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Impact of pH Variation on Coag-flocculation Behaviour of Chitin Derived Coag-flocculant in Coal Washery Effluent Medium

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ABSTRACT

This work investigates the influence of pH variation on coag-flocculation kinetics and performance of Chitin Derived Coag-flocculant (CDC) in removal of Suspended and Dissolved Particles (SDP) from Coal washery effluent (CWE) medium. Key parameters such as rate constant K_m, half life $\tau_{1/2,}$, and pH etc. were investigated. The best coag-flocculation performance is recorded at $K_{m,}$ of 0.007 l/mg.min, $\tau_{1/2,}$ of 0.0362min, pH of 8, dosage of 100mg/l and efficiency E(%) of 99.933. Minimum efficiency (%) > 94.00 was achieved at 30 minutes of coag-flocculation, establishing CDC as an effective water treatment agent at the conditions of the experiment.

Keywords: *Coal effluent, coag-flocculation, coagulation, chitin, chitosan*

1. INTRODUCTION

The biosphere is increasingly exposed to pollution threats in spite of the global efforts to protect it. Anthropogenic activities are the significant and dominant sources of these threats. The growing human needs and ceaseless drive to satisfy them have led to the production of varying forms of harmful wastes that ultimately rest in our aqua systems. The implication is that much of the water cannot be used without a form of treatment. This situation brings to the fore the needed impetus to focus on challenges inherent in hydro management, especially in developing countries where discharge of effluent such as CWE is common.

CWE, emanating from washery unit of coal mining operation depicts elevated concentrations of organic and inorganic loads [1,2]. Such loads include kaolinite, illite, muscovite, quartz, bacteria, colloids, virus, color, nitrogen, aromatics, sulphur, phosphorus etc. These contaminants make CWE a significant environmental pollutant, and thus subject to removal during treatment processes such as coag-flocculation [3,4].

Coag-flocculation as a treatment procedure has existed for years. The procedure is accomplished by the addition of ions having opposite charge to that of the particles. Typically, the ion species are from metal salts, capable of destabilizing stable colloids in suspension, such that they can agglomerate into settleable floc [5,6]. The application of Al and Fe salts are well established in the practice, though they are linked with health and cost challenges [6].

Attempts to confront these challenges highlight the persistent search for new substitutes to metal salts and the current drive to improve the efficiency of existing substitutes [7,8,9]. Among the established existing substitutes is chitin derived coag-flocculant (CDC), popularly known as chitosan. CDC is obtained from chitin of crustaceans such as crawfish and crab. CDC, a polycationic, biodegradable, non-toxic and high molecular weight linear copolymer of glucosamine and N-acetyl glucoseamine, is soluble and positively charged in acid media and may therefore be used as eco-friendly coag-flocculant [10,11].

CDC has been widely used as an effective coag-flocculant for a wide variety of suspended solids in various food and fish processing industries [12,13,14] and suspension containing mineral colloids in water [11,15,16,17,18]. The reactivity of CDC during coag-flocculation of suspended and dissolved particles (SDP) results from several mechanisms, including electrostatic attraction, sorption and bridging. The contribution of each mechanism depends on the pH of the suspension.

In this presnt study, the influence of CDC dosage and CWE pH on the kinetics and coag-flocculation efficiency of the process were examined. It is expected that the kinetics results will enrich the existing kinetic data towards development of more efficient and robust coag-flocculation units that ensure the conservation of the environment.

2. THEORY.

The rate of successful collision between particles of sizes i and j to form particle of size k is [19]:

$$\frac{dn_k}{dt} = \frac{1}{2}\sum_{i+j=k} \beta_{BR}(i,j)n_i n_j - \sum_{i=1}^{\alpha} \beta_{BR}(i,k)n_i n_k \qquad \ldots 1$$

where $\beta_{BR(i,j)}$ is Brownian aggregation factor for flocculation transport mechanism, $n_i n_j$ is particle aggregation concentration for particles of size i and j, respectively.

It has been established that [19,20]:

$$\beta_{BR} = \frac{8}{3}\varepsilon_p \frac{K_B T}{\eta} \quad \ldots 2$$

where K_B,T ,η, ε_p are Boltzmann constant, temperature, viscosity and collision efficiency factor, respectively.

It can be shown that:

$$\frac{1}{2}\beta_{BR} = \varepsilon_p K_R = K_m \quad \ldots 3$$

$$-\frac{dN_t}{dt} = K_m N_t^{\alpha} \quad \ldots 4$$

K_R is defined as Von Smoluchowski rate constant for rapid coagulation. K_m is Menkonu coag-flocculation rate constant accounting for Brownian coag-flocculation transport of destabilized particles at α^{th} order. N_t is the concentration of SDP at time, t [9,21,22].

Graphical representation of linear form of equation 5 at α=2 provides K_m from the slope of equation below:

$$\frac{1}{N} = K_m t + \frac{1}{N_0} \quad \ldots 5$$

where N_0 is upper limit of N_t at t>0. N_0 is N_t at t=0.

Equation 6 can be solved to obtain coag-flocculation period, $\tau_{1/2}$

$$\tau_{1/2} = (0.5 N_0 K_m)^{-1} \quad \ldots 6$$

Equation 2 solved exactly results in generic expression for microscopic aggregation

$$\frac{N_{m(t)}}{N_0} = \frac{\left[1/\tau_{1/2} \right]^{m-1}}{\left[1 + \frac{t}{\tau_{1/2}} \right]^{m+1}} \quad \ldots 7$$

m=1(monomer), m=2(doublet),m=3(triplet)

Efficiency of coag-flocculation is expressed as:

$$E(\%) = \left[\frac{N_0 - N_t}{N_0} \right] 100 \quad \ldots 8$$

3. MATERIALS AND METHODS

3.1. Materials Collection, Preparation and Characterization

3.1.1. Coal washery effluent

The effluent was taken from a coal mine located in Enugu, Enugu State, Nigeria. The characterization of the effluent presented in Table 1 were determined based on standard method [23].

