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Performance Prediction of Coag-Flocculation of Bentonite, Chitosan, and Sawdust Formulation for the Remediation of Crude Oil-Polluted Surface Water Using Anfis Technique

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ABSTRACT: The complexity of non-linear systems has prompted an in-depth research into different statistical approach that can accurately and most flexibly models such systems. In this study, a conventional statistical approach and a relatively new soft computing method known as the Adaptive Neuro Fuzzy Inference system (ANFIS) was employed in the modelling and prediction of turbidity removal efficiency of Tympanotonus fuscatus extract (TFE), sawdust, and Bentonite in the remediation of crude oil-polluted surface water by coag-flocculation process. TFE, a polycationic composite was extracted from periwinkle shell by deproteinisation, demineralization, and deacetylation for use as coagulant with bentonite and sawdust as coagulant aids at a combined ratio of 0.375:0.375:1. The coag-flocculation performance was investigated using a jar test apparatus at room temperature for three operational parameters: pH (2-12), Dosage (3-11) g/l and settling time (3-30) minutes and particulate oil removal efficiency monitored as process response. Following the set of predefined fuzzy logic rules originated from the central composite design (CCD) matrix, the optimum particulate oil removal efficiency of 87.90% was recorded at process conditions of 19.20 minutes, 9.19g/l and at pH of 10.9. This research exposes the potential of the mix as excellent coagulants and the use of ANFIS technique in the modelling of coag-flocculation process.

KEYWORDS: Remediation, ANFIS Technique, Coag-Flocculation, Crude Oil-Polluted Surface Water ,Bentonite.

I. INTRODUCTION

The remediation process of coagulation–flocculation is considered as the most important process in water surface treatment, which can be used as pre-treatment, post-treatment or even a main treatment. During the flocculation process, the flocculation effects mainly pend on the choice of flocculants directly [1]. A number of flocculants are commercially available, but some of them have not received the required acceptability due to their negative environmental consequences and potential health impacts. For example, the use of inorganic salts, such as aluminum chloride or aluminum sulfate, is now disputed due to their potential contribution to Alzheimer's disease [2] and production of large scale of sludge [3]. Polyacrylamide-based materials are also frequently used; however, the possible release of monomers is now considered harmful because they can enter the food chain, causing the potential health impacts (e.g., carcinogenic effects) [4]. The search for a better substitute to conventional flocculants has become an important challenge in the water treatment process, with the aim of minimizing the detrimental effects associated with the use of such flocculants. Several studies have focused on the use of chitosan for dye wastewater [5,6], latex particles [7,8], microorganisms [9], microalgae [10] and food industry [11,12], as well as colloidal particles [2,13–

18]. The properties of chitosan, including its cationic behavior and molecular weight, may be used both for coagulation (particle aggregation induced by electrolyte addition) and flocculation (aggregation resulting from the linking or bridging of several particles by a polymer chain). However, one difficulty with the use of chitosan is that it is commercially available with a wide range of molecular weight and degree of deacetylation [19]. Moreover, during the N-deacetylation process, despite numerous attempts, the N-acetyl groups cannot be completely removed without inducing degradation of the polysaccharide backbone [20]. At the same time, the physicochemical properties of chitosans, such as chain flexibility in solution [21], charge density [7,8], the rheological properties [22], crystal size and crystalinity [23] depend on structural parameters such as the molecular weight (Mw), degree of deacetylation (DD) and the distribution of the two kinds of residues constituting the chain. And all these properties affect the coagulation–flocculation properties. This study successfully used environmentally friendly materials to remediate crude oil polluted surface water as well as recover some amount of oil.

