

Catalytic degradation of naphthenic acid in aqueous solution: A review

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Abstract

Naphthenic acids are among the water, oil and soil contaminants mostly by accident. The review was carried out to examine the types and sources of Naphthenic acids. The toxic nature of naphthenic acids is mostly attributed to their surface characteristics due to the presence of a hydrophobia alkyl group and hydrophilic carboxylic group in their salts. Different method based on the use of different test organism like bacteria, aspen, fish, zooplankton and rat have been used by researchers to measure the level of toxicity of naphthenic acid in substances. Naphthenic acid caused corrosion in the oil sand refining process. Many analytical procedures have been use for the characterization and quantification of naphthenic acids was discussed. The chemical treatment methods have been explained and prove effective for degradation of naphthenic acid in water. The plants used in phytoremediation of contaminated water was examined and discussed. Photocatalysis method that uses UV 252 radiation has the most potential for reducing naphthenic acids and increasing their bio availability has been reported. Naphthenic acid is one of natural constituent of asphalt and crude oil and mainly obtained as the by-product of petroleum refining process with inconstant composition and ingredient. In conclusion, certain properties and characteristic of Naphthenic acid have been partially reviewed.

Keywords: Toxicant; Naphthenic acids; hydrophilic; Corrosive; Bioremediation

1. Introduction

Naphthenic acids are among the most inefficient water contaminants in tailing pond water as a result significant environmental and regulatory attention is focused on naphthenic and fraction of oil, sands material due to their persistence in the environment and aquatic toxicity in tailings panel water [1]. Being a natural constituent of bitumen and become concentrated as a by-product of petroleum refining. Naphthenic acids are a complex mixture of alky – substituted cyclo-aliphatic acids.

Significant environmental and regulatory attention has been addressed this challenges and potential hazards. Biological chemicals and photolytic treatments of water contaminated with naphthenic acid and been studied, but are either time consuming or involve significant capital investment. There is a growing need to develop more efficient and cost effective treatment methods based on existing literature, microwave and photo catalysis for degradation of naphthenic acids in an aqueous solution may be one solution. Part of this work included evaluation of the physical and chemical properties of naphthenic acid [2].

Occurrence, analysis, toxicity and biodegrading of naphthenic acid were reported by [2]. These sodium salts of naphthenic acid are toxic to microorganisms with 30% (V/V) EC₅₀ [3]. The purity as it limits the choice of materials concerns process affected water requires treatment prior to disposal. There is an insufficient amount of information of separation and techniques for naphthenic acid mixture.

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However photolysis using ultraviolet and visible spectrum, of light has been reported by [1], as one potential supplementary remediation method for naphthenic in natural surface water. [2] Reported photo catalysis using TiO_2 as one of the efficient naphthenic acid remediation methods under natural sunlight in this context. Recent literature suggested that naphthenic acid could be separated from diesel fuel using microwave radiation [5];[6]. Similarly removal of naphthenic acid from vacuum cut, distillate oil of dangling using microwave has also been reported [2].

2. Review of Literature

Physical and chemical properties of naphthenic acids obtained as a byproduct of petroleum refining. They are composed of substituted cyclo aliphatic carboxylic acid that include single rings and fused multiple rings. [2] Suggested that there are multiple carboxylic structures of naphthenic. The carboxyl group in the structure is generally attached to a side chain acid strength of naphthenic acids is lesser than low molecular weight carboxylic acid [8]; [9]; [1].

Typical physical and chemical properties of naphthenic acids are given in the 1.1 stoichiometrically naphthenic acid are represented by the formula $\text{C}_n\text{H}_{2n+2}\text{O}_2$ Where "n" indicate the number of carbon atoms and where H in the formula represent the hydrogen atoms. Naphthenic acids extracts contains a higher percentage of higher molecular [2] suggested that oil sand process water naphthenic acids contains larger naphthenic like compounds with unsaturated rings within their structures.