3.1.2. Crab shell sample

Crab Shell samples (precursor to CDC) were sourced from Nsugbe, Anambra State, Nigeria. CDC was prepared according to procedure reported by Fernandez-Kim [24]. The characteristics of the sample on the bases of AOAC standard method [25] are presented in Table 2.

Table 1: Characteristics of coal washery effluent

Parameters	Values
pH	2.5200
Turbidity (NTU)	5387.0000
Total hardness(mg/l)	358.0000
Ca hardness (mg/l)	306.0000
Mg hardness (mg/l)	52.0000
Ca^{2+}(mg/l)	122.4000
Mg^{2+}(mg/l)	15.6000
Fe^{2+}(mg/l)	0.2500
SO_4^{2-}(mg/l)	72.0000
NO_3^{2-}(mg/l)	Nil
Cl^-(mg/l)	184.3400
E.cond(μm/m^2)	805.2000
TDS (mg/l)	450.9120
TSS (mg/l)	109.6000
T.Coliform	Nil
Plate Count	4.0000s
E-Coli	Nil
BOD_5	1001.0110

Table 2 : Characteristics of coag-flocculant

Parameter	CDC
Moisture content (%)	9.7700
Ash content (%)	2.6800
Lipid content (%)	27.1800
Crude protein(%)	44.3800
Carbohydrate(%)	16.2600

3.2. Coag-flocculation Experiments

Experiments were conducted using conventional jar test apparatus. Appropriate dosage of CDC in the range 100-500mg/l was added directly to 200ml of CWE. The suspension, tuned to pH range 2-10 by application of H_2SO_4/ NaOH was subjected to 2 minutes of rapid mixing(250rpm),20minutes of slow mixing (20rpm) and followed by 30 minutes of settling. During settling, samples were withdrawn from 2cm depth and turbidity (converted to SDP in mg/l) changes measured for kinetic analysis. .

4. RESULTS AND DISCUSSION

The results of the investigation on the coag-flocculation of CWE by CDC are presented and discussed sequentially as presented below:

4.1 Coag-Flocculation Kinetics

Presented in tables 3-7 are functional kinetics parameters obtained for the coag-flocculation of CDC in CWE at pH 2, 4, 6, 8, 10 for 100, 200, 300, 400, 500mg/l CDC dosages. Linear regression coefficient (R^2) was employed in evaluation of the level of accuracy of fit of the experimental data on the considered model equation 5. Tables 3-7 indicate that data (with majority of $R^2 > 0.9$) were significantly described by the linearized form of equation 4 expressed as equation 5.

K_m , determined from the slope of equation 5 is a vital factor that determines the rate of reaction. Higher K_m translates to higher rate of coag-flocculation. K_m is evaluated by fitting the experimental data on the plot of (1/N) or (1/SDP) against time as can be deduced from equation 5. Representative results for the various dosages and pH as displayed in tables 3-7 are graphically depicted in Figure 1. It should be noted that the trends for the various dosages and Ph(not shown) are identical. $K_m(=0.5\ \beta_{BR})$ as expressed in equation 3 and shown in tables 3-7 recorded maximum and minimum values of 0.007 and $3x10^{-5}$ l/mg.min, respectively. It can be observed that least values of K_m were obtained at pH 2. One possible explanation is the likelihood of excess protonation of the particles, leading to partial or total charge reversal. The consequence is the prevalence of repulsion of the particle and the attendant poor performance observed in pH 2. From pH 4 to alkaline condition, CDC can perform satisfactorily but to a different extent [26,27]. This explains why high and low values of K_m were obtained at both acidic and alkaline conditions of CWE.

Another two essential parameters are ε_p and K_R. From equations 2 and 3, ε_p and K_R could be evaluated, respectively. It can be deduced from equation 2 that K_R is a function of K_B, temperature and viscosity. Mathematically, it can be expressed as K_R=fn(T, η). Values of K_R obtained from Tables 3-7 indicate there is no significant practical variation among the values. This trend follows minimal variation in the values of temperature and viscosity. At approximately constant K_R, ε_p relates directly to $2K_m = \beta_{BR}$ (equation 3). Thus, high ε_p results in high kinetic energy providing particle momentum to ensure the overcoming of the electrostatic repulsive forces by the coag-flocculating particles. It should be noted that high repulsive forces translate to high zeta potential, which in this present study is relatively high at pH 2. From theoretical point of view, $\tau_{1/2}$, K_R and ε_p are believed to be effectiveness factor, understood to be accounting for the coagulation efficiency before the commencement of flocculation.

The coag-flocculation period, $\tau_{1/2}$, is evaluated from equation 6. It can be inferred that $\tau_{1/2}$, =fn(N_0). It implies that the higher the N_0, the lesser the $\tau_{1/2}$. This accounts for high settling rate prevalent among waters with high initial turbidity load. On a broad base, the discrepancies noted in the results of the functional parameters are due to unattainable assumption that mixing of CWE particles and CDC throughout the dispersion is 100% efficient before aggregation occurs [22, 28, 29]. Second account is the interplay between Van der Wall's forces and the hydro dynamic interactions which typically alters the theoretical predicted values by a factor of ± 2.