II. EXPERIMENTATION

Materials

Bentonite (Aqua-gel) sample was obtained from the Petroleum Training Institute (PTI) Effurun-Otuoke Bayelsa State and was containerised to avoid contamination due to its hygroscopic nature. The Periwinkle Shells were obtained from Otuoke, Bayelsa state, Nigeria. Crude oil was sourced from Otuoke Refining and Petrochemical Company Limited. The sample of crude oil was characterised as a dark viscous liquid, insoluble in water, with density of about 0.88 g/cm^3, vapour pressure less than 1kpa at 20°C and boiling point above 350°C (A processed blend of Ughelli Quality Control Centre (UQCC) and Escravos sweet and light Crude oil blend, commercially used as refinery feed stock). The calcium hydroxide is a white powder from J.T. Baker, Phillipsburg, NJ (Product 1372-01). It contains 97.0% $Ca(OH)_2$.

Water Sample Preparation

Raw surface water was obtained from Otuoke River in Bayelsa state, Nigeria. 500ml of the raw water was spiked with 5ml of Excravos/UQCC crude and was agitated vigorously for 24 hour with a magnetic stirrer until a constant turbidity was observed. Oil-in-water emulsion with suspended oil particles in the water bulk and oil sleek on the water surface was generated as a model suspension to provide the desired turbidity. The resulting suspension was found to be colloidal and used to typify crude oil polluted non-process water.

Preparation of Sawdust

Sawdust collected from local sawmill in Otuoke, Bayelsa State was washed with hot distilled water to remove dust-like impurities and dried in the sun. The resulting material was further heated in the oven at 100 ^{0}C for 5 hours to ensure it is entirely moisture free. The sample was then ground to further reduce the particle size and increase the surface area. Thereafter it was containerized to avoid water adsorption after been sieved with ASTM sieve mesh size of 0.350mm.

Preparation of Periwinkle Shell Sample

Periwinkle shell Sample, (precursor to PSE) was sourced from Otuoke, Bayelsa State Nigeria. 3kg of the sample was continuously and thoroughly washed with warm distilled water until impurities; soluble organics and adherent proteins were removed and subsequently dried in an oven at 90^{0}C for 13hrs to a constant weight. After drying, the 3kg sample was ground with a milling machine and sieves with a US ASTM standard sieve to obtain a ground-dried shell of 0.841-0.425 mm and subsequently stored in a desiccator for further use.

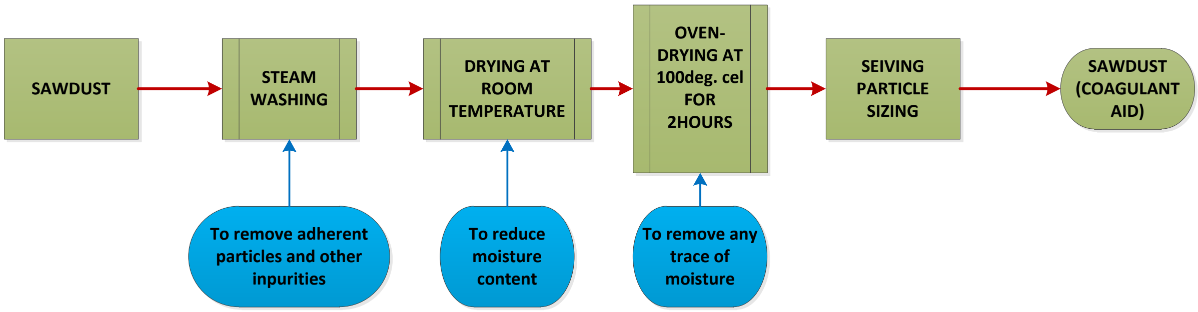

Fig. I Detailed Material Flow for the Preparation of Sawdust

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Extraction of Chitosan from Periwinkle Shell