The z =-4 series of naphthenic acid predominant in Athabasca oils sand tailing pond water [1]; [10] amend are more toxic than other naphthenic acids fractions. The physical, chemical and toxicological properties of these compounds are directly related to the molecular weight and structure. Polarity and non-volatility of naphthenic acid are affected by Molecular weight (Herman et al., 1994 Brient et al., 1995, Mc Martin et al, 2004 Headley et al., 2004). The solubility of naphthenic acids is related to media P^{H} , with nearly complete solubility between 9-11 [11; 12].

Table 1 Physicochemical Properties of the Naphthenic Acid [13].

Property	Grades		
	Crude	Refined	Highly refined
Acid number, mg KOH/g	150-200	220-260	225-310
Acid number (oil fuel)	170-230	225-270	230-315
Unsaponifiable Kt%	10-20	4-10	1-3
Phonologic compound Wt%	03-1.0	0.01-0.1	0.1-0.08
Water, Wt%	03-1.0	0.01-0.1	0.1-0.08
Specific gravity at 20%	0.95-0.98	0.95-0.98	0.95-0.98
Viscosity at 40°C, op	40-80	40-80	50-100
Refractive index, ND^{20}	1-482	1-478	1-475
Average molecular weight (oil free)	240-330	210-250	180-250
Boiling point	250-350°C	-	-

3. Source of Naphthenic and Contaminations

Naphthenic acid are a complex mixture of alkali substituted cyclo aliphatic carboxylic acids. Naphthenic acids are natural constituents of bitumen. They are oxidative products of petroleum hydrocarbons and may be the byproducts of original plant transformation to oil [1]. The concentration of the naphthenic acid in aquatic environment is usually low at 0.4 to 51mg/l [14].

4. Naphthenic Acid Toxicity

The toxic nature of naphthenic acids is mostly attributed to their surface characteristics due to the presence of a hydrophobia alkyl group and hydrophilic carboxylic group in their salts [15]; [14]; [2]. Naphthenic acids of low

molecular weight are the most significant contaminants in the tailings pond of water [15]. The lower molecular weight naphthenic acids can more easily interact with biological tissue and thus have higher toxicity.

[14] toxicity of any given naphthenic and source is a function of birth and composition, toxicity also decrease with the increase in carbon number content and structural complexity of the compound there is structural difference between lower and higher molecular weight naphthenic acid which contribute to the difference in their toxicity [16]; [17]; [1]; [2]. [17] report that function with carbon number $n < 22$ are responsible for much of the toxicity of naphthenic, naphthenic acids with $z = -4$ and low carbon number (n) exhibit relatively toxicity [6] naphthenic acid friction with more rings (higher z value) and branches are relatively less toxic. Multiple rings with a higher number of carbon branches are relatively more resistance to microbial degradation lower molecular weight less branched and lower carbon number naphthenic acid are more bio available to micro be which this naphthenic friction thus shifting the proportion of high molecular weight higher carbon naphthenic to higher side well again [17]. [2] also suggested that there is greater carboxyl acid content within the higher molecular weight and cyclic structure acid content within the higher molecular weight and cyclic structure of naphthenic acid the present multiple carboxylic group within their structure makes the higher molecular weight naphthenic acid more ionizable and less hydrophobic and account for lower toxicity of higher molecular weight naphthenic acid than lower molecular weight acid.

Toxicity of naphthenic acid also depend on the production and mining source communally available naphthenic acid are more phyto toxic than those from the AOS process [18]. this difference was attributed to the molecular weight distribution in naphthenic acid mixture have a highest concentration of lower molecular weight compound and thus are more toxic than the oil sand process water naphthenic compound along with some impurities aromatic naphthenic acids like compound of similar range of molecular weight [2] further suggested that oil sand process water naphthenic acid contain large naphthenic acids like compound with unsaturated ring within their structure.