Table 3 : Coag-flocculation kinetic parameters of CDC in CWE at varying pH and 100 mg/l dosage

Parameters	pH=2	pH=4	pH=6	pH=8	pH=10
α	2.0000	2.0000	2.0000	2.0000	2.0000
R^2	0.9363	0.9574	0.9284	0.9828	0.9268
$K_m\left({}^{l}/_{mg.min}\right)$	4E- 05	0.001	0.0009	0.0022	0.0014
$\beta_{BR}\left({}^{l}/_{mg.min}\right.$	8E – 05	0.002	1.8×10^{-3}	0.0044	0.0028
$K_R(l/min)$	7.1668×10^{-12}	9.4422×10^{-12}	9.4263×10^{-12}	9.7352×10^{-12}	7.5623×10^{-12}
$\varepsilon_p\left({}^{1}/_{mg}\right)$	1.1162×10^{7}	2.1181×10^{8}	1.9095×10^{8}	4.5196×10^{8}	3.7025×10^{8}
$\tau_{1/2}(min)$	2.5368	0.0781	0.1128	0.0461	0.0724
$N_0(mg/l)$	10000.0000	322.5806	204.0816	86.9565	476.1905
$(Np)_0(/l)$	6.0220×10^{24}	1.9425×10^{23}	1.2289×10^{23}	5.2365×10^{22}	2.8676×10^{23}

Table 4 : Coag-flocculation kinetic parameters of CDC in CWE at varying pH and 200 mg/l dosage

Parameters	pH=2	pH=4	pH=6	pH=8	pH=10
α	2.0000	2.0000	2.0000	2.0000	2.0000
R^2	0.7962	0.9908	0.9129	0.9209	0.9872
$K_m\left({}^{l}/_{mg.min}\right)$	3E- 05	0.0020	0.0023	0.0024	0.0015
$\beta_{BR}\left({}^{l}/_{mg.min}\right)$	6E – 05	0.004	0.4600	0.0048	3×10^{-3}
$K_R(l/min)$	1.0992×10^{-11}	1.0474×10^{-11}	8.8758×10^{-12}	9.5713×10^{-12}	7.9004×10^{-12}
$\varepsilon_p\left({}^{1}/_{mg}\right)$	5.4631×10^{6}	3.8187×10^{7}	5.1826×10^{8}	5.0149×10^{8}	3.7972×10^{8}
$\tau_{1/2}(min)$	3.3825	0.5074	0.5074	0.0422	0.0677
$N_0(mg/l)$	10000.0000	3333.3333	285.1142	57.4713	84.0336
$(Np)_0(/l)$	6.0220×10^{24}	2.0073×10^{24}	1.7206×10^{23}	3.4609×10^{22}	1.85663×10^{22}

Table 5 : Coag-flocculation kinetic parameters of CDC in CWE at varying pH and 300 mg/l dosage

Parameters	pH=2	pH=4	pH=6	pH=8	pH=10
α	2.0000	2.0000	2.0000	2.0000	2.0000
R^2	0.7970	0.8805	0.7721	0.9349	0.9388
$K_m\left({}^{l}/_{mg.min}\right)$	3E- 05	0.0009	0.0017	0.0019	0.0006
$\beta_{BR}\left({}^{l}/_{mg.min}\right)$	6E – 05	1.8×10^{-3}	3.4×10^{-3}	3.8×10^{-3}	1.2×10^{-3}
$K_R(l/min)$	9.8944×10^{-12}	1.0878×10^{-11}	1.0291×10^{-11}	7.8483×10^{-12}	7.9061×10^{-12}
$\varepsilon_p\left({}^{1}/_{mg}\right)$	6.0663×10^{6}	1.6546×10^{8}	3.3038×10^{8}	4.8418×10^{8}	1.5178×10^{8}
$\tau_{1/2}(min)$	3.3825	0.1128	0.0596	0.0534	0.1691
$N_0(mg/l)$	50000.0000	322.5806	2564.1025	2500.0000	2500.0000
$(Np)_0(/l)$	3.0110×10^{25}	1.9426×10^{23}	1.5441×10^{24}	1.5055×10^{24}	1.5055×10^{24}

Table 6 : Coag-flocculation kinetic parameters of CDC in CWE at varying pH and 400 mg/l dosage

Parameters	pH=2	pH=4	pH=6	pH=8	pH=10
α	2.0000	2.0000	2.0000	2.0000	2.0000
R^2	0.9828	0.9576	0.9821	0.9963	0.8194
$K_m\left({}^{l}/_{mg.min}\right)$	4E- 05	0.0006	0.0028	0.0010	0.0018
$\beta_{BR}\left({}^{l}/_{mg.min}\right)$	8E – 05	1.2×10^{-3}	5.6×10^{-3}	0.0020	3.6×10^{-3}
$K_R(l/min)$	1.0180×10^{-11}	1.0335×10^{-11}	8.7400×10^{-12}	8.5143×10^{-11}	8.5552×10^{-12}
$\varepsilon_p\left({}^{1}/_{mg}\right)$	7.8585×10^{6}	1.1610×10^{8}	6.4072×10^{8}	2.3489×10^{8}	4.2079×10^{8}

$\tau_{1/2}(min)$	2.5368	0.1691	0.0362	0.1014	0.05663
$N_0(mg/l)$	25000.0000	555.5556	263.1578	88.3333	104.1667
$(Np)_0(/l)$	1.5055 x 10^{25}	3.3456 x 10^{23}	1.5847 x 10^{23}	5.0183 x 10^{22}	6.2727 x 10^{22}

Table 7 : Coag-flocculation kinetic parameters of CDC in CWE at varying pH and 500 mg/l dosage