Periwinkle shell chitosan (PSC) was prepared according to a modified method of [4]. 400g of ground periwinkle shell (PS) was steam washed to remove adherent proteins and other impurities. Demineralisation was carried out by constantly stirring the residue in 1litre of 1M HCl solution for 4 hours at 50 ^{o}C. The PS-HCl mixture was separated using filter paper and washed with distilled water for 30 minutes to neutralise the acidity of the resulting solid. The demineralised solid residue was then deacetylated by constantly stirring in 10 M concentrated NaOH solution applied at 1:10 (w/v) solid to solution ratio at 15 psi for 3 hours at 122 ^{0}C. On cooling, the mixture was separated (using filter paper) The resulting sample residue after deacetylation was washed to pH 7 in running water, rinsed with distilled water and oven dried for 2 hours at 70 ^{0}C. This processing product of PS was referred to as periwinkle shell extract (PSE). The detailed material flow for the extraction is shown by fig. III

Appropriate dosage of Bentonite, chitosan and sawdust blend (0.375:0.375:1) in the range of 2-11 g/l was added directly by manual sprinkling to 500 ml of the simulated effluent and was tuned to pH range of 4-12 by the application of H_2SO_4/$Ca(OH)_2$. Thereafter was subjected to 10 minutes of slow mixing (70 rpm) to ensure complete dispersion of coagulant and 20 minutes of slow mixing (10 rpm) and followed by 30 minutes of settling. During settling, samples were withdrawn from 2 cm depth and changes in turbidity (in NTU) were measured using the nephlometric turbidity meter. The aggregation kinetics readings at room temperature were monitored and collected at

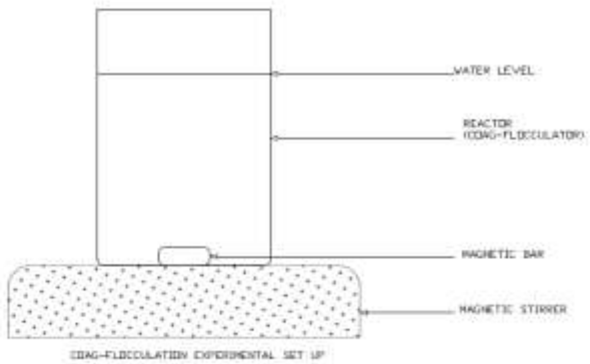

Fig. II Coag-flocculation set up

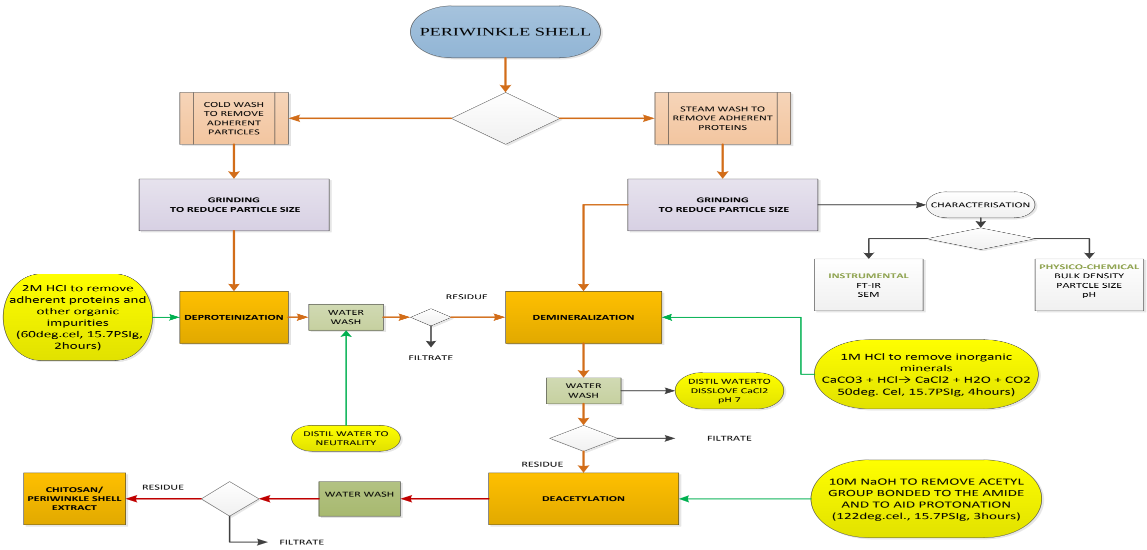

Fig. III Detailed material flow for the extraction of chitosan from periwinkle shell Jar Test Experiment

