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Coag-flocculation kinetics of phosphorus containing effluent using *Corchorus Olitorious* seed

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Abstract: Corchorus olitorius, (CR) an environmentally friendly biomass was used as a coagulant in this work for the treatment of phosphorus containing effluent using Nephelometric method. The research evaluates the coag-flocculation efficiency of CR coagulant as well as kinetic parameter response of CR to varying pH and dosage of the waste water effluent. Coag-flocculation reaction order α, coag-flocculation rate constant K, and coagulation period τ were determined. The maximum coag-flocculation performance is recorded at rate constant, K of $5x10^{-5}$ l/mg.mm, dosage of 500mg/l, pH of 6 and coagulation period of 5.4 mins. While the coag-flocculation efficiency obtained E > 70% at the condition of the experiment.

Keywords: Coagulation*,* *Corchorus Olitorius*, Kinetics, Phosphorus

1. Introduction

Coagulation is the destabilization of colloids by neutralizing the forces that keep them apart. Cationic coagulants provide positive electric charges to reduce the negative charge (Zeta potential) of the colloids. As a result, the particles collide to form larger particles (flocs). Rapid mixing is required to disperse the coagulant throughout the liquid. Care must be taken not to overdose the coagulants as this can cause a complete charge reversal and re-stabilize the colloid complex. Flocculation is the action of polymers to form bridge between the flocs, and bind the particles into large agglomerate or clumps [1]. Many coagulating agents are used in processes for treating water, such as inorganic coagulants (salts of aluminum and iron), synthetic and natural organic polymers [2].Aluminum sulphate is widely used worldwide as a coagulant, but recently its use has been questioned due to evidence that Alzheimer's disease may be as a result of extensive intake of alum [3, 4].Moreover, aluminum is not biodegradable, and can cause disposal problems and require treatment of the generated sludge [5]. The search for an environmentally friendly and inexpensive coagulant as a viable alternative to conventional coagulants has therefore become an important challenge in the water treatment process. Some of these natural coagulants and flocculants that have been investigated by other researchers include: chitosan, aqueous extracts of the seed of *Moringa Oleifera* and extracts of Okra seed [6, 7, 8]. This study proposes the use of *Corchorus Olitorius* seed as a viable alternative for conventional coagulants in the treatment of industrial waste water.

Corchorus Olitorius called "ayoyo" in Hausa and "ewedu" in Yoruba is a popular green vegetable plant [9]. The vegetable is also known by several names in different countries including Jews mallow or Jute mallow in English, Egyptian spinach, and Bush okra in South Africa [10].

Aqueous extracts of the seeds of *Corchorus Olitorius* were reported to possess peripheral and central anti-nociceptive, anti-inflammatory and anti-pyretic activities [11]. The seeds are used as a purgative and have been found to contain cardenolide glycosides on preliminary analysis while the methanol extracts of the seeds have been reported to possess a broad spectrum of antibacterial activity [12].

Although much work has not been reported on coagulating application of CR to phosphorus removal, CR is available in large quantities in our local communities in Nigeria.

2. Materials and Methods

The turbid effluent was collected from the Federal Superphosphate fertilizer company, Kaduna, Nigeria. A 20-litre polyethylene bottle was thoroughly cleaned and rinsed with effluent sample before the final sample collection, after which the bottle was tightly closed and taken to the laboratory for experimental work.

The sample of the CR seed was sourced from a local market in Ibadan, Oyo State. The shell or covering testa of the seeds was removed and winnowed in order to separate the shell from the cotyledon of the seeds. The cotyledons were then dried at 100^0c for 2hrs in a hot air oven. The dried seeds were then ground and processed into a coagulant using standard method. The jar test was conducted based on standard Bench scale Nephelometric method (single angle procedure) for the examination of water and waste water [13,14] using model WZS-185Turbidimeter, Gulen hamp magnetic stirrer and Delta 320 pH meter.