Parameters	pH=2	pH=4	pH=6	pH=8	pH=10
α	2.0000	2.0000	2.0000	2.0000	2.0000
R^2	0.9552	0.9501	0.8531	0.9320	0.9862
$K_m(l/mg.min)$	4E- 05	0.0006	0.0018	0.0026	0.0070
$\beta_{BR}(l/mg.min)$	8E – 05	1.2 x 10^{-3}	3.6 x 10^{-3}	5.2 x 10^{-3}	0.0140
$K_R(l/min)$	9.4882 x 10^{-12}	1.089 x 10^{-11}	1.0188 x 10^{-11}	1.0155 x 10^{-11}	9.1790 x 10^{-12}
$\varepsilon_p(1/mg)$	8..4314 x 10^{6}	1.1894 x 10^{8}	3.5335 x 10^{8}	5.1206 x 10^{8}	15252 x 10^{9}
$\tau_{1/2}(min)$	2.5368	0.1690	0.0566	0.0390	0.1449
$N_0(mg/l)$	12500.0000	1428.5714	142.8571	238.0952	212.7659
$(Np)_0(/l)$	7.5275 x 10^{24}	8.6031 x 10^{22}	8.6031 x 10^{22}	1.4338 x 10^{23}	1.2812 x 10^{23}

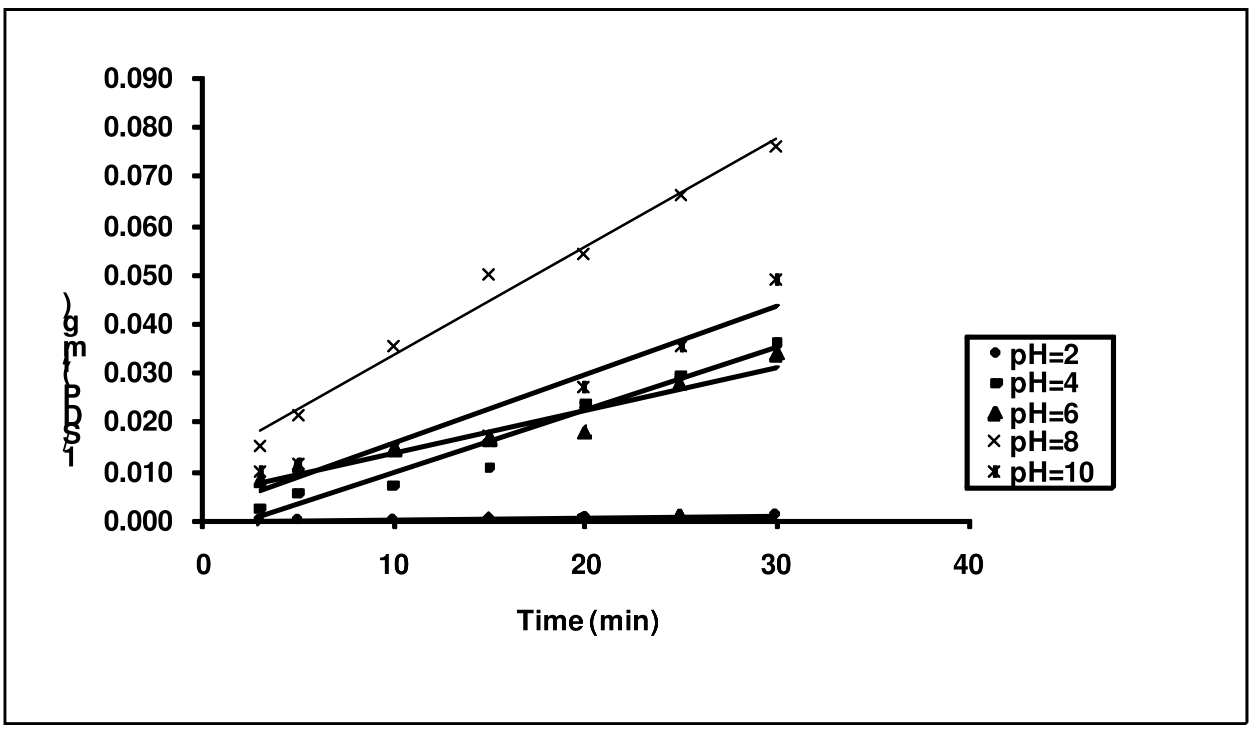


Fig. 1: Kinetic profile of SDP removal from CWE by CDC at 100mg/l

4.2 Time Evolution of Cluster Size Distribution.

The time evolutions of cluster size distribution are presented in the graphical form of number of particles as a function of time. By substituting K_m from equation 5 into 7, the particle aggregation at a microscopic levels can be predicted graphically by the interaction of singlets (m=1), doublets (m=2) and triplets (m=3). The singlets, doublets and triplets are composed of single, double and triple monomers, respectively. Representative results are shown in Figures 2 and 3. The perceived difference in the nature of the curves in response of two different $\tau_{1/2}$ of 0.0362 and 3.382minutes are demonstrated as case I and caseII, respectively.

Case I This is shown graphically as Figure 2. In this case , the singlet and total particle sum can be seen to decrease more rapidily. This is evidence of high rate of coag-flocculation supported by low half life. This can be accounted on the bases of sweep-floc or/ and massive instantaneous destabilization of the particles. With prevalent low zeta potential in the fluid, the CDC sweep-floc the particle out of the suspension [30].

Case II This is particle distribution that is associated with coag-flocculation process where there is absence of excessive entrapment and high shear resistance. The dominating aggregation mechanisms are charge neutralization in conjunction with low bridging to ensure moderate speed of coag-flocculation associated with moderate energy barrier in view of gentle nature of the curves.