Toxicity of naphthenic acid is also affected by P^H of the oil sand process water. The Pka value naphthenic acid is in between P^H s 5.2 and 6.0 if the P^H s of oil sand process water is higher than the Pka value naphthenic acid are highly polarized and cannot pass through biological membrane and this are less toxic when P^H s is below the Pka value naphthenic acids are uncommon in the natural forms as such they are more soluble in biological membrane and therefore more toxic salinity of the medium reception also affects toxicity as naphthenic acids are known to be toxic to microorganism with an EC_{50} of 30% (V/O) [19].

5. Toxicity Measurement of Naphthenic Acids

Different method based on the use of different test organism like bacteria, poisonous plant, fish, zooplankton and rat have been used by researchers to measure the toxicity of naphthenic acid [14]. Microtox toxicity assay is one of such method that uses *Viobrio fisheri*, a luminescent bacterium as the test organism. Possibility exists for other organisms to respond differently than fisheri. [20] compared three test organisms (Rainbow truel, Dapahinia magna and *V. fisheri*) to measure the toxicity of oil sand tailing pond water. However they reported to be more reproducible compared to the trout and D. Magnas assays. [21] reported microtox method as quicker, easier and less expensive than other toxicity assays. Because of these observations, this assay has commonly been used to monitor toxicity of the oil sands tailing after and naphthenic acid solutions [14].

6. Corrosiveness of Naphthenic Acids

In addition to contributing to tailing pond water toxicity naphthenic acid cause corrosion in the oil sand refining process. Most natural naphthenic acid cause corrosion in the oil sans refining process, most natural naphthenic acid occur in their sulfide form, mainly responsible for corrosively. [22] reported that corrossivity of naphthenic acid depends on ion the total acid numbers of the crude oil. Availability of carboxylic group in the naphthenic acid structure to react with metal ions determined the extent of corrosiveness.

Corrosiveness is also temperature dependent under favorable conditions between 220 to 400°C. Naphthenic acids salts cause chelations of the metal ion leading to corrosion of metal material at higher temperature (>400°C). Naphthenic acid and their salts decompose and the corrossivity decreases [2] reported efforts made to limit corrosion cause by naphthenic acid. The approaches available including:

Changing the refining process top reduce the acidity of crude oils.

Controlling the characteristics such as velocity and flow.

Using bacteria and components that are more corrosion resistance.

Any treatment unit design must include appropriate choice of materials to avoid damage or structural compromise due to naphthenic acid corrosively.

7. Techniques for Naphthenic Acid Analysis

Naphthenic acid are highly mixtures of compound following the general formular $C^n H^{2n+2} O_2$ for each carbon number (n) there is more than one isomeric form of naphthenic acid. Analytical methods to identify separate and quality of those vast forms have not yet been reported, however method to quantify the overall concentration of (m/z) distribution are available [22].

Analytical procedures such as high performance liquid chromatography, electro spray ionization mass spectrometry and forces transform, infrared Fourier transform of ion, cyclotron resonance proton, nuclear magnetic resonance, spectroscopy and high performance liquid chromatography, high- resolution mass spectrometry has been use for the characterization and quantification of naphthenic acid [24]; [12]; [25]; [26] ; [1]; [8] [23] ; and [2] a recent study of [23] compared the low and high resolution mass spectrometry and suggested that electrospray ionization is efficient for the characterization of commercial naphthenic acids but it is substantial false positive detection and misclassifications in oil sand process water naphthenic acid.

Electrospray ionization mode is used by water science and technology directorate of environment Canada to qualify and characterize naphthenic acid. Concentration following the standard the standard produce proposed by [11] this method allows a detection limit of 0.01 mg/l. The electrospray ionization was used to quality analysis and characterizes naphthenic acid samples in this research because of its availability.

