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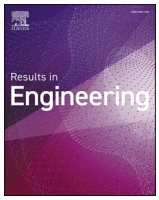

Experimental investigation and comparative environmental impact analysis of conventional and naturally occurring kinetic hydrate inhibitors in offshore environments using toxicity and bioconcentration tools

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ABSTRACT

In this present study, an *in vivo* experiment was carried out to determine the tendencies of a naturally occurring high-phenolic compound red-onion skin extract (HPC-ROSE) and conventional N-Vinylcaprolactam (N-VCAP) kinetic hydrate inhibitors (KHIs) to bio-accumulate in offshore environment through the analysis of their uptake and depuration kinetics by a Fish-Chemical Model using *Cyprinus carpio* marine invertebrate. This test was performed in the laboratory in a flow through experimental set up according to the guidelines by [49] (Fish-chemical exposure test). The uptake duration was 10 days with a depuration period of twenty days. The inhibitor toxicity test was evaluated by determining the 50 % lethal concentration (LC_{50}) as highlighted by OSPAR Commission protocols. The solubility of the inhibitors was determined by a column elution technique. Similarly, a proton-enabled nuclear magnetic resonance (^{1}HNMR) technique was used to measure the partitioning characteristics of the inhibitors in an immiscible mixture of octanol and water (*Kow*) by ^{1}HNMR spectroscopy using a benchtop low-field NMR spectrometer. OSPAR Commission and ASTM standard protocols were used for the laboratory investigation of the static sediment toxicity tests. A reference chemical substance of known BCF and solubility (Ethyl Acetate, EtOAc) was used as control to check the experimental progression. The stock solution was prepared by solid phase desorption mechanisms. The HPC-ROSE does not constitute environmentally significant risk to aquatic life owing to its lower BCF values between 215 L/kg - 251.5L/Kg, Log-Kow of 1.2 and higher lethal concentration of 25140 mg/L. Unlike the NVCAP which is very toxic with lower lethal concentration of 1280 mg/L and higher BCF values in the range of 442.5L/Kg to 485 L/kg with Log-Kow of 1.5. Furthermore, Nuclear magnetic resonance (^{1}HNMR) is a simple and reliable method of estimating partition coefficient characteristics (Kow) because the obtained Log-Kow values showed good agreements with that of shake flask and high-performance liquid chromatography techniques. Also, the chemical concentration in water has an inverse relationship with uptake rate constant (K_1) and steady-state bioconcentration factor (BCFss). Finally, the theoretically estimated BCFs were higher than the steady-state (BCFss) values that were obtained from laboratory experiments for the different inhibitor samples and at all concentrations. This is due to the route by which Log-Kow was estimated since most of the empirical models are usually one-factor model consisting of partition coefficient and BCF.

1. Introduction

Oil and gas production activities have metamorphosed from shallow oil and gas fields to deep water offshore environment with significant amount of hydrocarbon reserves. These offshore fields are inherently characterized by low temperature and high pressure and thus a huge tendency for gas hydrates formation in oil and gas pipelines during crude oil transportation. Hydrates are formed whenever there is presence of water in the pipeline system which result in the trapping of the

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List of abbreviations

ECETOC	European center for ecotoxicology and toxicology of chemicals
HNMR	Proton enabled nuclear magnetic resonance
KHIs	Kinetic hydrate inhibitors
OSPAR	Oslo and Paris commission
BCF	Bioconcentration factor
K_{OW}	Octanol-water partition coefficient
NVCAP	N-Vinylcaprolactam
HPC-ROSE	High phenolics compound red onion skin extract
BCF_{SS}	Steady state bioconcentration factor
BCF_K	Kinetic bioconcentration factor
EIA	Environmental impact assessment
EtOAc	Ethyl acetate
EOCs	Emerging organic compounds
POCs	Persistent organic compounds
OECD	Organization for economic cooperation and development
ASTM	American society for testing and materials
OGP	Oil and gas practitioners

List of Symbols

K_1	Inhibitor uptake rate constant into fish ($L{\cdot}kg^{-1}{\cdot}day^{-1}$)
K_2	Inhibitor depuration rate constant from fish (day^{-1})
K_g	Fish growth rate constant ('growth dilution') (day^{-1})
K_m	Metabolic transformation rate constant (day^{-1})
K_e	Faecal egestion rate constant (day^{-1})
C_W	Concentration of the chemical inhibitor in water ($mg{\cdot}L^{-1}$)
C_F	Concentration of the chemical inhibitor in fish ($mg{\cdot}kg^{-1}$ wet weight)
*C*f-ss	Concentration of the inhibitor in fish at steady-state (mg kg^{-1} wet weight)
*C*w-ss	Concentration of the inhibitor in water at steady-state (mg L^{-1})

gas molecules within the hydrate shell (hydrates-forming cage-like structure) [1]. Thus, agglomeration of hydrate shells occurs as a result of capillary attraction, leading to the formation of hydrate plugs [2].

There are different inhibitors that have been developed in order to mitigate this serious flow assurance catastrophe. These inhibitors can be thermodynamic hydrate inhibitors such as methanol, amino acids, glycols (mono-ethylene glycol (MEG) and ionic liquids. There are also low-dosage hydrate inhibitors which can be subdivided into kinetic hydrate inhibitors and anti-agglomerants [3]. The most common of these kinetic inhibitors are different polymers and co-polymers such as NVCAP (N-Vinylcaprolactam)., IPMA (N-Isopropyl-meth-acrylamide) and 2-(Dimethyl amino) ethyl methacrylate [4]. The anti-agglomerants are zwitterionic surfactants and bio-surfactants as well as quaternary phosphonium and ammonium salts among others. In recent advances, extensive research has been conducted on the possibility of using locally sourced materials as kinetic hydrate inhibitors [5–11].

A serious concern about emerging synthetic organic chemicals that are used in methane hydrate inhibition particularly in North Sea countries is the tendency of the organic compounds to bio-accumulate in the aquatic organisms and thereby deface marine animals of commercial interest [12,13]. It is pertinent to note that an organic compound may bio-accumulate in the tissues of marine organisms if the organisms are exposed to bioavailable forms of the chemical in the ambient water, sediment, or food [14]. A chemical is bioavailable if it is in a form that can move through or bind to the surface coating (e.g., skin, gill epithelium, gut lining, cell membrane) of an organism [15]. Prevention of hydrate formation using some conventional chemical inhibitors in offshore environments may result in several environmental pollution issues. One of such concerns apart from chemical-toxicity is the tendency of some emerging organic chemicals (EOCs) to bio-accumulate in tissues of marine organisms and thus constitute threats to the growth, development and survival of the organism and ultimately creating serious ecological imbalances.

The potential risks that are associated with the use of hazardous chemicals as kinetic hydrate inhibitors in offshore environments are mainly on the influence of the toxic chemicals on aquatic species, population assemblages and ecosystem imbalances through modification of different ecological parameters such as biodiversity, biomass and productivity. These marine species and ecosystems are known to have low resilience and recovery characteristics when subjected to chemical and biological disturbances from different industrial processes including oil and gas production activities. Moreover, these toxic chemicals may contain dispersants which invariably creates two supplementary impacts on the offshore aquatic life. These are the toxic effects of the chemical dispersant itself [16] and secondly the multiplier contamination effect in case of prior hydrocarbon spillage in the offshore environment under consideration due to dispersal of crude oil. These dispersants are known to promote the concentration of hydrocarbon in the environment [17] and invariably increases the availability of oil compounds in the environment and thus enhance toxic effects [18,19]. Hence, the potential impacts of any chemical hydrate inhibitors on the environment are broadly appraised through a well detailed EIA process.

The various environmental tools that are of utmost importance in the assessment of the persistence and environmental friendliness of organic and inorganic chemicals are biodegradability, bioaccumulation and toxicity [20–24]. Bioconcentration factor (BCF) is one of the most important environmental risk assessment criteria that is required by environmental regulatory agencies in the determination of the fate or persistence of an organic chemical compound in the aquatic environment. This factor serves as an important guide in human and aquatic organisms' exposure to any new or existing chemicals.

