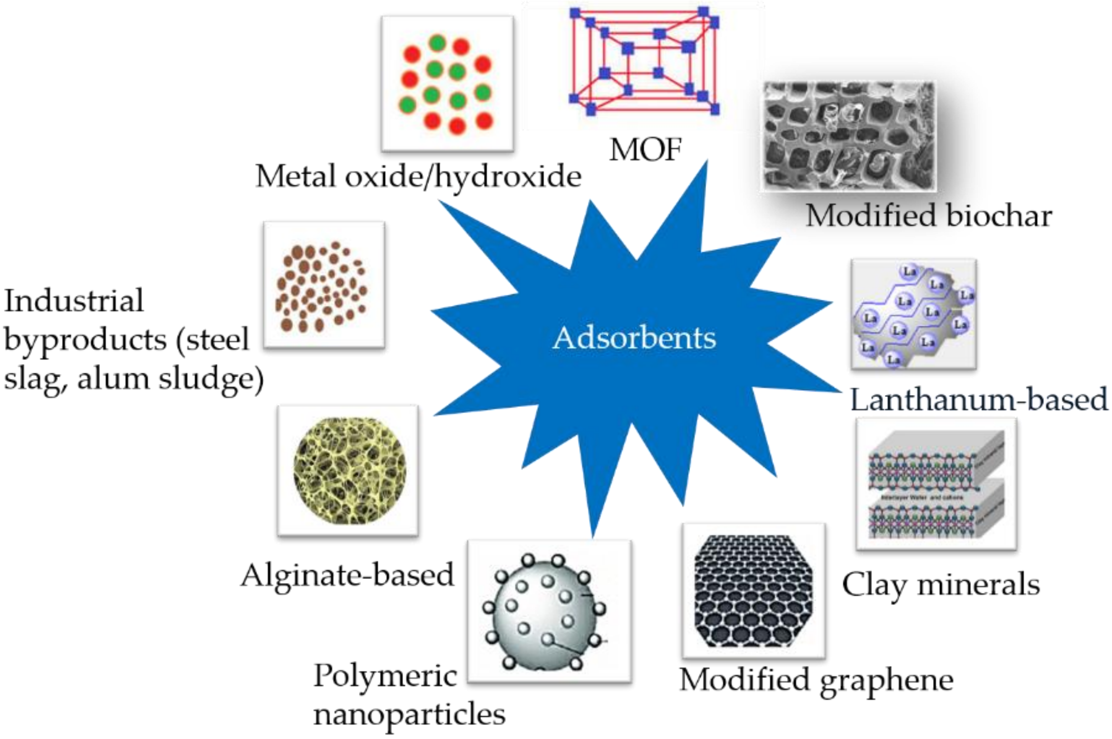

Figure 1.5 Common adsorbents used in phosphate adsorption method.

1.6 Nanofibrillated Cellulose: A versatile biomaterial

Cellulose is a ubiquitous polysaccharide which is easily available from lignocellulosic waste products like sugarcane bagasse, rice husk, wheat bran, sorghum straw, corn stalks etc. It is derived from D-glucose units consisting of a linear chain of condensed $\beta(1 \rightarrow 4)$ linked glycosidic bonds, referred as cellobiose. Each unit of cellobiose carries three hydroxyl groups which form hydrogen bonds from one chain, with oxygen atoms of the same or neighbouring chain, imparting high tensile strength [74,75]. Native cellulose shows lesser adsorption capacity as compared to modified celluloses. Despite various modifications, the adsorption capacity does not vary much since it is not compatible with hydrophobic polymer matrix and prone to form aggregates during its processing with composites [52,53]. Also, it is not long-lasting and lacks uniformity limiting its scope in polymer reinforcement [78,79]. However, this can be surmounted by an elementary building block of cellulose called nanocellulose [78,80]. Recent literature has confirmed nanocellulose as a next-generation material and a promising candidate for many technological applications. A comparative data of properties of cellulose and NFC has been illustrated in Table 1.4 that proves the superiority of NFCs.