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Central Composite Design

Centre composite design (CCD) was used for experimental study. Three process variables viz. Dosage, pH, and settling time were set using small CCD. Eight star points (α = ± 1), eight axial points (α = ±1) and five replicates at the centre point (α = 0) were chosen as experimental points. A total of 20 experiments were performed. Central points were used to check the reproducibility and stability of results. The runs were conducted in randomized manner to guard against systematic bias.

III. RESULTS AND DISCUSSION

Crude oil-polluted surface water characteristics

Table 1 details the main characteristic of crude oil polluted surface water sample used in this experiment and it shows that COD, turbidity, TSS and pH levels were present in significant quantities with maximum concentrations of approximately 83 mg/L, 404 NTU, 930 mg/L and 6.5, respectively. These high values indicate that the surface water can be categorized as been polluted since it exceeded the National Environment (Standards for Discharge of Effluent into Water or on Land) Regulations, of the federal republic of Nigeria maximum effluent discharged limit. It can be concluded that the surface water was quite concentrated and full treatment is necessary.

SEM analysis

Scanning electron microscopy (SEM) analysis was conducted on the precursor and coagulant using SEM machine with model number Hitachi S-3400N to produce topological images of the samples. This machine has maximum resolution of 30000 times and can scan images up to 50 nm. The structural morphology of the samples shows how the micropores of the samples are interconnected. The degree of compaction and porosity determines the ease of particles to adhere to the surfaces available as less compacted structures have smaller surface area available to aid the coagulation of particles. In fig. I above the coagulant precursor have little or no pores available for the adherence of particles due to its compacted mesh structure unlike the PSC that provides better surface area as shown in fig. II. The change in structure could be attributed to the pre-modification and modification process (deproteinisation and deacetylation) which exposes the micropores, which leads to the existence of bridge structures.

Table 1 Characteristics of crude oil-polluted surface water

	Surface water	After pollution	Treated effluent	Effluent discharge standard
COD (mg/l)	15	83	69	NA
Ph	6.2	6.5	11.2	6-8
TSS (mg/l)	140	930	148.05	100
Turbidity (NTU)	60	404	65	300
TDS (mg/l)	20	70	51.5	1200