The coagulant and the effluent samples were characterized and the results of their characterization are presented in Table 3.2 and 3.1 respectively.

The percentage of turbidity removal was calculated using equation (1)

Removal efficiency:

$$E(\%)=(C_0-C_1)/C_0 x100 \tag{1}$$

where C_0 and C_1 are the initial and residual concentration of the waste water effluent respectively, mg/l.

2.1. Theoretical Principles

The rate of flocculation is a function of the particles (count) concentration C, and the intensity of Brownian motion characterized by the diffusivity D. Consideration of the particle diffusion flux in a mono dispersed system toward a particle of radius ‘a’ (chosen as the central one) on the basis of Fick’s equation yields an expression for the rate of decrease in the particle number.

$$dC/dt = -KC^{\alpha} \tag{2}$$

Integrating Eq (1) gives

$$\ln\left(-dC/dt\right) = \ln K + \alpha \ln C \tag{3}$$

From which K and α can be determined from a plot of $\ln\left(dC/dt\right)$ against $\ln C$.

In eq. (2), K is coagulation rate constant/collision frequency

α is the order of coagulation reaction

C is the concentration of the particles (TSS),mg/l

It has been shown by some researchers that for the conditions described above [16]

$$K = 8\pi R' D \tag{4}$$

Where $R' = 2a$

From Einstein’s equation [15, 17]

$$D = K_B\left(T/B\right) \tag{5}$$

Where B is the friction factor, T is the absolute temperature (^{0}K) and K_B is the Boltzman constant (Molar gas constant per particle).

For the simplest case of a smooth spherical particle of radius ‘a’ immersed in a fluid of viscosity μ, B is given by Stoke’s relation [15]

$$B = 6\pi\mu a \tag{6}$$

Putting Eq(6) into Eq(5) gives

$$D = K_B T/6\pi a\mu \tag{7}$$

But $R' = 2a$

Therefore

$$D = 2K_B T/6\pi\mu R' = K_B T/3\pi\mu R' \tag{8}$$

Putting Eq(8) into Eq(4) gives

$$K = 8\pi R'\left(K_B T/3\pi R'\mu\right) = 8/3\left(K_B T/\mu\right) \tag{9}$$

Putting Eq(9) into Eq(2) when $\alpha = 2$ yields

$$dC/dt = -8/3\, C^2\left(K_B T/\mu\right) \tag{10}$$

Applying the method of separable variable and integrating Eq (2) within the following limits:

At t = 0, C = C_o at t = t, C = C, yields

$$-dC/dC^2 = Kdt \tag{11}$$

Integrating Eq (11) above yields

$$1/C = 1/C_0 + Kt \tag{12}$$

Multiply both sides of Eq (12) by C_o to give

$$C_0/C = 1 + C_0 Kt \tag{13}$$

Making ‘C’ the subject of the formular, yields

$$C = \frac{C_0}{1 + C_0 Kt} = \frac{C_0}{\left[1 + \frac{t}{\left(1/C_0 K\right)}\right]} \tag{14}$$

Let

$$\left(1/C_0 K\right) = \tau \tag{15}$$

Therefore Eq(14) becomes

$$C = \frac{C_0}{1+ {}^{t}\!/_{\tau}} = \tau \qquad (16)$$

When $t = \tau$ then Eq(16) becomes

$$C = \frac{C_0}{1+1} = \frac{C_0}{2} \qquad (17)$$

Thus at $t = \tau, C = \frac{C_0}{2}$ .This quantity is called the coagulation period, which is the time during which the initial concentration of particles is halved