There are basically three categories of nanocelluloses; (i) nanocrystalline cellulose (NCC), (ii) nano-fibrillated cellulose (NFC), and (iii) bacterial nanocellulose (BNC). Considering its different origins of biomass and production techniques, all these types have similarity in chemical composition but vary in particle size, crystallinity, and morphology [81–83]. NCCs and NFCs are produced from mineral plants, animals, wood, or agricultural residual wastes while BNCs are derived from microbes like *Gluconacetobacter xylinus* (BC), *Acetobacter xylinum, Gluconacetobacter hansenii, Sarcina ventriculi* etc. [84]. NCCs are needle-shaped crystalline fibrils having a diameter of 5-10 nm and a length of 150-300 nm. These are an assembly of amorphous and crystalline domains. The extraction method includes acid hydrolysis of bleached cellulose fibres to disintegrate amorphous cellulose (in particular) into suspension and liberate crystalline domains [80,85,86]. NFCs are entangled cellulose nanofibers, having diameter in range from 5 to 60 nm and length is micrometer range. NFCs have a higher surface area as they have a long-chain form and enormous amount of hydroxyl groups on their surface [87]. Bacterial celluloses are excreted as exopolysaccharides by the bacteria that are cultivated in aqueous nutrient media. It is pure as it is devoid of lignin and hemicellulosic material [84,88]. BCs have high molecular weight, high crystallinity index, and good mechanical stability [88,89].

Table 1.4 A comparative data of properties of cellulose and NFC.

Properties	Cellulose	Nanocellulose	References
Fibre length	10-15 µm	≤50 nm	[74]
Crystallinity index	56.7 %	55 - 90 %	[90,91]
Degree of polymerization	970-1050	500 - 15000	[84,92]
Young’s modulus	20	50 - 130 GPa	[91,93]
Specific surface area	~2 m^2 g^{-1}	>30 m^2 g^{-1}	[94]

In the combined field of biotechnology and nanotechnology, nanofibrillated cellulose has become a new generation biomaterial that has many potential applications. It is evident by the increasing number of research articles and patents recorded in the scientific databases [95]. NFC has an outstretched range of applications in the field of biomedical, sensor technology, cosmetics, catalysis, energy harvesting, water remediation, paper industries, oil and gas industries, etc. [96–98] due to its outstanding properties such as high specific surface area, exquisite surface functionalization property (due to presence of high density of surface hydroxyl groups), high aspect ratio, high mechanical strength, biodegradability and abundant availability makes it a novel material for water treatment processes [99]. In addition, researchers have found to increase the efficacy of NFC by chemically modifying the surface or the structure of nanomaterial and polymer reinforcement. Such modifications help in improving the binding affinities and thereby, enhancing the adsorption capabilities towards contaminants [97]. The properties of NFCs are described in the following points:

- Surface functionalization flexibility: NCs possess high density of -OH linkages which enable easy functionalization with different functional groups. These methods include esterification, carboxylation, oxidation, etherification, quaternization, surface hydrophobization by silylation or acylation, cationic surface functionalization, polymer grafting, etc. [100,101]. It helps in binding of pollutant ions (adsorbate) to the adsorptive sites of the adsorbent by different chemical processes such as chelation, complexation, coordination, hydrogen bonding, etc. [96,98,102].