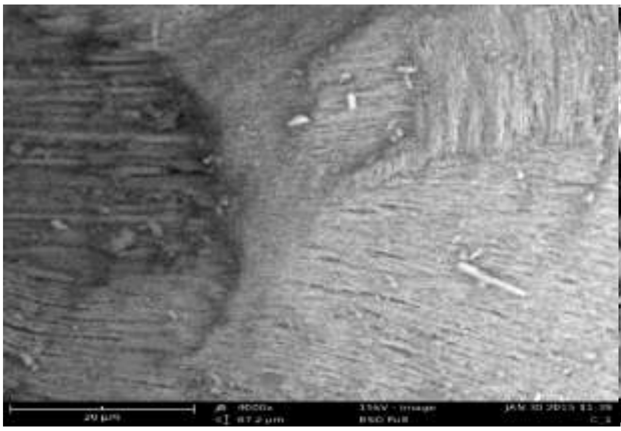

Plate I SEM Image of PS

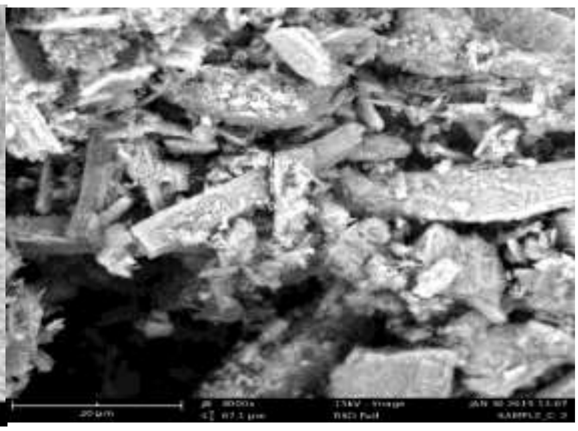

Plate II SEM Image of PSC

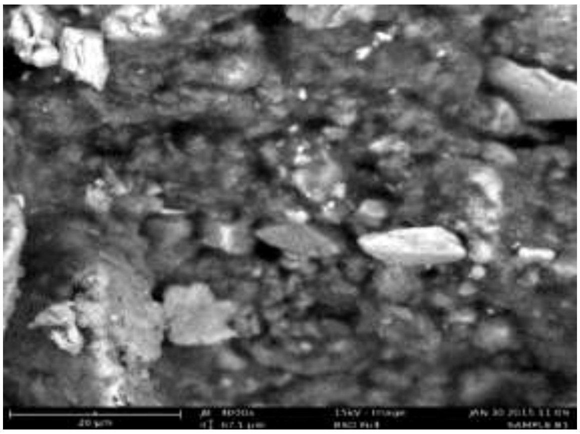

Plate IIISEM morphology of Bentonite

ANFIS Modelling Procedure and Response Prediction

The fuzzy logic toolbox of MATLAB 2009a 7.0.1 was used for ANFIS modelling of the turbidity removal efficiency of the Coag-flocculation process using PSE, Bentonite and Sawdust in Crude oily non-process water. In this present study, a Sugeno model was employed. Different membership functions were tried and the result shows that the Gaussian membership functions had comparatively reliable results and also are more common in fuzzy systems literature as they are both simple and flexible.Therefore the Gaussian membership function (equation 1) was used for the input variable.

$$f(x:\sigma,c) = e^{\frac{-(x-c)^2}{2\sigma^2}} \quad (1)$$

Where x is the input variable, σ and c are the adjustable parameters of the membership function (premise parameters). Linear membership function was considered for the output (i.e. turbidity removal efficiency). There are 27 rules in the used ANFIS architecture as shown by fig. IV. Since each selected membership function has two adjustable parameters shown by equation 1 above, there are 3×3×2 adjustable parameters (premise parameters) for the membership function of inputs. In layer 3 the number of consequent parameters is 27 (3×9) as there are 27 linear membership functions of the output parameters corresponding to the 27 rules. Hybrid optimization method was employed in order to estimate the parameters of the membership functions.