Bioaccumulation basically refers to an increase in the concentrations of the contaminants or chemicals in marine organism after an uptake from different environmental media such food, nutrient or water. It is concerned with contaminant uptake and elimination in aquatic organisms. This concept is different from bio-availability in the sense that while bioaccumulation is concerned with the differences in the concentrations of the chemicals/contaminants in the living tissue of an organism, bio-availability represents the fraction of contaminants that is potentially available for uptake or actually taken up from the environment. Bioavailability represents the portion of chemical/contaminants in the environment that is required for bio-accumulation to occur. The two concepts are however inter-related.

There are two types of quantitative data that are used to evaluate bioaccumulative characteristics of persistent organic compounds. These are the octanol-water partition coefficient (Kow) and the bioconcentration factor (BCF). The octanol-water partition coefficient, often expressed as Log Kow is a physico-chemical measure of a chemical's tendency to partition into octanol relative to water [25]. Whereas, bioconcentration factor (BCF) is an essential parameter in environmental risk assessment because it provides quantitative information pertaining to the ability of an organic chemical to be taken up by aquatic species from the water. It is frequently used as one of the first screening criteria for persistent organic compounds (POCs), bio-accumulative, and toxic chemical substances analysis. However, BCF is not a constant or a factor as it is commonly portrayed but a variable that depends on different environmental and biological conditions. It is inversely related to the concentration of the contaminant in the water (for metals) or the octanol-water partitioning coefficient (*K*ow) (for organic substances) [26,27].

Toxico-kinetic studies are concerned with the identification of organic chemicals tendencies to accumulate to likely toxic levels on the organism alone or probably behave as toxicity source in higher organisms [28]. In aquatic species, it may involve the study of either accumulation of chemical substances through the exposure of such compound to only water in process that is referred to as bio-concentration or through exposure to both water and food (diet). This latter process is called bioaccumulation or bio-magnification [29,30]. In fish, water or dietary exposure tests, the chemical of interest is allowed to attain steady state equilibrium conditions within the required period of time in the aquatic organism where the rate of chemical uptake is equal to the rate of its depuration (loss). Nonetheless, the uncertainties in the duration to reach steady-state have led to the concept of kinetic bioconcentration factor in which uptake and elimination rates are estimated [31]. This factor can be evaluated in two ways: (1) as a ratio of the compound concentrations in the organism and the water phase at steady-state, or (2) as the ratio of the uptake rate constant ($k1$) and elimination rate constant ($k2$) [32,33].

The initial kinetic BCF model took into consideration several uncertainties such as water volume through the fish gills, rate of assimilation and the body weight of the fish [34]. Whereas, present models have been improved upon to account for water and lipid phase resistance, the partition characteristics of the chemical compound of interest as well as lipid content of the organism [35]. A widely accepted model that is employed in the evaluation of the bioaccumulation of organic chemical in fish via aqueous and dietary exposure is outlined in OECD 305 guidelines [36]. This experiment usually last for twenty days. However, recent investigations for BCF evaluation use shorter exposure times with experimental duration of only 4–7 days in order to determine the likelihood for substance to bio-accumulate in aquatic organisms [37, 38].

Finally, all these eco-toxicity tests are of utmost importance to direct future risk assessment and essential when considering contaminant monitoring in water, sediment and living-organism. Fig. 1 is the pictorial representation of gas hydrates formation in pipelines.

1.1. Materials and method

1.1.1. Red onion skin extract

The red onion skin extract (HPC-ROSE) is abundant in nature. It has higher value of naturally occurring phenolic compounds in the form of vanillic and gallic acids (about 4315.81–6183.5 mgGAE/100g). It also has appreciable quantity of total flavonoids (about 93.51–121.49 mgQE/g) which is present majorly as quercetin. The total tannins content is in the range of 121.48–136.17 mg catechin/g with total anthocyanin value of 748.90–847.47 mg/100g [40]. These compounds are known to inhibit hydrate formation at controlled concentrations.

1.1.2. Determination of the solubility of the inhibitor samples

The solubility of the natural chemical inhibitors was evaluated by column elution technique.

1.1.3. Evaluation of sediment toxicity of the inhibitor samples

The sediment toxicity test was conducted in order to determine the concentration of the inhibitor sample which killed 50 % of the exposed aquatic organism within ten (10) days exposure period. This concentration is referred to as fifty percent lethal concentration (10d LC50). The test was carried out in the laboratory by using the protocols highlighted by **OSPAR Commission** and **ASTM** standard guidelines for conducting 10-day static sediment toxicity tests [41–44]. The experiment involved the monitoring of burrowing and swimming activity of fish species which were exposed to a sediment containing varying concentrations of the organic chemical substances for a period of ten days. The population of surviving organisms at the surface of the sediments and those that were actively swimming after sieving the organisms from the sediment was then recorded.

2.1.4Octanol. -Water partition coefficient (kow) determination by nuclear magnetic resonance technique (1HNMR)

A nuclear magnetic resonance technique (^{1}HNMR) was used to measure the partitioning characteristics of the inhibitors in an immiscible mixture of octanol and water (*Kow)*.

About 50 mg of the inhibitors were dissolved in 750 μL of water at room temperature in a nuclear magnetic resonance (NMR) tube. A pure spectrum of the chemical-water mixture was taken and recorded after which an equal amount of 1-octanol (750 μL) was added to the chemical mixture in the test vessel and the two immiscible phases were adequately mixed by simply inverting the tube for a period of 30 min. The mixture was then allowed to separate for about ten (10) minutes and the NMR spectrum of the aqueous (lower) phase was then carried out and also recorded. A characteristic peak of the tested inhibitor was integrated against the water peak in both spectra. The NMR tube was not shaken during the experiment to prevent emulsification. The aqueous phase was then analyzed by ^{1}HNMR spectroscopy using a benchtop low-field NMR spectrometer. The benchtop ^{1}HNMR analyzer has a frequency of 42.5 MHz with a standard thin-wall tubes of internal dimension of 890 mm^2. The experiment was carried out at laboratory temperature of 25 °C. The schematic representation of the analyte partition between the water and 1-octanol inter-phases at equilibrium is shown in Fig. 2.

Finally, the chemical singlet at $\delta = 2.2$ ppm was integrated against the water peak at $\delta = 4.8$ ppm, whose relative intensity is set to 1.000 in each spectrum for the two ^{1}HNMR spectra.

The octanol-water partition coefficient was then evaluated by using equation 1a.

$$\mathrm{KOW} = \frac{\text{Initial RI} - \text{RI at Equilibrium}}{\text{RI at Equilibrium}} \tag{1a}$$

Where:

Initial RI = the Inhibitor-water mixture spectrum.

RI at Equilibrium = the octanol-water-chemical spectrum.

1.1.5. Bioconcentration test evaluation

The bioconcentration test was performed in the laboratory in a flow through experimental set up according to the guidelines by Ref. [46] (Fish-chemical exposure test). The test is made up of two distinct stages.

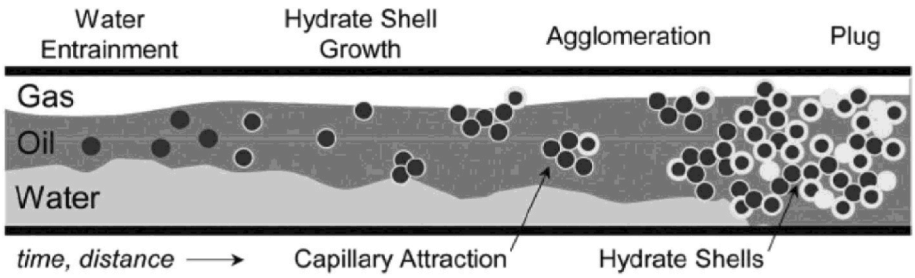

Fig. 1. Hydrates formation in pipelines [39].