- High specific surface area: Because of their nanometric scale, cellulose nanofibrils display a high specific surface area [103–106], typically more than 30 m^2/g, while native cellulose has only 2 m^2/g [94]. The high surface area of nanocelluloses leads to increased number of contact points between adjoining fibres which makes the material rigid and ultra-superior.
- Aspect ratio (length/diameter): High aspect ratio of NFC is depicted by entangled nano-fibrous network strongly held by strong hydrogen bond [96,99]. It increases the mechanical strength of the adsorbent.
- High mechanical stiffness: NFCs are high-grade materials with extensive mechanical stiffness having young’s modulus of around 130 GPa, which is much higher than glass fibres [74,91,107]. Apart from this, the specific Young's modulus (ratio between Young's modulus and the density) is 65 J/g which is more than that of steel which is about 25 J/g [91].
- Well-defined crystallinity: NFCs have crystallinity index of around 60 %, which improves its resistivity and decreases its solubility even in high polar solvents [108,109].
- Biocompatible and biodegradable: NFCs are biodegradable polymeric nanomaterial that do not cause any harmful changes in the adsorption process [110].

1.6.1 From Waste-to-Resource: Sugarcane bagasse as a sustainable lignocellulosic source for production of NFC

Selection of precursor material for cellulose recovery is very important as it should possess high cellulosic content, and are plentily available and accessible. Agro-industries such as sugar, tea, coffee, vegetable oil, cotton, paper, and fruit canning industries generate a tremendous number of residual wastes such as rice and corn husk, vegetables and fruits peel-offs, wheat brans, sugarcane bagasse, etc. during their production process [111,112]. These wastes are mostly lignocellulosic compounds that are prime source of cellulose. Various research work has been conducted where lignocellulosic wastes have been utilized for the removal of pollutants from wastewater [103,113–117]. Among many lignocellulosic materials, sugarcane bagasse (SCB) has always been in demand as it is low-value agricultural residue, superabundant, easily available, reproducible, and environmentally compatible [118]. It comprises approximately 40-50 % cellulose, 20-25 % hemicellulose, 15-20 % lignin and, remaining other extractives [90,119–121]. There is a significant commercial advantage in using sugarcane bagasse as a cellulosic precursor as it is widely produced in India. This minimizes the cost of collection and transportation of bagasse which will certainly be higher for other lignocellulosic residues.

Food and Agriculture Organization of the United Nations (UNFAO STAT, 2021) [122] made a statistical analysis of the annual crop production where global sugarcane production is 1.9 billion tonnes which is equivalent to 21 percent of total crop production worldwide and India accounts for a total of 20 percent of sugarcane production [122]. Each ton of sugarcane generates around half of the amount as moisture, more than 250 kg of bagasse, and approximately 200 kg of straw on average, for the generation of sugar and ethanol [123,124]. Sugar industries, inadvertently produce large amounts of bagasse as byproduct. Either it is dumped on the roadside or in nearby waterbodies. Also, the bagasse that is obtained from domestic houses and local shops are not properly discarded. The wastes have an inconsiderate impact on the environment if not advocated properly. Therefore, it becomes important that the wastes are managed aptly in a way that the unvalued wastes would result in the production of a definite high-value product. In line with sustainable waste management practices, this research explores the use of sugarcane bagasse-derived nanofibrillated cellulose for efficient phosphate removal from wastewater.

1.6.2 Production methods of nanofibrillated cellulose and its characterization techniques

Lignocellulosic biomass primarily consists of three major components; cellulose, hemicellulose, and lignin. One of the key steps in recovering cellulose from lignocellulosic biomass is pretreatment, that plays a vital role in disrupting the lignin-carbohydrate complex and recalcitrant structure of the biomass. Effective pretreatment facilitates hemicellulose and lignin removal and enhances the accessibility to cellulose, allowing for their conversion into nanofibrillated form.

Various pretreatment strategies have been developed to solubilize hemicellulose and lignin and enhance cellulose recovery. These include physical methods (e.g., milling and refining), chemical approaches (e.g., alkaline, acidic), physico-chemical techniques (e.g., ammonia fiber expansion (AFEX), and steam explosion), biological treatments (enzymatic, microbial digestion), green solvents (deep eutectic solvents, ionic liquids, organosolv) and hybrid processes. An efficient pretreatment strategy disrupts the supramolecular architecture of lignocellulose and alters the interactions between carbohydrates and the lignin matrix. Traditional methods, such as acidic and alkaline pretreatments, have shown effectiveness but suffer from several drawbacks, including equipment corrosion, high costs related to effluent treatment, generation of inhibitory compounds and cellulose recovery challenges.