In electrospray ionization the solution is bombarded to produce ions that can be mass separated and detected by mass to charge ratio. The sample cone is kept at a different voltage (7KV) then the surrounding was. These smaller charge particles move through a capillary tube and increase as particle that are also evaporated by the nitrogen drying gas the process continues until the molecules are reduced to their quass-molecular ionic from and are passed from mass analysis and production of mass spectral. The negative ions electrospray ionization is comparatively more useful for the quantities analysis of naphthenic acid [1]; [12].

The treatment method for naphthenic acid concentration in aqueous solution, many methods have been reported to date, to reduce concentration of organic and inorganic contaminants in water including chemical treatment and microwave treatment. Method that have potential to be used for treating water containment with naphthenic acid these methods are discussed in details in the following subsection.

8. Chemical Treatment

Chemical treatment of water is a well-established process by which organic and inorganic containments and harmful microorganism are treated by the addition of chemical agent to the water, chemical treatment can promote pathogen removal, colour, odor and taste removal, iron and manganese oxidation, algal and biological growth prevention in water distribution [1]; [11].

The most common chemical treatment process used for drinking water is chlorination to eliminate bacteria viruses protozoan and other organic/ inorganic contaminant [27]. However, the accumulation of undesirable byproduct such as (nitrogen) trihalomethanes formed during the treatment process reducing the amount of chlorine use.

The chemical treatment methods have been explained and prove effective for degradation of naphthenic acid in water. [28] explained two approach including

Altering the P^H of the solution to favor coagulation on conditions and flocculation of naphthenic acid using anionic polyelectrolyte.

Allowing natural process that degrades naphthenic acid to reduce water concentration over one to two during which tailing water is placed in shallow well aerated pit.

[28] reported that ozonation of sediment free oil sand process water and high cost of ozone production must be considered however when evaluating the practically of large scale of ozonation.

The chemical treatment method of naphthenic acid appears to be either an overly complicated procedure as demonstrate by these approaches.

Also a small fraction of reaction naphthenic acid remain after the chemical to find other solution for the treatment of tailing pond water that are more cost and time saving.

9. Bio-Remediation

Bio-remediation occur when plant and microbe remove metals and other contaminate from soil and water is part of their normal metabolic process, some plant and microbes are capable of taking up naphthenic acids from aqueous phase therefore bioremediation may be a viable option for remediation of naphthenic acid contaminated tailoring pond water. The challenges with bio-remediation are that a significant residual concentration of approximately 19mg/l remains and it is considerably slower process [27] result show that lower molecular weight naphthenic acid ($n < 22$) or more readily biodegrade than higher the commercial weight naphthenic acid, additionally the commercial naphthenic acid mixture are more biodegradable than oil sand process water naphthenic acid. This is likely since the commercial mixture tend to contain more low – molecular weight naphthenic acid than typical Athabasca oil sand naphthenic acid mixture. The plant used in phytoremediation of contaminated water selectable uptake naphthenic acid molecules limiting the usefulness of this method therefore plants alone are not capable of fully remediating tailing pond water. [29]; [21] reported photo-remediation as one potential method for metabolizing organic to an non-toxic form, plant can also be generally modified to metabolize toxic from plant can also be generally modified to metabolize toxic contaminants [21] toxicity reduction naphthenic acid by the attributed to the biotransformation of naphthenic acid by the microbes in the root zone [13] determined the effectiveness of rhizosphere microorganism at different wetland plant significantly can reduce toxicity of naphthenic acid.

[30], reduce the potential for bio-generation with selected bacterial to degrade the more refractory for classes of naphthenic acid here the use of attachment material such as clays to concentrate both naphthenic acid degrading bacteria in surface or pore synergist association and bio-stimulation with nutrient to promote the growth and activity of microorganism may further increase the degradation of naphthenic acid in oil sand process water. Indigenous aerobic microbial communities in oil sand tailing pond biodegrade naphthenic acid [19]; [14]; [13]; [19] reported that aerobic bacterial degrade naphthenic acid by oxidizing the carboxylate aliphatic oxide chain which subsequence the cycloaliphatic ring o naphthenic acid several published research result show that various microorganism are capable of breaking down the majority of the naphthenic acid within so clap of being introduced to the system [20]; [30]. These results also show that microorganism cannot readily break down the more complex structure naphthenic acid.