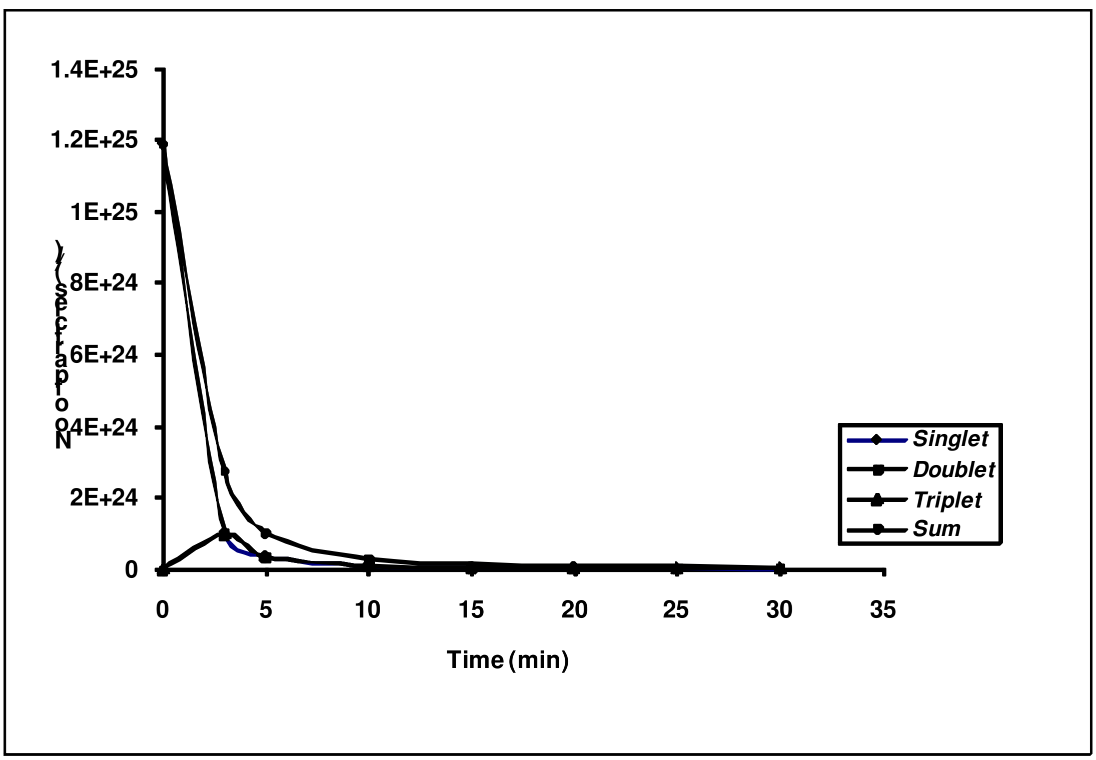


Fig. 2:Temporal particle aggregation profle at minimum half life of 0.0362min

4.3 Time Course % Removal Efficiency for Varying pH and CDC Dosages.

The process efficiency graphically presented in Figures 3-7 are obtained based on the evaluation of equation 8. They depict the variation of efficiency E(%) as a function of time and pH for various CDC dosages of 100, 200, 300, 400 and 500mg/l. It was observed that the trends for all the cases studied are almost identical but with different percentages of efficiency achieved for particular pH and dosages. This coag-flocculation process was very fast initially with about 99% efficiency recorded at 3minutes for all cases. The only exception was recorded at pH 2 where E(%) range between 40 and 60 for Figures 4-8. Practically, 99% of initial SDP load of 19709.20mg/l was removed at 3minutes of coag-flocculation.

The possible explanation for the poor performance at pH 2 could be attributed to hyper protonation and interactions among numerous chemical species present in CWE. This could affect the charge balance following complex reaction likely to have been undergone by the CWE. Arguably, this condition can generate restabalized colloids, causing electrostatic repulsion among the suspended solids. It could also be observed that the CDC recorded satisfactory performance from pH 4-10, but to a different extent. It is reported that CDC performs well in acidic medium because the amine group of CDC is usually protonated by H^+ produced from dissociation of H_2SO_4 . On the other hand, one possible explanation for the good alkaline performance is that alkaline cation can favor delamination of the SDP in suspension, which thereby displays highly accessible surface [11,26]. Another important factor that impacted the CDC performance in this study is the CDC dosage. Basically, insufficient dosage or over dosage when confronted with chemical interaction among the chemical species involved in the process could affect the perceived performance of CDC. At unfavorable conditions, excess CDC dosage ensures that excess polymer is adsorbed on the particles surfaces, producing restabalized colloids. The implication is the absence of sites available on the particles surfaces for the formation of inter particle bridge. However, at favorable conditions, excess CDC can lead to particle enmeshment that can instantaneously sweep away the SDP from the suspension. Mechanism of aggregation has possible effects on the influence of dosage on the aggregation process. It has been reported that effective coag-flocculation could be achieved with much lower doses of CDC ,especially when complete charge neutralization is not required and the process guided by combine effects of electrostatic patch and bridging mechanism [11].