3. Results and Discussion

Table3.2 shows the characterization results of the CR coagulant. In all the analyzed parameters (moisture content, ash content, lipid content, crude protein, carbohydrate and crude fibre) protein happens to be the active agent responsible for the coagulation in these substrates [18]. The percentage protein content of CR is 31.25%. Wastewater effluent before and after treatment was characterized and the results obtained are presented in Table 3.1. The result of the wastewater sample indicates that some heavy metals such as iron, lead and copper which are 2.75mg/l, 0.90mg/l and 12.00mg/l before treatment respectively were totally removed during the coagulation process. Between 85% and 91% of magnesium, sulphates, chlorides and phosphates were also removed during the process. Figs.1 to 5 show the effect of coagulant dosage on turbidity removal at various pH. It can be observed from the figures that the removal of turbidity increases with increase in coagulant dosage. Fig 1-3 show the removal efficiency as a function of time for various CR coagulant dosages at pH of 2.4 and 6 respectively. It is observed from the figures that the rate of removal increases very fast within the first ten minutes for a particular dosage particularly as from pH of 4, after which the rate of increase begins to reduce. The sharp increase in removal efficiency at the early stages of coagulation is a product of either floc mechanism or combination of entrapment bridging mechanism[18].The decrease, thereafter in the rate of removal efficiency was due to the fact that as the reaction proceeds the amount of the suspended particles available for coagulation decreases.

The figures also show that the removal efficiency of CR coagulant increases with dosage. However, in fig. 4-5, it was observed that as pH was increased further from 6 to 10, the rate of removal began to decrease. It could be deduced from the observation that the optimum turbidity removal of CR coagulant occurred at the optimum pH of 6 and 400 mg/l.

The values of coag-flocculation kinetic parameters at various dosages and pH are presented in tables 1-5. The R^2 and coagulation rate constant K contained in the various tables were determined from the linear kinetic plots $1/C_t$ versus time as shown in figures 6-10. The values of R^2, being grater than 0.9000 with the exception of few are satisfactory and this confirms the theory of perikinetics as the controlling mechanism of coag-flocculation under study[18] It is observed that high value of K corresponds to low value of τ a relationship that establishes a link among collision efficiency ε_p, coagulation period τ and coagulation rate constant K .This is supported by the highest value of K= $5x10^{-5}$ ^{1}/mg.min, and the lowest value of τ = 5.4000mins recorded ,at the dosage of 500mg/l, coagulation period τ = 5.4000mins and at pH of 6 as presented in Table.5.However, at pH of 2 the high value of τ with the corresponding low value of ε_p and K indicate repulsion in the system.

Table 3.1. *Characterization result of waste water effluent before and after treatment.*

Parameter	S.I. Unit	Before coagulation	After coagulation
Colour	Hazen	250	18.50
pH		8.0	10
Conductivity	μ/ cm^3	1.88×10^4	2.1×10^4
Turbidity	NTU	Not clear	Mild clear
Total solid	mg/l	6530	471.8
Acidity	mg/l	30	20
Alkalinity	mg/l	485	505
Manganese	mg/l	410.7	3.35
Potassium	mg/l	420	1.28
Chloride	mg/l	996.43	150
Nitrogen	%	27.65	1.93
Chemical oxygen demand	mg/l	289.77	71.77
Dissolved Oxygen	mg/l	28.52	76.50
Biochemical oxygen demand	mg/l	318.29	48.27
Sulphate	mg/l	185	18.6
Nitrate	mg/l	0.1	N.D
Copper	mg/l	12	N.D
Phosphorus	mg/l	378.34	35.67
Total Hardness	mg/l	80	50
Lead	mg/l	0.9	N.D
Magnesium	mg/l	19.46	12.16
Iron	mg/l	2.75	N.D

N.D: Not detected

Table 3.2. *Characterization results of coagulants.*

Parameter	CR
Moisture content (%)	10.00
Ash content (%)	14.50
Lipid content (%)	19.63
Crude protein (%)	31.25
Carbohydrate (%)	35.05
Crude fibre (%)	20.00