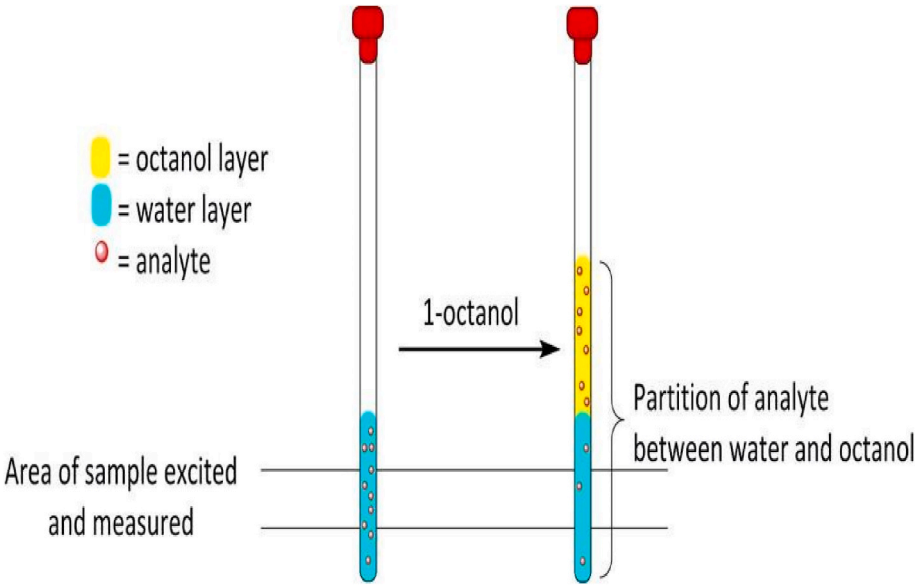

Fig. 2. Schematic representation of Analyte Partition between the water and 1-octanol Inter- Phase at Equilibrium [45].

In the first stage that is referred to as the uptake or exposure phase, a chemical substance of known concentration was introduced into identical small fishes (*Cyprinus carpio*) in a water-containing medium for the ingestion or intake of the chemical compound. While the fishes are then taken to a new medium that is devoid of the tested chemical substance in a post-exposure phase that is known as the depuration or loss phase. This post-exposure phase is very significant except in a situation whereby the amount of chemical uptake by the fish is too unrealistic for any depuration to occur. The chemical substance concentration in the tissues of the aquatic animal was then monitored throughout the two-phases.

For efficient experimental control, a substance of known bioconcentration factor (BCF) was introduced into another set of the aquatic organism under the same laboratory conditions and to link possible errors or adverse effects observed in the bioconcentration test to a matching control group and to obtain background concentrations of the test [47]. In the exposure stage, the duration of test substance intake is dependent on the time in days that steady-state equilibrium was reached. This is usually about twenty-eight (28) days. Although, there are mathematical models that can predict the time of attainment of steady-state equilibrium and by extension the duration of the uptake phase. A twenty-day (20) depuration was maintained.

In the depuration period, further exposure of the test chemical substance was ceased and the fish was transferred to a clean vessel in the absence of the test chemical substance.

The laboratory steady-state BCFss was then measured as the ratio of the chemical concentration in the fish (*Cf*) to its initial concentration in the water (*Cw*) at steady-state. Whereas the kinetic bioconcentration factor (BCFK) was estimated as the ratio of the uptake rate constant ($k1$) and depuration rate constant ($k2$) assuming the reaction follows first order kinetics [48].

The experiment was conducted in a flow through apparatus to enhance continuous dispensing and dilution of the test chemical stock solution (Fig. 3). The apparatus consists of a metering pump, proportional diluter and a saturation system (Fig. 3). The Fish species is *Cyprinus carpio*. Stock solutions of varying concentrations ranging between 50 and 90 mg per litre of the HPC-ROSE was prepared by mixing and agitating each test chemical substance in dilution water while a solid phase desorption dosing mechanism was used to prepare the NVCAP (N-Vinylcaprolactam) stock solutions owing to solubility differences. In the case of the conventional inhibitors, ethanol was used as solvents while 0.01 % of methylcellulose was used as dispersant (solubilizing agent). The solvent concentration in the final test vessel was the same in all

Fig. 3. Bioconcentration experimental set up.

treatments notwithstanding the inhibitor concentration. During the test, the concentration of the inhibitor was maintained below the solubility limit of each inhibitor chemical in the test vessel regardless of the use of solvent or dispersing agent. The test concentration was delivered to the test chambers by a solid phase desorption apparatus. The flow rates of stock solutions and dilution water were checked twice on daily basis during the experiment. The dilution water was at room temperature and was continuously monitored to avoid abysmal variation which in turn may adversely affect the normal functioning of biological factors that are important for chemical uptake and depuration by the aquatic life. For this purpose, a temperature variation of ± 2 °C is acceptable for the purpose of this experiment [49].

Similarly, the concentration of dissolved oxygen was maintained above 60 % saturation. It was ensured that the test substance concentration in the vessel was maintained within ± 20 % of the average value during the exposure phase. At the end of the experiment, the fish mortality rate was less than 10 % in both the control and the natural inhibitors while about 40 % mortality rate was observed in NVCAP.

At the end of the experiment, the important parameters that characterize chemical bioaccumulation were deduced. These include the uptake rate constant ($k1$), depuration or loss rate constant ($k2$), the

steady-state bioconcentration factor (BCFss) and the kinetic bio-concentration factor (BCFK).

1.1.6. Evaluation of bioconcentration factor (BCF) from the laboratory experiment

Considering the equilibrium partitioning model in Fig. 4a, at the end of the depuration phase, the experimental steady-state BCFss was then measured as the ratio of the inhibitor concentration in the fish (*Cf*) to its initial concentration in the water (*Cw*) at steady-state (eq. (1b)).

$$\mathrm{BCF} = \frac{\mathrm{Cf} - \mathrm{ss}}{\mathrm{Cw} - \mathrm{ss}} \tag{1b}$$

Where:

Cf-ss = Concentration of the inhibitor in fish at steady-state (mg kg^{-1} wet weight).

Cw-ss = Concentration of the inhibitor in water at steady-state (mg L^{-1}).

1.1.7. Kinetics of bioconcentration reaction

The general differential bioaccumulation model that characterizes the rate of change in fish-chemical concentration (mg·kg^{-1}·day^{-1}) can be mathematically described in terms of uptake and loss (elimination) processes by equation (2) as shown in Fig. 4b [46].

$$\frac{dCf}{\mathrm{dt}} = \mathrm{K1} * \mathrm{CW} - (\mathrm{K2} + \mathrm{Kg} + \mathrm{Km} + \mathrm{Ke})\,\mathrm{CF} \tag{2}$$

Where:

$\frac{dCf}{\mathrm{dt}}$ is the rate of change in fish-chemical concentration (mg·kg^{-1}·day^{-1}).

Assuming the continuous process is considered to occur in first order reaction.

K_1 = Inhibitor uptake rate constant into fish (L·kg^{-1}·day^{-1}).

K_2 = Inhibitor depuration rate constant from fish (day^{-1}).

K_g = Fish growth rate constant ('growth dilution') (day^{-1}).

K_m = Metabolic transformation rate constant (day^{-1}).

K_e = Faecal egestion rate constant (day^{-1}).

C_W = Concentration of the chemical inhibitor in water (mg·L^{-1}).

C_F = Concentration of the chemical inhibitor in fish (mg·kg^{-1} wet weight).