In recent years, the focus has shifted towards developing milder, environmentally friendly, and sustainable pretreatment technologies suitable for industrial applications. Natural Deep eutectic solvents (NADES) have emerged as promising green solvents for biomass pretreatment due to their favourable characteristics, such as simple synthesis, high purity, low toxicity, biodegradability, low melting points, thermal stability, non-flammability, low volatility, and strong air stability. NADES align well with the principles of green chemistry, offering an eco-conscious alternative for biomass processing. Also, it is reported that NADES has greater solubility towards biomass components especially hemicellulose. A deep eutectic mixture is a combination of two or more solid components at fixed molar ratios that interact through hydrogen bonding to form a homogenous liquid at mild temperatures and pressure conditions [125]. These solvents have melting point lower than that of individual components when combined. The components of eutectic solvents are hydrogen bond donor (HBD) and hydrogen bond acceptors (HBA) [126]. NADES are formed due to delocalization of charge between HBA and HBD component via hydrogen bonding [127]. The delocalization of charge brings about the decrease in melting point of the combined mixture in respect to the melting points of the individual raw components [128]. NADES are subordinate class of DESs. These are termed “natural” as the components of the mixture are plants primary metabolites like sugars, amino acids, choline derivatives, polyols, and organic acids etc. Recently, organosolv fractionation such as use of organic solvents such as alcohols, acids, and phenols have gained attention for their gentler, more efficient fractionation compared to conventional alkalis and inorganic acids. Among them, acetic acid stands out for effectively in delignifying biomass and hydrolysing hemicelluloses completely, enhancing cellulose accessibility and reducing inhibitor formation [129]. Notably, the organic solvents used in this process can be easily recovered and reused.

The effectiveness of green solvents in biomass pretreatment depends on factors such as the NADES type and its molar ratio, organosolv type, processing conditions, and the specific characteristics of the biomass, which can vary in structure, lignin content, and recalcitrance [130]. Understanding the molecular interactions of NADESs and organosolv can support their tailored design for improved performance. For production of nanofibrillated cellulose, integrating solvent pretreatment with other intensification techniques, such as microwave, ultrasound, ball milling, high pressure homogenization is important to reduce the size of cellulose effectively. Process intensification techniques, such as ultrasound, can be combined with pre-treating solvents to enhance the efficiency of NFC production and significantly reduce reaction time [131]. This thesis explores the use of green solvents for producing nanofibrillated cellulose (NFC), aiming to obtain high-purity cellulose with minimal degradation and high yield by integrating high-intensity ultrasonication. The produced NFCs are characterized with the help of various state-of-the-art analytical techniques. Figure 1.6 represents various characterization techniques used in the analysis of produced NFCs as adsorbent for phosphate removal from wastewaters.