Table 1. *Coagulation Kinetic Parameters of CR at varying pH and 100mg/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	0.9650	0.8330	0.9610	0.9860	0.9550
K (l/mg.min)	1x10^{-5}	3x10^{-5}	4x10^{-5}	3 x10^{-5}	3 x10^{-5}
β_{BR}(l/mg.min)	2.0 x10^{-5}	6.0 x10^{-5}	8.0 x10^{-5}	6.00 x10^{-5}	6.0 x10^{-5}
ε_p (l/mg)	1.8x10^{12}	5.4 x10^{12}	7.3 x10^{12}	5.4 x10^{12}	5.4 x10^{12}
τ(min)	26.8000	9.0000	6.7000	9.0000	9.0000

Table 2. *Coagulation Kinetic Parameters of CR at varying pH and 200mg/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	0.9140	0.7940	0.9610	0.9770	0.9530
K (l/mg.min)	1x10^{-5}	3x10^{-5}	4x10^{-5}	4x10^{-5}	3 x10^{-5}
β_{BR}(l/mg.min)	2.0 x10^{-5}	6.0 x10^{-5}	8.0 x10^{-5}	8.0 x10^{-5}	6.0 x10^{-5}
ε_p (l/mg)	1.8x10^{12}	5.4 x10^{12}	7.3 x10^{12}	7.3 x10^{12}	5.4 x10^{12}
τ(min)	26.8000	9.0000	6.7000	6.7000	9.0000

Table 3. *Coagulation Kinetic Parameters of CR at varying pH and 300mg/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	0.9230	0.9730	0.9870	0.9870	0.9390
K (l/mg.min)	1x10^{-5}	4x10^{-5}	4x10^{-5}	4 x10^{-5}	4 x10^{-5}
β_{BR}(l/mg.min)	2.0 x10^{-5}	8.0 x10^{-5}	8.0 x10^{-5}	8.0 x10^{-5}	8.0 x10^{-5}
ε_p (l/mg)	1.8x10^{12}	7.3 x10^{12}	7.3 x10^{12}	7.3 x10^{12}	7.3 x10^{12}
τ(min)	26.8000	6.7000	6.7000	6.7000	6.7000

Table 4. *Coagulation Kinetic Parameters of CR at varying pH and 400mg/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	0.9120	0.9470	0.9760	0.9720	0.9320
K (l/mg.min)	1x10^{-5}	4x10^{-5}	4x10^{-5}	4 x10^{-5}	4 x10^{-5}
β_{BR}(l/mg.min)	2.0 x10^{-5}	8.0 x10^{-5}	8.0 x10^{-5}	8.0 x10^{-5}	8.0 x10^{-5}
ε_p (l/mg)	1.8x10^{12}	7.3 x10^{12}	7.3 x10^{12}	7.3 x10^{12}	7.3 x10^{12}
τ(min)	26.8000	6.7000	6.7000	6.7000	6.7000

Table 5. *Coagulation Kinetic Parameters of CR at varying pH and 500mg/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	0.7570	0.9740	0.9940	0.9570	0.9530
K (l/mg.min)	1x10^{-5}	3x10^{-5}	5x10^{-5}	4 x10^{-5}	4 x10^{-5}
β_{BR}(l/mg.min)	2.0 x10^{-5}	1.00 x10^{-6}	8.0 x10^{-5}	8.0 x10^{-5}	8.0 x10^{-5}
ε_p (l/mg)	1.8x10^{12}	9.1 x10^{12}	7.3 x10^{12}	7.3 x10^{12}	7.3 x10^{12}
τ(min)	26.8000	7.4000	5.4000	6.7000	6.7000