1.1.8. Estimation of the uptake rate constant and duration

Since the bio-chemical reaction is assumed to be a first order, before conducting the Fish-bioaccumulation experiment, it is imperative to make a rough estimate of depuration rate constant *k*2 from which an approximate time that may be required by the bio-chemical reaction to reach steady-state may be deduced from the mathematical relationships between *k*2 and *Kow* or *k*1 and BCF. Therefore, the rate of chemical inhibitor uptake by water (R_1) and inhibitor depuration in fish (R_2) can be represented by a first order kinetics in Eqs (3) and (4) respectively:

For chemical inhibitor uptake by water, neglecting the depuration term of equation (2), then,

$$\textit{Rate of Inhibitor uptake by water}\ (R_1) = K_1 * C_w \tag{3}$$

Similarly, from eq (2), assuming steady-state behaviour and neglecting the growth, metabolism and Faecal egestion (K_g, K_m, *and* K_e) *rate constants respectively*.

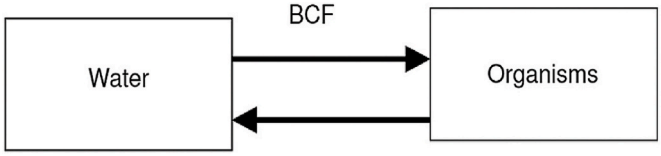

Fig. 4a. Equilibrium partitioning model for bioconcentration factor.

The rate of inhibitor depuration is thus expressed by equation 4

$$\textit{Rate of Depuration in fish}\ (R_2) = K_2 * C_f \tag{4}$$

At steady state, the inhibitor uptake rate is equal to the rate of its depuration (loss) as shown in equation (5),

$$R_1 = R_2 = K_1 * C_w = K_2 * C_f \tag{5}$$

Therefore, equation (6) is the simplified form of equation 5

$$\text{Hence,}\ \frac{C_{f-ss}}{C_{w-ss}} = \frac{K_1}{K_2} \tag{6}$$

The ratio *k*1/*k*2 is referred to as the kinetic BCF (BCFK) (eq (7)) and it is equal to the steady-state BCF (BCFSS) obtained from the ratio of the steady-state concentration in fish to that in water.

$$(\mathrm{BCFK}) = \frac{K_1}{K_2} \tag{7}$$

1.1.9. Mathematical relationship between n-octanol partition coefficient (k_{ow}) and inhibitor uptake and depuration rate constants (K_1 and K_2)

Different mathematical models are available for the estimation of BCF, inhibitor uptake and depuration rate constant (K1 and K2 respectively) (day^{-1}) [51–54].

The relationship between Log K_{OW} and depuration rate constant (K2) according to Ref. [51] is mathematically described by equation (8).

$$Log\ K_2 = 1.47 - 0.414\ Log\ K_{OW}\ r^2 = 0.95 \tag{8}$$

Similarly [53], gave the empirical relationship between the chemical uptake rate constant (K1) and the average weight of the Fish sample according to equation 9

$$K\_(1) = 520 * \widehat{W}(-0.32)\ \ (\text{for substances with Log KOW>3}\ \hat{r}(2) = 0.85 \tag{9}$$

The Bioconcentration factor (BCF) can be expressed in terms of partition characteristics by equation (10) below

$$BCF = 10^{0.910 log K} OW - 1.975 \log(6.8 * 10^{-7} K_{OW} + 1) - 0.786)\ r^2 = 0.90 \tag{10}$$

W = mean weight of the treated fish (grams wet weight after uptake/immediate beginning of depuration.

1.1.10. Prediction of the duration of the depuration phase

The time that is required to attain a certain percentage of steady-state may be obtained by integrating the general kinetic bio-accumulation model with respect to first order reaction.

Equation (11) is the simplified expression of equation (2) by assuming that growth, metabolism and Faecal egestion (K_g, K_m, *and* K_e) *rate constants respectively* are negligible in the general bio-accumulation model.

$$\frac{dcf}{dt} = K_1 * C_w - K_2 * C_f \tag{11}$$

Where,

K_1 = Inhibitor uptake rate constant into fish (L·kg^{-1}·day^{-1}).

K_2 = Inhibitor depuration rate constant from fish (day^{-1}).

C_W = Concentration of the chemical inhibitor in water (mg·L^{-1}).

C_F = Concentration of the chemical inhibitor in fish (mg·kg^{-1} wet weight).

Equation (12) is the Integral solution of equation (11) and assuming that the concentration of the inhibitor in water C_W is constant,

$$C_F = \frac{K_1}{K_2} * C_W\left(1 - e^{-k_2 t}\right) \tag{12}$$

At steady state, $t \rightarrow \infty$ and $C_F = C_{f-ss}$

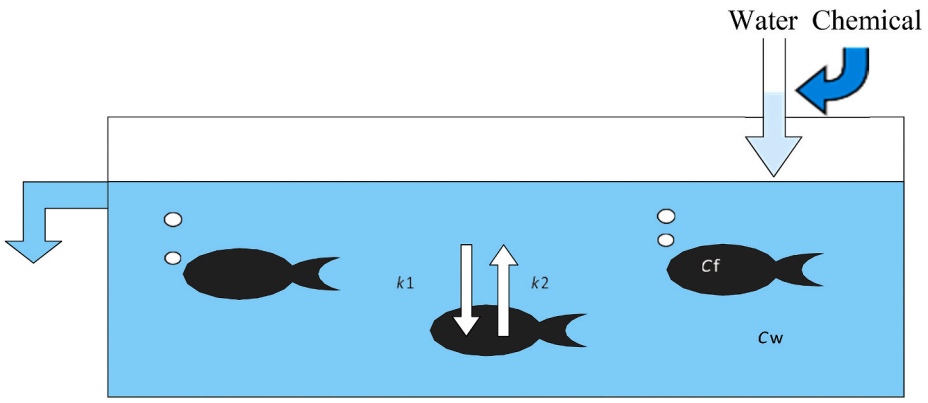

Fig. 4b. Kinetic Bioaccumulation Model for bioconcentration [50].

Hence, equation (12) is then simplified into eq. 13

$$C_{F-ss} = \frac{K_1}{K_2} * C_W \tag{13}$$

By replacing $\frac{K_1}{K_2} * C_W$ with C_{F-ss} in equation (13), gives equations (14) and (15) respectively

$$C_F = C_{f-ss}\left(1 - e^{-K}2t\right) \tag{14}$$

$$\text{Therefore,} \frac{CF}{Cf - ss} = 1 - e^{-K}2t \tag{15}$$

Where: C_F is the initial Chemical inhibitor concentration in fish ($mg{\cdot}kg^{-1}$ wet weight).

C_{f-ss} = Final inhibitor concentration in fish at steady-state ($mg\ kg^{-1}$ wet weight).

1.1.11. Half-life of a first-order biochemical reaction

The half-life of a chemical/biochemical reactionis the time taken for the initial concentration of the reactant(s) to transform into half of its initial concentration (time to reach 50 % percent completion).

The final steady state concentration is expressed by equation 16

$$\left[C_{f-ss}\right] = \left[C_f\right]^{-Kt} \tag{16}$$

For first order reaction, the final concentration can be expressed in terms of its initial value by equation 17

$$\text{Since } C_{f-ss} = 1 - C_f \tag{17}$$

Therefore, substituting eq. 17 into 16, we have eq 18

$$\text{Hence, } C_f = 1 - e^{-Kt} \tag{18}$$

At time (t) = $t\frac{1}{2}$, (that is time to reach 50 % steady state), the final concentration is expressed by eq 19

$$\boldsymbol{C}_{f-ss} = \left[\frac{Cf}{2}\right] \tag{19}$$

Substituting for C_{f-ss} in equation (16), we have eq 20

$$\left[\frac{Cf}{2}\right] = [Cf]e^{-Kt\frac{1}{2}} \tag{20}$$

Solving equation (20) gives us eq 21

$$t_{50} = \frac{In2}{K_2} = \frac{0.693}{K_2} \tag{21}$$

Equation (21) is the time required for 50 % steady state condition.