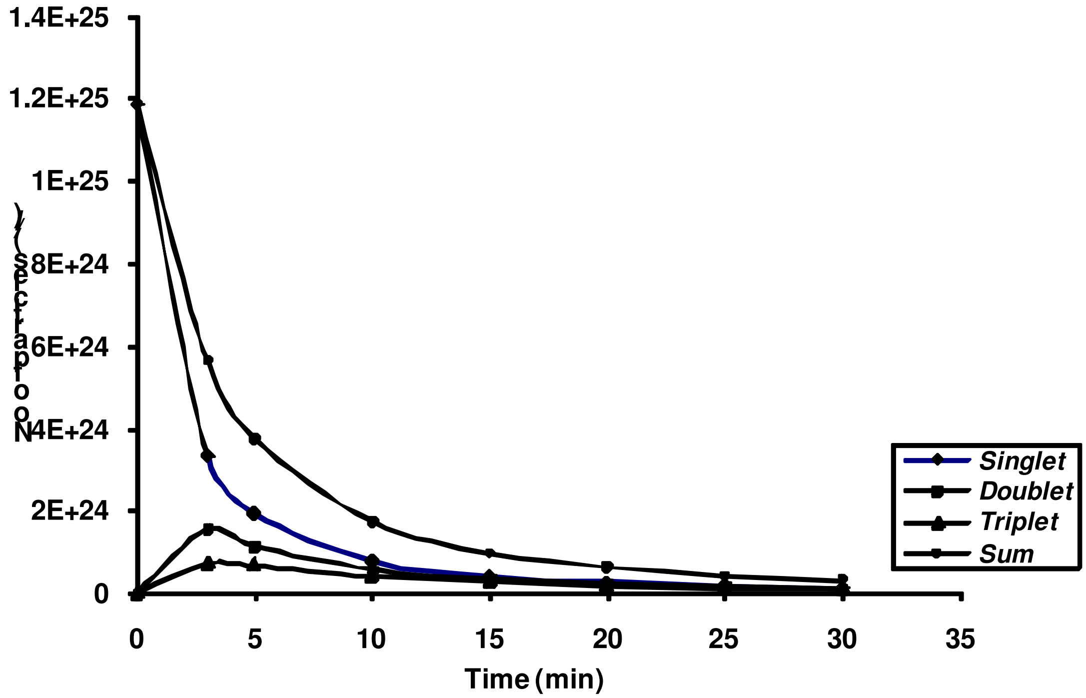


Fig.3:Temporal particle aggregation profile at maximum half life of 3.3825min

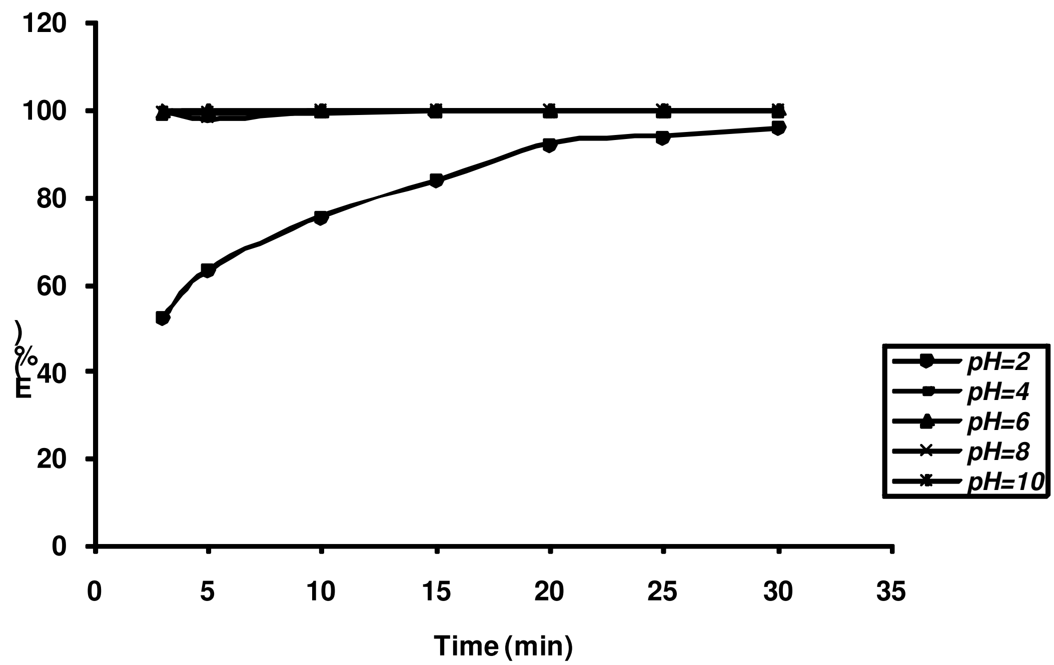


Fig. 4: Temporal coag-flocculation efficiency profile at 100mg/l and pH varying CWE.

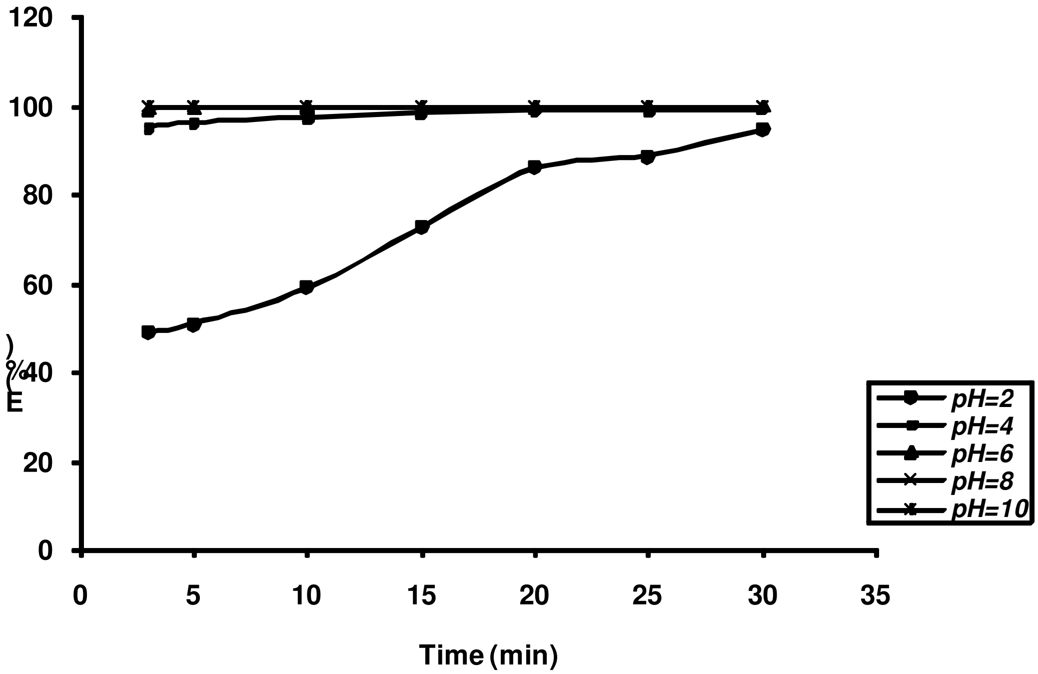


Fig.5: Temporal coag-flocculation efficiency profile at 200mg/l and pH varying CWE