[31] used high performance liquid chromatography for analysis naphthenic acid and reported the influence of naphthenic acid structure of bio degradation kinetic they suggested that commercial naphthenic faster than oil sand process water naphthenic acid the slower degradation rate of oil sand process water naphthenic acid was attributed to the recurrent friction of naphthenic and present predominantly in oil sand process water naphthenic used acid also to the high alkyl branching of these naphthenic acid they also reported decrease biodegrading rate of both types of naphthenic (commercial and oil sand process water extract) with increased number of ring (more negative z value-naphthenic acid family classification indicating hydrogen deficiency).

10. Photocatalysis

Photocatalysis is one of the most promising alternate for water treatment [29]; [32] photocatalysis is a chemical process in which a catalyst accelerate and electron hole pairs light source both visible and ultraviolet (UV) light used as the source of photons of most photocatalytic process. UV light is emitted in wave length in the range of 100 to 400nm.

According to [33].much of the water treatment value of UV light can be attributed to the UV-B (230 to 315nm) and UV –C (200 to 230nm) sun range [23] reported that UV 252 radiation has the most potential for reducing naphthenic acids and increasing their bio availability.

A number of semiconductors are used as photocatalysis and are capable of providing electron when they are attributed at their band gap energy level by the incident UV- US radiation [34]. Titanium dioxide (TiO_2) is the preferred photocatalyst because of its activity. Non toxicity stability in aqueous solution and relatively low cost [31] t 10z is widely

available in three crystalline structure namely rutile anatase and brookite anatase exhibits better photocatalytic efficiency due to the lower recombination probability of electron hole pairs [29] ; [31]. This structure required 3.2eV for activation, requiring the use of UV light for activation. The nitrile structure however has a band gap value of 3.2eV meaning it can be activated by solar radiation. In heterogeneous catalysis, suspensions of TiO₂ are irradiated with UV wavelengths shorter than 390 nm, to produce photo energy greater than 3.0eV sufficient to initiate the photocatalytic reaction [29].

The scope of micro wave assisted heterogenous photocatalysis has also been reported by [35] they have integrated a photolytic reactor system with a wave guide which allow concurrent application of microwave at 2.45 GHz and photocatalysis with higher conversion as compared to only photocatalysis for ethylene oxidation.

11. Conclusion

Naphthenic acid are natural constituent of bitumen and crude oil and predominantly obtained as the by-product of petroleum refining with variable composition and ingredient. Naphthenic acid are composed of alkyl- substituted cycloaliphatic carboxylic acid with smaller amount of cyclic aliphatic acid naphthenic acid become a significant part of the tailing pond of water after separation from oil sand materials. Naphthenic acid are soluble in water and are converted in oil sand process as a result of caustic oil sand extraction process significant environment and regulatory attention has been focused on the naphthenic acid.

Recommendations

- Naphthenic acid should be considered as hazardous substance but rather a substance used for purification in industries therefore further research on naphthenic should take note of that.
- Despite the importance of naphthenic acid it not react available hence naphthenic acid other petrochemical should be manufactured in Nigeria rather than importing them.
- The federal government of Nigeria should also encourage developed of technologies necessary for the production of naphthenic acid and aromatic compound such as benzene xylene.
- The federal government of Nigeria should make and implement laws that will check indiscriminate impartation of good that can be provided locally this will boost that growth of local industries.
- For Nigeria to achieve her goal of being on the list of top 20 most industrialized nation of the world develop some important basic chemical industries in order to meet the chemical requirement of the existing manufacturing process.
- There is growing need to develop more efficient and cost-effective treatment methods.

Compliance with ethical standards

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Disclosure of conflict of interest

The authors declare no conflict of interest.

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