Also, equation (22) is the time required for 90 % steady state behaviour,

$$t_{90} = \frac{In10}{K_2} = \frac{2.30}{K_2} \tag{22}$$

2. Results and discussions

2.1. Toxicity of inhibitors

The solid-phase (sediment) tests were performed to assess the potential risks of inhibitor exposure to pelagic and benthic organisms. For the N-VCAP conventional inhibitor, lower lethal concentrations (LC50) of less than 1500 mg/L was able to kill 50 % of fish species within 24-h window period during sediment toxicity test (Table 1). Whereas, the HPC-ROSE naturally occurring inhibitor sample has a higher lethal concentration of greater than 20000 mg/kg for mortality of 50 % of the exposed organism during a 10-day window period. This indicates its high non-toxicity. Similarly, the ethyl acetate reference chemical (EtAOc) is not toxic with a high lethal concentration of 15750 mg/L (Table 1). The toxicity of most organic chemicals is mainly due to the presence of appreciable quantities of amide as indicated in their FTIR [55].

2.2. Octanol-water partition coefficient through ^{1}HNMR

The ^{1}HNMR spectra of NVCAP is shown in Fig. 5a and b. The assignment of individual peaks for the proton types a, b, c, d and e for the initial resonance image (RI) ranges between 1.5 ppm and 7.1 ppm while that of the equilibrium ranges between 0.85 ppm and 4.5 ppm. The logarithm of octanol water partition coefficient of the NVCAP from these proton peaks was estimated as 1.50. Whereas, the Log Kow of the ethyl acetate reference substance (EtOAc) is 0.70 with a spectrum band in the range of 0.50 and 5.0 ppm in water while a spectrum band in the range of 1.2 ppm and 4.2 ppm was observed in octanol-water mixture at equilibrium (Fig. 6a and b). The HPC-ROSE (Fig. 7a and b) has a Log Kow of 1.2 with an initial resonance between 1 ppm and 7 ppm. Whereas, it was in the range of 1 ppm and 5 ppm at equilibrium. The results showed good agreement with that of shake flask and high-performance liquid chromatography techniques with ethyl acetate Log Kow value of 0.71 in comparison with 0.70 that was obtained by ^{1}HNMR [49,56,57]. The octanol-water partition coefficient (Kow) measures the

Table 1
Toxicity of inhibitor and reference chemical substance.

Chemical Sample	HPC-ROSE	EtAOc (Reference)	N-VCAP
LC50 (Mg/L)	25140	15750	1280
Interpretation	LC50 was greater than 25000 mg/L	LC50 was greater than 15000 mg/L	LC50 was Less than 1500 mg/L
Remarks	Highly Non-Toxic	Non-Toxic	Highly-Toxic

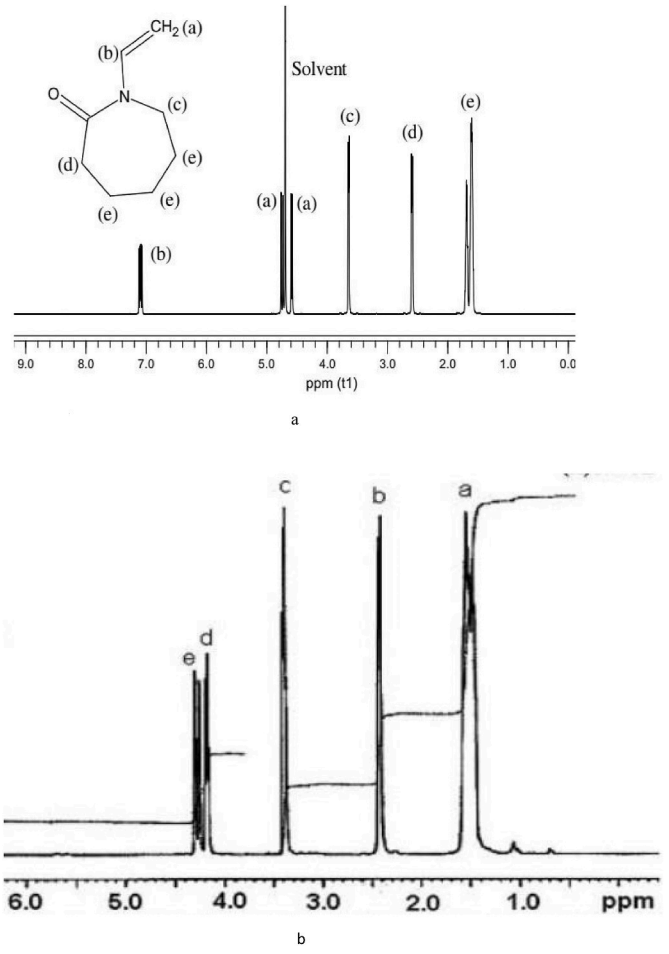

Fig. 5. a: Nuclear Magnetic Resonance (^{1}HNMR) Spectrum of N-VCAP in Water, b: Nuclear Magnetic Resonance (^{1}HNMR) Spectrum of N-VCAP in Octanol-Water Mixture.

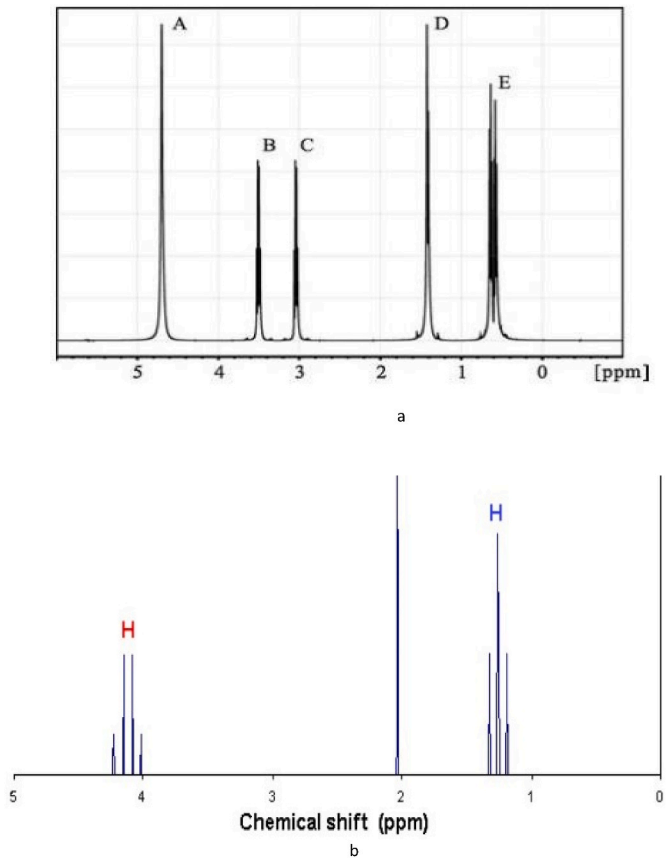

Fig. 6. a: Nuclear Magnetic Resonance (^{1}HNMR) Spectrum of Ethyl Acetate in Water mixture, b: Nuclear Magnetic Resonance (^{1}HNMR) Spectrum of Ethyl Acetate in Octanol-Water mixture.

hydrophobicity or lipophilicity of the inhibitor samples and it is an important characteristic of any chemical substance and it is crucial in determining the fate of the inhibitors on the environment and in living organisms [58–60]. It is imperative to know that bio-chemical factors such as bio-accumulation and toxicity are determined by Kow to a significant extent. Generally, a chemical compound with a (***Log*** (***Kow***)) values between 3 and 6 has the potential to bio-accumulate significantly. However, organic compound with octanol/water partition coefficient (***Log*** (***Kow***)) values that are lesser than 3 are not readily adsorbed/absorbed into the octanol and thus readily desorb back into the water phase. Hence, such compounds do not readily bio-accumulate [14,25].