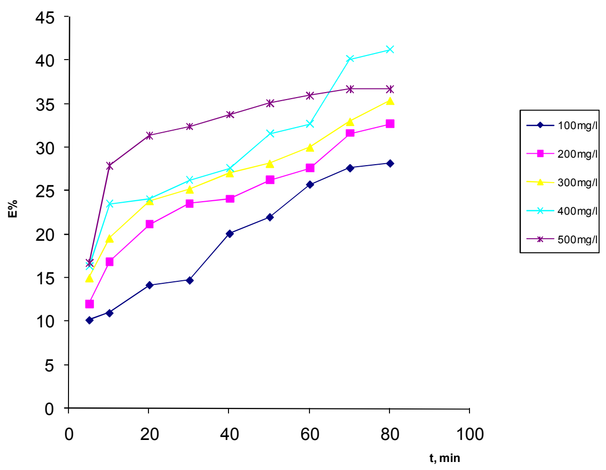

Fig. 1. *Coagulation efficiency profile for varying CR dosage at pH=2.*

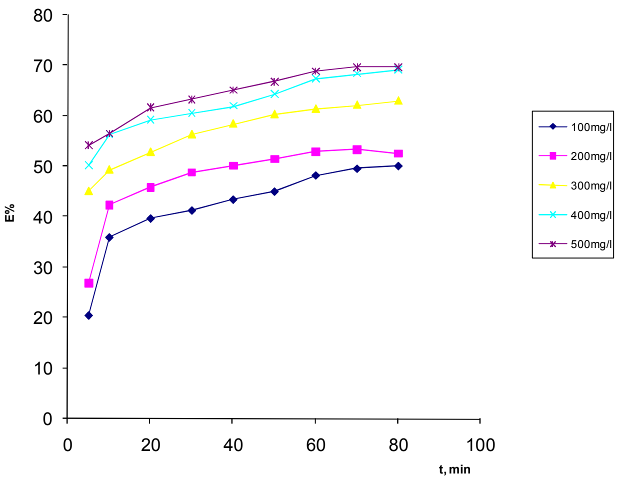

Fig. 2. *Coagulation efficiency profile for varying CR dosage at pH=4.*

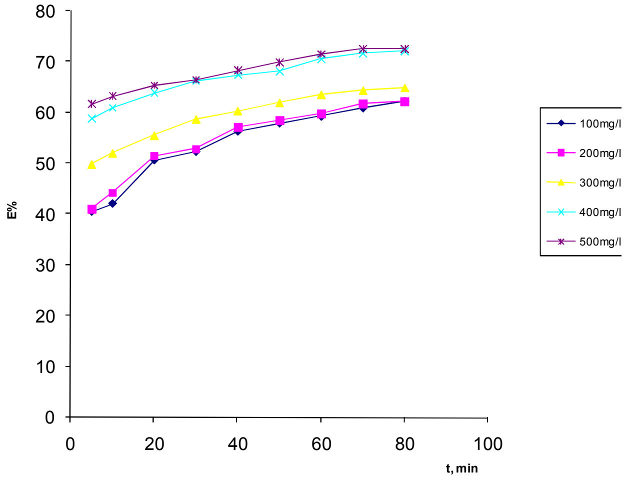

Fig. 3. *Coagulation efficiency profile for varying CR dosage at pH=6.*

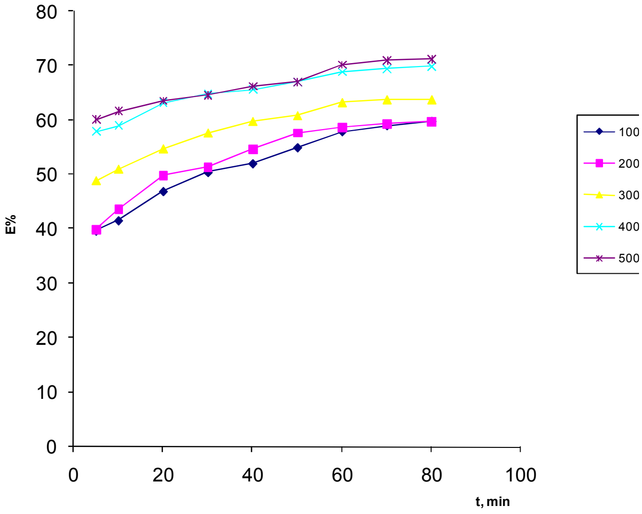

Fig. 4. *Coagulation efficiency profile for varying CR dosage at pH=8.*

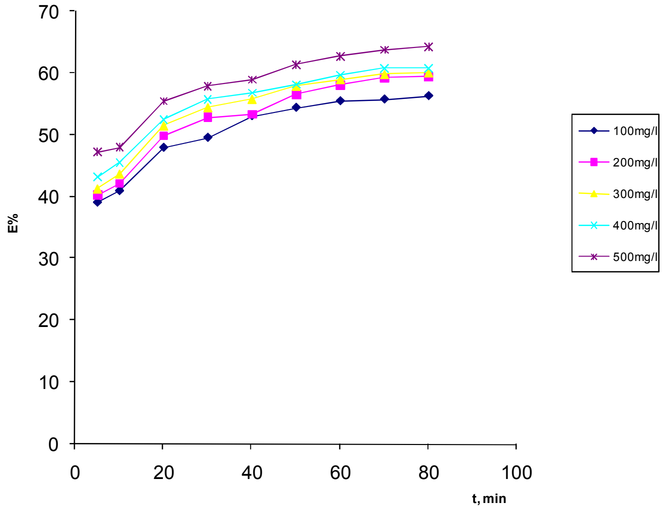

Fig. 5. *Coagulation efficiency profile for varying CR dosage at pH=10.*

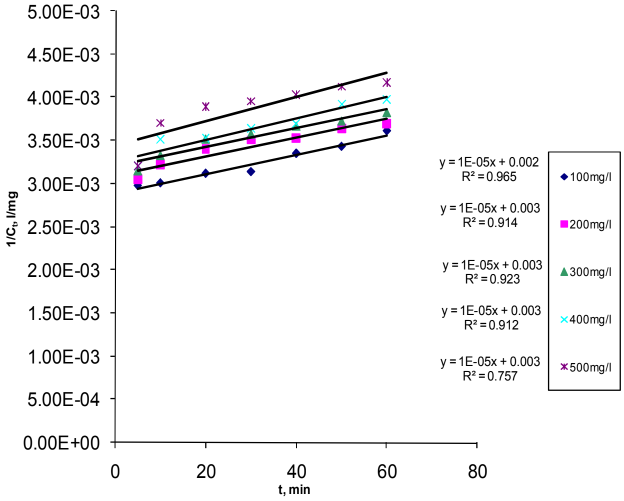

Fig. 6. *Kinetic plot of* $1/c_t$ *versus time for varying CR dosage at pH=2.*