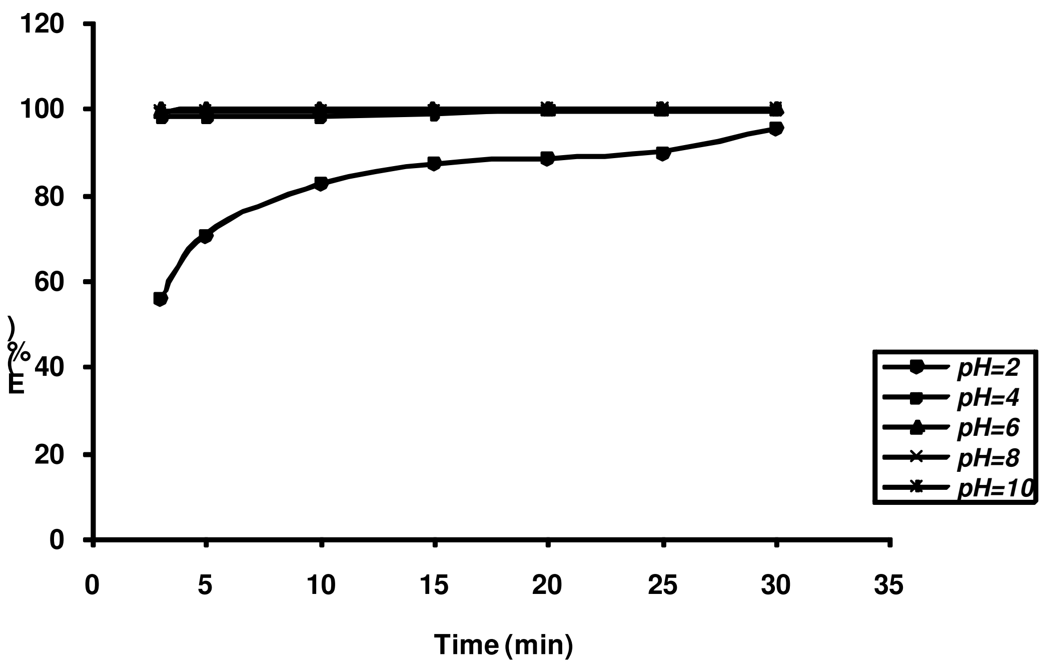


Fig.6:Temporal coag-flocculation efficiency profile at 300mg/l and pH varying CWE.

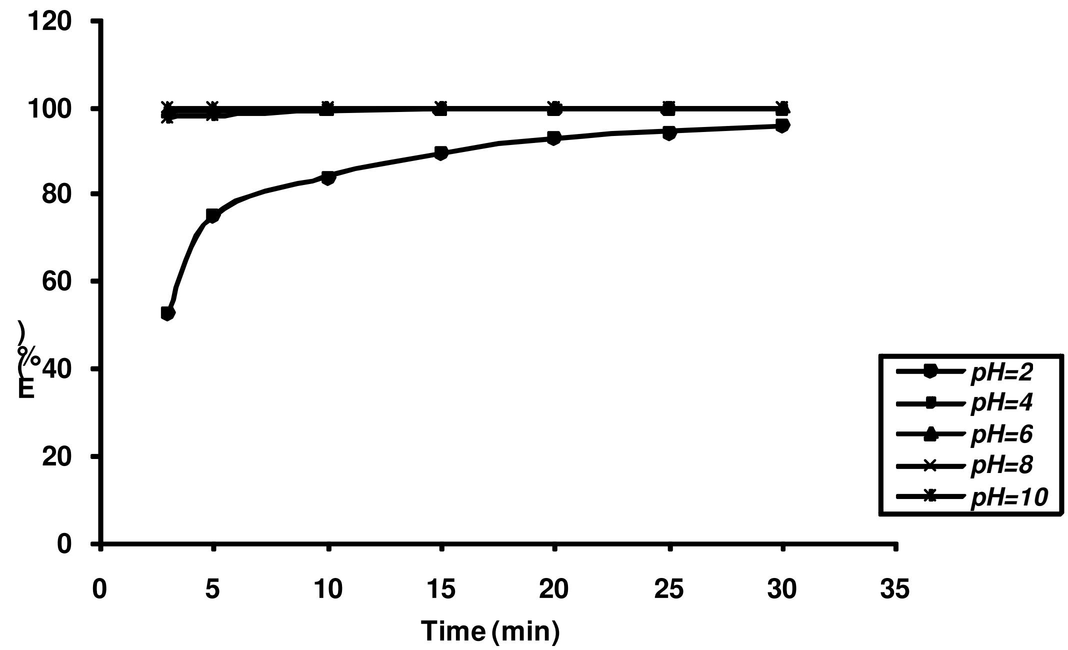


Fig.7 :Temporal coag-flocculation efficiency profile at 400mg/l and pH varying CWE.