2.3. Relationship between solubility, Log Kow and Bioconcentration factor

There is an inverse relationship between log Kow and aqueous solubility. The ethyl acetate reference chemical (EtOAc) has highest aqueous solubility and thus lowest log Kow and BCF values. The ethyl acetate has aqueous solubility of 8 *10^{-1} mg/L and a lower Log Kow value of 0.70. Thus, lower BCF values of 88.50 and 80.15 L/kg (Table 3). The naturally occurring high-phenolic red onion skin extract (HPC-ROSE) has high aqueous solubility of 0.728*10^{-1} mg/L and a Log Kow value of 1.2 with lower steady state BCF values of 251.5 and 215 L/kg at chemical-water concentration of 50 and 90 mg/L respectively (Table 2). However, the NVCAP has aqueous solubility of 0.62*10^{-1} mg/L and a higher Log Kow value of 1.50 with higher steady state BCF values of 485 and 452.5L/Kg at Chemical-water concentration of 50 and 90 mg/L respectively at steady state (Table 4).

Therefore, the tendency of the different chemicals to bio-accumulate is in the order:

EtOAc < HPC-ROSE < NVCAP

2.4. Steady state bioconcentration factor

Bioconcentration factor (BCF) evaluation is an *in vivo* measure of bio-accumulative potential. Fundamentally, an organism, usually fish, is exposed to a constant concentration of the test chemical in water until equilibrium is attained between the concentration in the water and that of organism tissues. The BCF is thus estimated as the tissue-chemical concentration divided by the water-chemical concentration at equilibrium.

From Table 2 and Fig. 8, the HPC-ROSE has a steady state bio-concentration factor in the range of 215–251 L/kg and a predicted BCF factor of 259.6L/kg. The Log BCF is in the region of.

2.332 and 2.401 (Fig. 9). However, observations from Table 4 and Fig. 8, the N-Vinylcaprolactam (NVCAP) Kinetic hydrate Inhibitor has a higher steady-state bioconcentration factor with values in the range of 485 L/kg and 442.05 L/kg for the tested chemical concentration amounts (50–90 mg/L) while the calculated value is 497 L/kg. Higher Log BCF numerical values (2.685 and 2.645) were also observed at steady state for the NVCAP (Fig. 9). The Ethyl Acetate, (EtOAc) standard reference chemical has the lowest steady state BCF value in the range of 88.50 and 82.75 L/kg with a predicted value of 91 L per kilogram (Table 3 and Fig. 8). The logarithm value was between 1.947 and 1.904 (Table 3 and Fig. 9).

The N-Vinylcaprolactam has a higher BCF values compared to the high-phenolic compound red onion skin extract (HPC-ROSE) but within

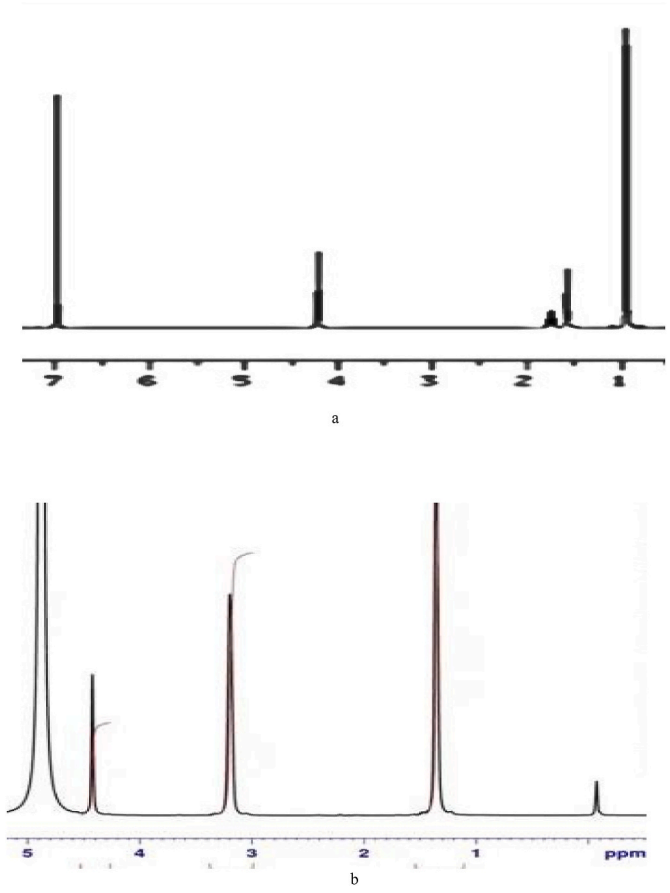

Fig. 7. a: Nuclear Magnetic Resonance (^{1}HNMR) Spectrum of HPC-ROSE in Water, b: Nuclear Magnetic Resonance (^{1}HNMR) Spectrum of HPC-ROSE in Octanol-Water Mixture.

Table 2
Bioconcentration parameter results for HPC-ROSE kinetic Inhibitor
Log Kow = 1.2, K2 = 9.402day^{-1}.

Cw−ss (mg L^{-1})	Cf−*ss* (kg kg^{-1} wet weight)	BCFss (L/Kg)	Log BCF	Uptake-Rate constant (K1) (L·kg^{-1}·day^{-1})	BCFcal (L/Kg)
50	12575	251.50	2.401	2364.50	259.6
60	14580	243	2.386	2284.6	259.6
70	16212	231.6	2.365	2177.50	259.6
80	17600	220	2.342	2068.44	259.6
90	19350	215	2.332	2021.43	259.6

Table 3
Results of bioconcentration parameters for ethyl acetate (EtOAc) reference Chemical
Log Kow = 0.70, K_2 = 15.14day^{-1}.

Cw−ss (mg L^{-1})	Cf−*ss* (mg kg^{-1} wet weight)	BCFss (L/Kg)	Log BCF	Uptake-Rate constant (K1) (L·kg^{-1}·day^{-1})	BCFCal (L/Kg)
50	4425	88.50	1.947	1339.89	91
60	5220	87.00	1.940	1317.18	91
70	5971	85.30	1.931	1291.44	91
80	6620	82.75	1.918	1252.08	91
90	7213.5	80.15	1.904	1213.47	91

manageable accepted limit because a BCF value that is greater than 1000 L/kg or log BCF that is greater than 3 may constitute serious environmental concerns [61,62]. Organic chemicals with BCF values of

Table 4
Result of Bio-centration Parameters for N-Vinylcaprolactam (NVCAP) Kinetic Inhibitor
Log Kow = 1.50, K2 = 6.996 day^{-1}.

Cw−ss (mg L^{-1})	Cf−*ss* (mg kg^{-1} wet weight)	BCFss (L/Kg)	Log BCF	Uptake-Rate constant (K1) (L·kg^{-1}·day^{-1})	BCFK (L/Kg)
50	24250	485	2.685	3378.51	497
60	28260	471	2.673	3295.12	497
70	32410	463	2.666	3239.15	497
80	36200	452.5	2.655	3165.69	497
90	39785	442.05	2.645	3092.58	497

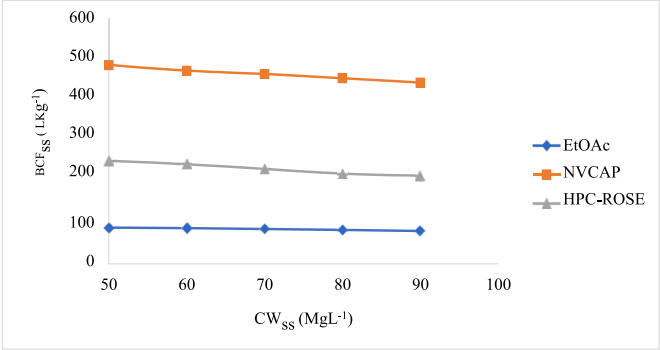

Fig. 8. Bioconcentration factor (BCFss) of contaminants/inhibitors variation with chemical concentration in water.