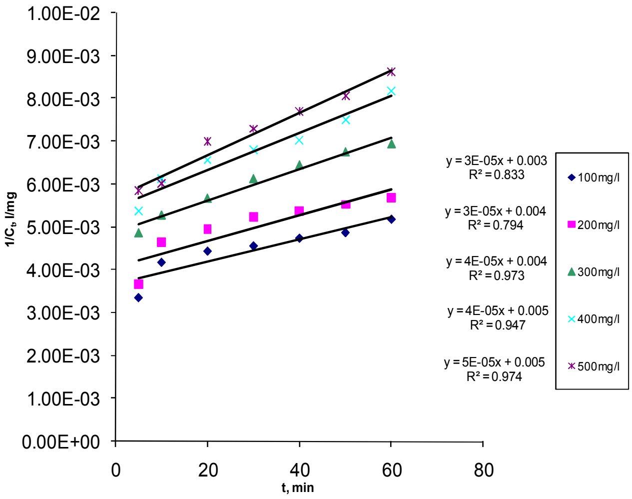

Fig. 7. *Kinetic plot of* $1/c_t$ *versus time for varying CR dosage at pH=4.*

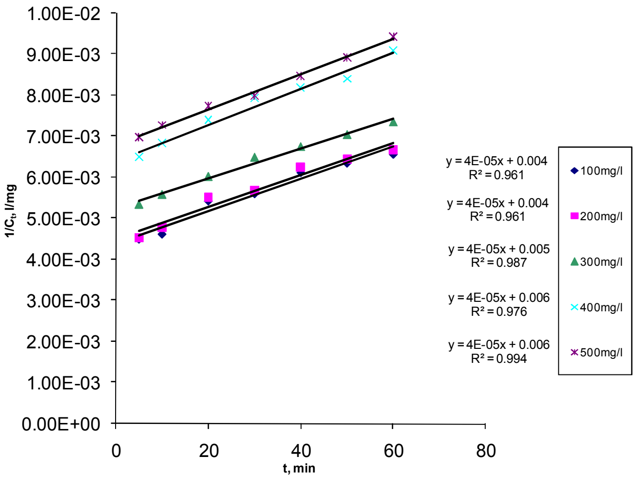

Fig. 8. *Kinetic plot of* $1/c_t$ *versus time for varying CR dosage at pH=6.*

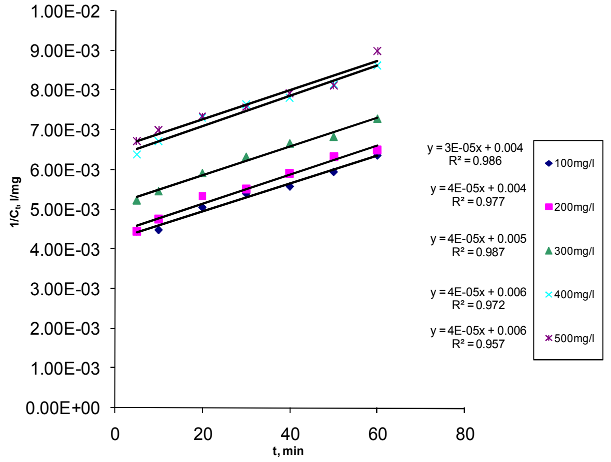

Fig. 9. *Kinetic plot of 1/c$_t$ versus time for varying CR dosage at pH=8.*

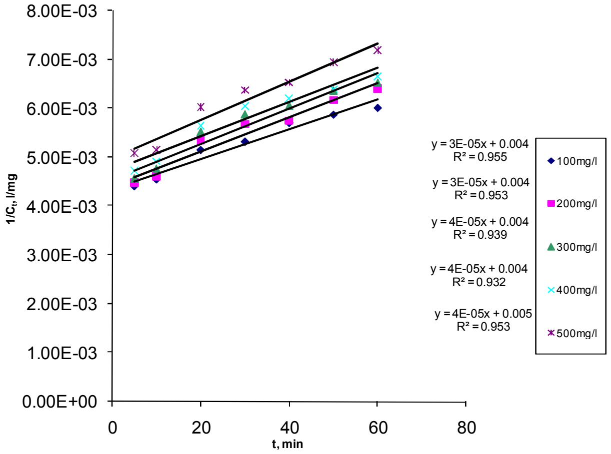

Fig. 10. *Kinetic plot of 1/c$_t$ versus time for varying CR dosage at pH=10.*

4. Conclusion

The obtained kinetic results of low coagulation period, high collision efficiency and high coagulation rate constant are satisfactory. The high values of R2 confirm the theory of perikinetics as the controlling mechanism of coag-flocculation under study. The removal efficiency E(%) > 70 recorded at the optimum pH of 6 and dosage of 500mg/l, its biodegradable and non-toxic nature present the potential of CR as a source of organic derived coagulant applicable in large scale water treatment.

Nomenclature

β_{BR}	Collision factor for Brownian transport
ε_p	Collision efficiency
$\tau_{1/2}$	Coagulation period /Half life
R^2	Coefficient of Determination
α	Coag-flocculation reaction order
CR	Corchorus olitorius
K	Coagulation rate constant
C	Concentration of particles

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