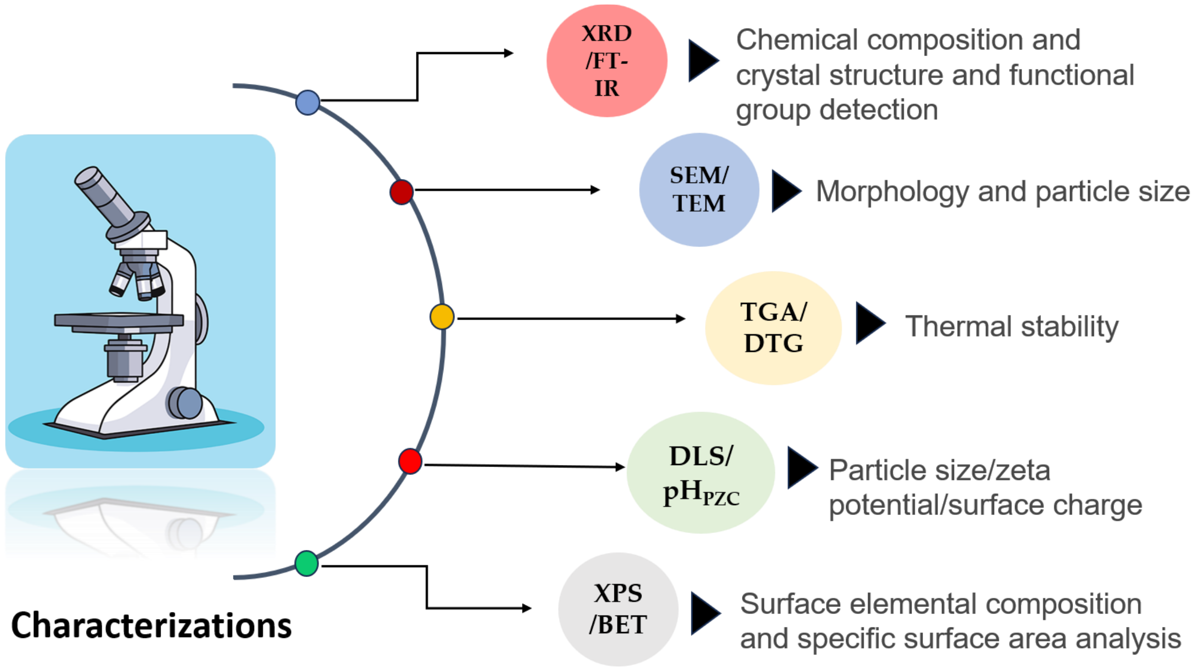

Figure 1.6 Characterization techniques used in the analysis of produced NFCs as adsorbent for phosphate removal from wastewater.

1.7 Motivation

The increasing demand for sustainable materials and effective wastewater treatment strategies has driven research toward eco-friendly, low-cost, and renewable solutions. Agricultural residues such as sugarcane bagasse, which are often underutilized or discarded as waste, represent an abundant and renewable source of cellulose. Transforming this agrowaste into value-added nanomaterials not only supports waste valorization but also aligns with the principles of a circular economy. NFC, in particular, has emerged as a promising material due to its high surface area, mechanical strength, and modifiable surface chemistry, making it suitable for a variety of environmental applications, including pollutant removal.

This study is motivated by the dual challenge of agro-waste management and phosphate contamination in aquatic systems. Excess phosphate in water bodies contributes to eutrophication, threatening ecosystems and water quality. By producing NFC from sugarcane bagasse using green solvents and high-intensity ultrasonication, this research aims to develop a sustainable and efficient adsorbent for phosphate removal from wastewater. Furthermore, modifying the NFC through environmentally benign methods is expected to enhance its adsorption capacity, offering a low-impact, high-performance alternative to conventional treatment approaches. The outcomes of this work have the potential to contribute significantly to sustainable environmental technologies and waste-to-resource innovations.

1.8 Objectives

The primary aim of this study was to produce NFC, characterize its properties, and explore its potential for phosphate removal from wastewater through various modification techniques to enhance its removal efficiency. To accomplish this, the study focused on the following key areas:

(i) Production of NFC from lignocellulosic waste utilizing green solvents and high-intensity ultrasonication, followed by comprehensive physicochemical characterization to evaluate the material's structural and functional properties.

(ii) Examination of phosphate adsorption behaviour of NFC modified with cationic surfactant; cetyltrimethylammonium bromide (CTAB), including optimization of experimental conditions and analysis of the underlying removal mechanisms and adsorption characteristics.

(iii) Assessment of phosphate removal efficiency using magnesium-doped NFC and bentonite clay, with optimization of relevant parameters and investigation into the adsorption mechanisms involved.