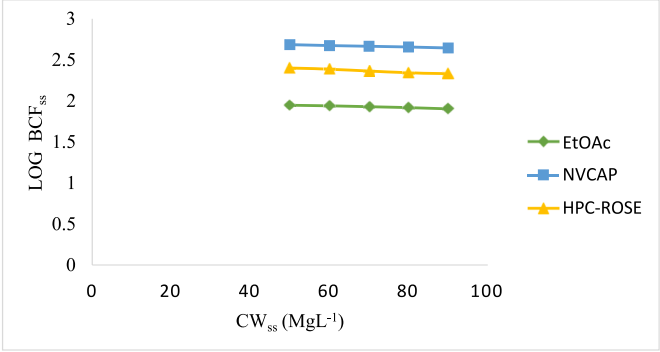

Fig. 9. LOG-BCFss of contaminants/inhibitors variation with chemical concentration in water.

less than 1000L/Kg or Log BCF that is below 3 are less likely to bioaccumulate in aquatic organism tissues owing to their relative high-water solubility characteristics. However, chemical compounds with intensely low water solubility have a likelihood to precipitate out of solutions or bind to suspended particles. All the inhibitor samples are hydrophilic with good solubility in water (Log Kow ≤1.60). These lower Log K_{OW} values greatly reduced uncertainties in the aqueous Fish-exposure bioconcentration test. However, in case of highly hydrophobic chemicals with (log *KOW* > 5 and a solubility below ~ 0.01–0.1 mg/L), this testing method may be marked with high degree of uncertainties. This may be due to inability to maintain constant aqueous concentration because of the following reasons. These are (1) Liquid sorption exposure vessel glass (2) rapid substrate uptake by the fish (3) low chemical concentration below analytical limit of quantification [63]. However, uptake may be hindered by low exposure concentrations due to low water solubility in the test while higher exposure concentrations can be attained with the dietary test. Thus, the use of dietary test is highly recommended for these highly hydrophobic chemicals in as

much as important regulatory and risk assessment procedures are satisfied [46]. The steady state bioconcentration factor depends on the type of organism, the pattern of contamination within the organism's range, the part of the organism considered (lipid tissue being higher), and the duration of exposure or maturity of the organism among other factors [64,65]. Relatively water-insoluble compounds will less efficiently reach equilibrium compared to those that are water soluble.

2.5. Effects of chemical concentration in water on uptake rate and steady state BCF

The NVCAP has the highest uptake rate constant (K_1) at all the tested chemical concentration (Fig. 10, Table 4) and thus highest steady state BCF. Whereas, the HPC-ROSE has lower uptake rate constant (K1) and lower bio-accumulation tendencies (Fig. 10, Table 3). The steady state bioconcentration factor has an inverse relationship with chemical concentration in water (Fig. 8). Similarly, the uptake rate constant has a negative relationship with chemical concentration in water (Fig. 10). The uptake rate, K_1, is closely related to the physiology of the organisms such as the body size of fish. Relatively small organisms display a higher uptake rate than larger ones [66,67]. Moreover, the uptake rate of a chemical compound can also be affected considerably by environmental factors. These include, salinity, temperature, dissolved organic matter (DOM) and dissolved oxygen among others. Most of these abiotic factors are due to changes in the speciation of the organic compound as well as the physiological and biochemical processes of the aquatic life.

Salinity is undoubtedly the best studied environmental factor affecting uptake rate (K1) [68]. Apart from salinity's direct effect on speciation, it can also trigger physiological changes [69]. The influence of dissolved organic matter in chemical uptake is dependent on the organism type, the nature of the organic chemical and its quantities. Higher amount of dissolved organic matter can invariably reduce the bio-available fraction of the chemical and thereby lower chemical uptake [70,71] Organic compounds bioavailability to marine organisms is contingent on the physical and chemical nature of the chemical. Organic chemicals in solution of marine water are more bio-available than when they are in complexed, adsorbed or solid form.

Non-polar organic compounds are termed hydrophobic or lipophilic compounds because they are usually characterized by low water solubility and higher lipids solubility. The rate and extent of hydrophobic compounds bioaccumulation by marine organisms depends on the relative affinity of the organic compounds for the water and lipid phases at ambient conditions. Bioconcentration factor is an important parameter that helps to define this affinity. The rates of absorption of the chemical and its desorption from the lipid phase are equal under equilibrium condition [72,73].

Chemical hydrophobicity is considered to be a significant factor which affects the uptake of chemicals into aquatic life (plants and animals) through diffusion [74]. The highest potential for uptake is observed in organic compounds with partition coefficient between 1 and 2.5. This is due to the balance of lipid and aqueous solubility in such compounds [75,76]. While ionic compounds exhibit a negative correlation between log Kow and BCF, the cationic moieties and neutral compounds have positive relationship between Log Kow and Bioconcentration factor (BCF) [77]. This indicates higher accumulation potential of cationic hydrophobic substance.

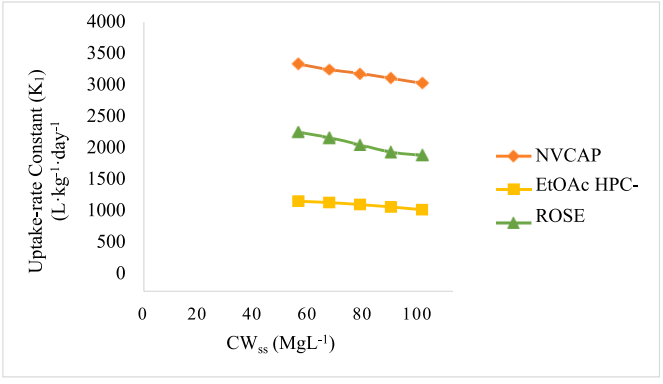

Fig. 10. Uptake-rate constant of contaminants/inhibitors versus chemical concentration in water.

Molecular ionization is another important factor that affects uptake of organic compounds apart from hydrophobicity. Charged molecules usually have a lower uptake potential because ionization can cause permeability reduction across cell membranes [78,79]. Also, uptake rate is significantly affected by different organism lipid concentration. There is a marked variation in the uptake of organic contaminants between different plants and animals' species. The uptake of hydrophobic organic contaminants in aquatic life is influenced by the lipid content [80].

There is a strong positive relationship between BCF and lipid contents. This is due to the hydrophobic partitioning governing the uptake of hydrophobic organic compounds. Nevertheless, this correlation may not hold for ionizable compounds. The lipid content is an important indicator of the ability of an organism to uptake many hydrophobic compounds.

The general mechanism for the uptake and elimination of non-ionizable organic compounds are: chemical transport to and from gill surfaces through water and blood media, diffusion of chemicals through epithelia cells, and chemical cleavage to water and blood components. In addition to these mechanisms [81], included three other processes in order to develop a new model for the uptake and elimination of ionizable organic chemicals at fish gills. These are alteration of PH by excretory products at gill surfaces, and thus affect the relative quantity of neutral and ionized molecules in comparison to that initially exposed water. Also, ionized molecules promote chemical flux to and from the membrane of the epithelial cell and thus influence uptake and depuration in impenetrable membrane through high diffusion gradients. Lastly, membrane obstructions are not totally impenetrable to ionized molecules. In fact, restricted permeability can have considerable influence on chemical flux.

2.6. Relationship between Log Kow and predicted BCF values

The Predicted BCF values were higher than the steady state BCF values for all the tested inhibitors and at all the concentrations (Tables 2–4, Fig. 11a–e). These values were obtained from the empirical relationship between log Kow and bioconcentration factor. Different linear regression models are available to predict the relationship between log Kow and log BCF for polar and non-polar compounds [82–84]. The primary source of error is due to the method of Log Kow estimation since most of the empirical models are usually One-factor model consisting of partition coefficient and BCF. The methods of Kow estimation are shake-flask method, NMR technique and reversed-phase high performance liquid chromatography technique. Hydrophobic compounds with log Kow values between 3 and 3.5 may bio-accumulate rapidly but not to high concentrations in aquatic organism tissues, most especially if they are readily biodegradable [85]. Whereas those with log Kow values between 6.5 and 7 do not bioaccumulate effectively from the water, because their solubility in both the water and lipid phases is very low [86]. Bio-availability is also size dependent. Large molecules with longer chain length may not be able to permeate biological membranes and therefore not bioavailable [87,88]. The ethyl acetate control sample is moderately soluble in water and has a low log Kow of 0.70 and thus bioavailable; nevertheless, they are readily biodegradable and do not bioaccumulate to biologically significant concentrations in tissues of marine animals.