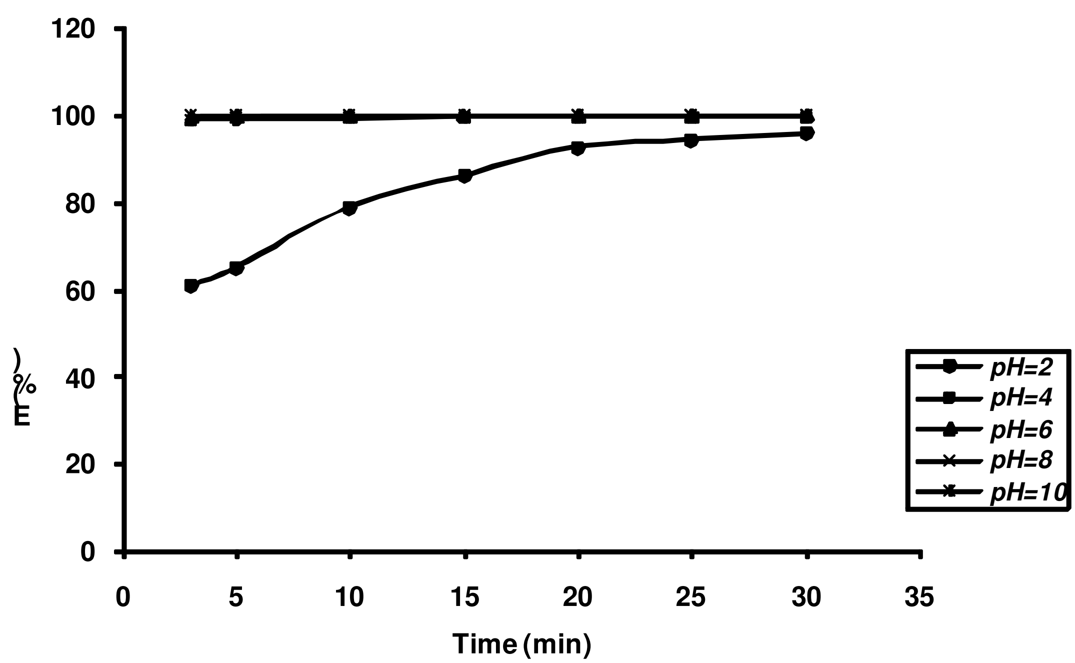
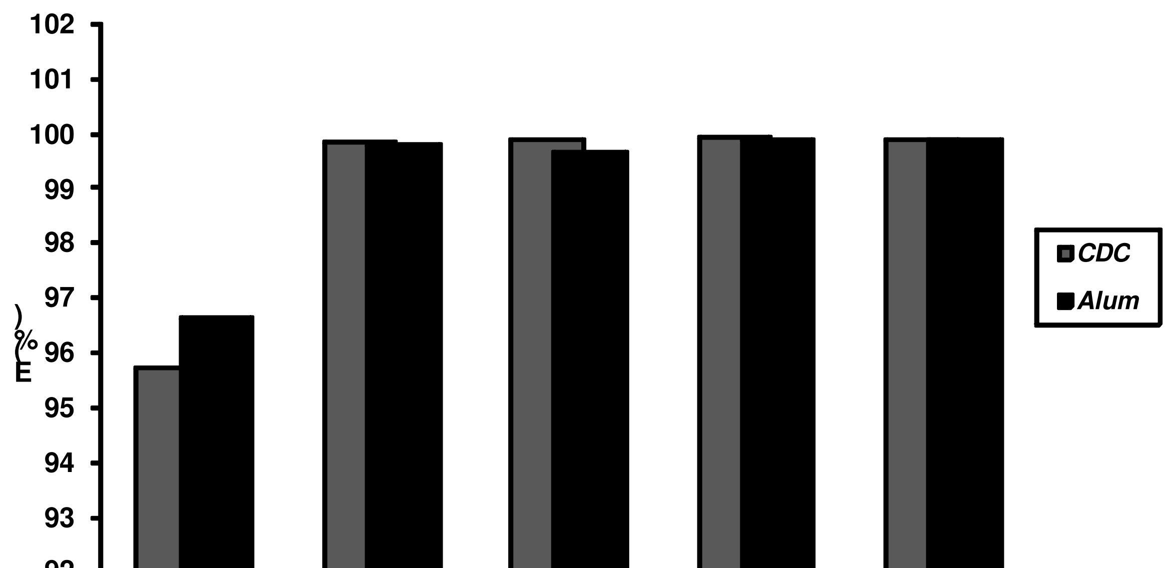


Fig.8: Temporal coag-flocculation efficiency profile at 500mg/l and pH varying CWE.

4.4 Comparative Coag-flocculation Performance Between CDC and Alum.

Figure 9 is the comparative performance chart between CDC and alum at varying pH, 100mg/l CDC, and 30minutes. The least performance is recorded at pH 2.This is explained by various reasons adduced earlier in this communication. However, the performance is about 94% for all the pH considered at this dosage. Similar results(not shown) were obtained for 200, 300, 400 and 500mg/l CDC dosages. The best performance was recorded at pH 8 and 99.933% while the least was recorded at pH 2 and 94.7537%. The fact is that CDC compares favorably with alum with advantage of being eco-friendly. Additionally, the use of CDC raises no health concerns, which is one of the major setbacks in the application of alum in water treatment.



	pH=2	pH=4	pH=6	pH=8	pH=10
CDC	95.7195	99.8597	99.8902	99.9333	99.8969
Alum	96.6256	99.8092	99.6661	99.9015	99.8922

Fig. 9: Representative comparative coag-flocculation performance between Alum and CDC for 100mg/l at 30 mins.

5. CONCLUSION

The high level of efficiency achieved within 30 minutes affirms the prevalence of rapid coag-flocculation, hence the dominance of perikinetics in the removal of SDP from CWE by CDC . The efficiency of CDC recorded establishes it at a pilot scale and within the experimental conditions as a veritable treatment agent for the removal of SDP from CWE. The best results were obtained at pH 8, 100mg/l dosage and 99.933% efficiency.

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