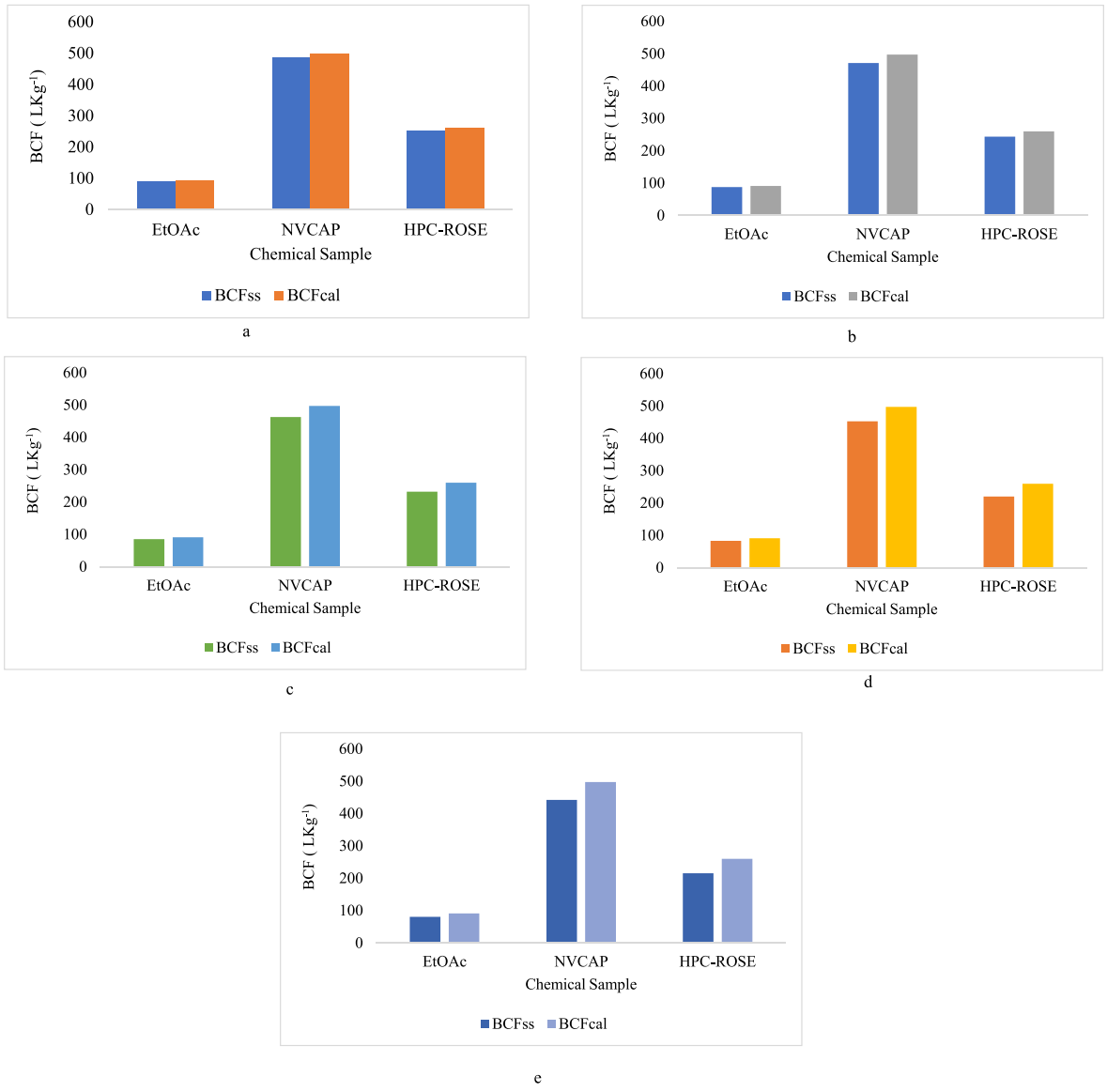

Fig. 11. a: Steady State and Calculated BCF at 50 mg/L Chemical Concentration, b: Steady State and Calculated BCF at 60 mg/L Chemical Concentration, c: Steady State and Calculated BCF at 70 mg/L Chemical Concentration, d: Steady State and Calculated BCF at 80 mg/L Chemical Concentration, e: Steady State and Calculated BCF at 90 mg/L Chemical Concentration.

3. Conclusion

i. The HPC-ROSE does not constitute environmentally significant risk to aquatic life owing to its lower BCF values between 215 L/Kg-251.5L/Kg and higher lethal concentration of 25140 mg/L unlike the NVCAP which is very toxic with lower lethal concentration of 1280 mg/L and higher BCF values in the range of 442.5L/Kg to 485 L/kg.

ii. The HPC-ROSE naturally occurring inhibitor sample has a higher lethal concentration of greater than 20000 mg/kg and thus highly-non-toxic. Whereas, the NVCAP hydrate inhibitor is highly toxic with Lower lethal concentrations (LC50) of less than 1500 mg/L which was able to kill 50 % of fish species within 24-h window period during sediment toxicity test.

iii. The HPC-ROSE naturally occurring kinetic inhibitor has a lower Log Kow value of 1.20 while the NVCAP has a higher value of 1.50. Nevertheless, the two kinetic inhibitors will not bio-accumulate in offshore environment.

iv. Nuclear magnetic resonance (^{1}HNMR) is a simple and reliable method of estimating partition coefficient characteristics (Kow) because the obtained Log-Kow values showed good agreements with that of shake flask and high-performance liquid chromatography techniques.

v. The NVCAP has the highest uptake rate constants (K1) at all the tested chemical concentrations and thus highest steady state BCF whereas, the HPC-ROSE has lower uptake rate constant (K1) and lower bio-accumulation tendencies.

vi. The chemical concentration in water has an inverse relationship with uptake rate constant (K_1) and steady-state bioconcentration factor (BCFss).

vii. The Predicted BCF values were higher than the steady state BCF values for all the tested inhibitors and at all the concentrations. This is due to the route by which Log Kow was estimated since most of the empirical models are usually one-factor model consisting of partition coefficient and BCF.

viii. The rate and extent of organic compounds bioaccumulation by marine organisms depend on the relative affinity of the organic compounds for the water and lipid phases at ambient conditions.
ix. It is therefore recommended that oil and gas operators must carry out environmental viability tests such as toxicity and bio-accumulation tests before any chemical whether new or existing is deployed in the offshore fields.

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CRediT authorship contribution statement

Okon Efiong Okon: Conceptualization, Data curation, Formal analysis, Funding acquisition, Investigation, Methodology, Validation, Visualization, Writing - original draft, Writing - review & editing. **Joseph Atubokiki Ajienka:** Conceptualization, Resources, Supervision, Writing - review & editing, Visualization. **Sunday Sunday Ikiensikimama:** Conceptualization, Resources, Supervision, Visualization, Writing - review & editing. **Onyewuchi Emmanuel Akaranta:** Conceptualization, Resources, Supervision, Writing - review & editing. **Virtue Urunwo Wachikwu-Elechi:** Conceptualization, Resources, Writing - review & editing.

Declaration of competing interest

Authors have declared that there is no conflict of interest. This manuscript has not been submitted to nor is under review at another journal or other publishing venue. The authors have no affiliation with any organization with a direct or indirect financial interest in the subject matter discussed in the manuscript.

Data availability

The data that has been used is confidential.

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