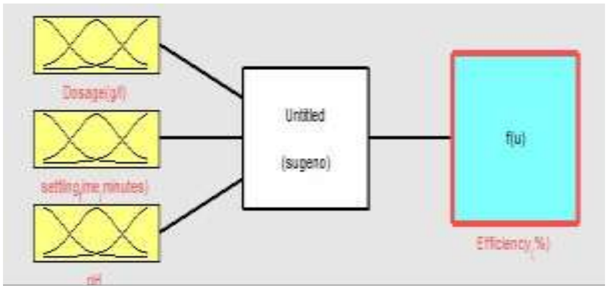

Fig. IV ANFIS input-output relationship diagram

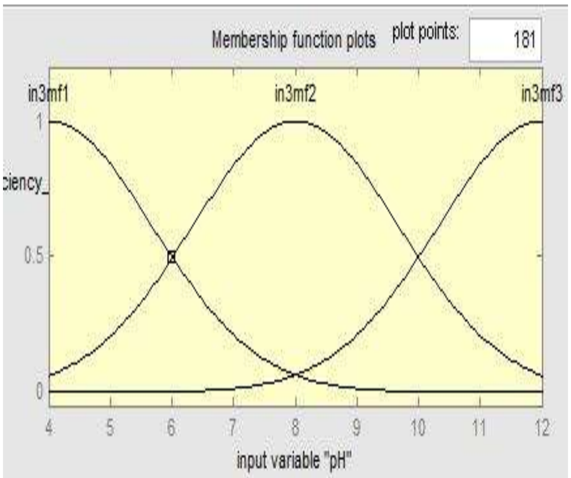

Fig. Va

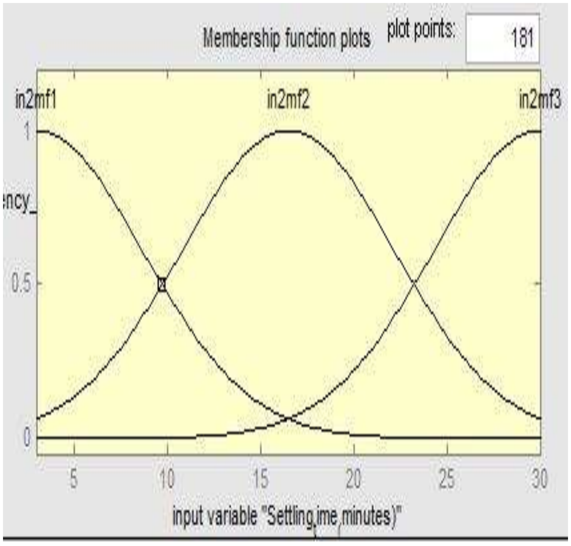

Fig. Vb

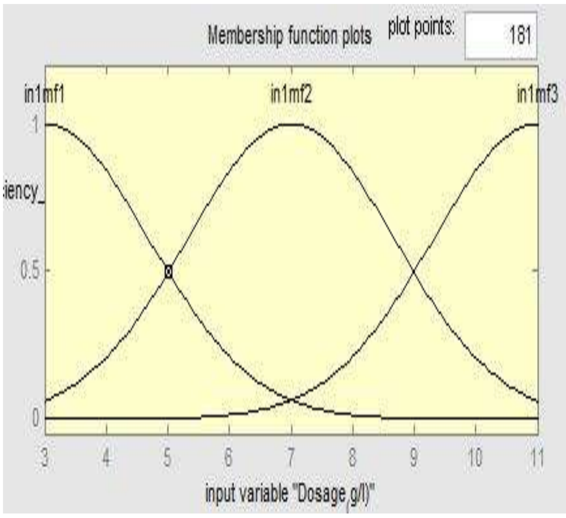

Fig. Vc

Fig. V(a-c) Settling time input with Gaussian membership function (gauss) plots

ANFIS Modelling Procedure

Appropriate selection of suitable membership function with proper number of fuzzy rules, are essential for ANFIS model development. Linear membership functions (mf) of the Gaussian type, number (3 3 3) for the input variables shown in fig. V was used for the modelling. To prevent overtraining, very large training dataset was not used during the learning process in the present study. Root mean squared error (RMSE) was used as statistical accuracy measure to analyse and compare the performance of the model. For the modelling procedure using ANFIS technique three input data set namely dosage (3, 5, 7, 9, and 11g/l), pH (4 6 8 10 12) and settling time (3 5 10 15 25 and 30 minutes) were used and the values of the empirical turbidity removal efficiency were used as the output values schematically shown by fig. VI.

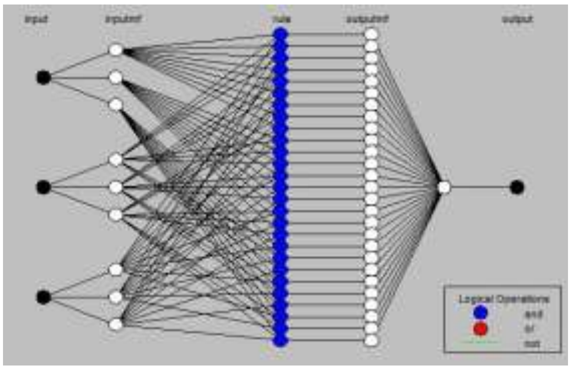

Fig. VI ANFIS architecture with membership functions and rules

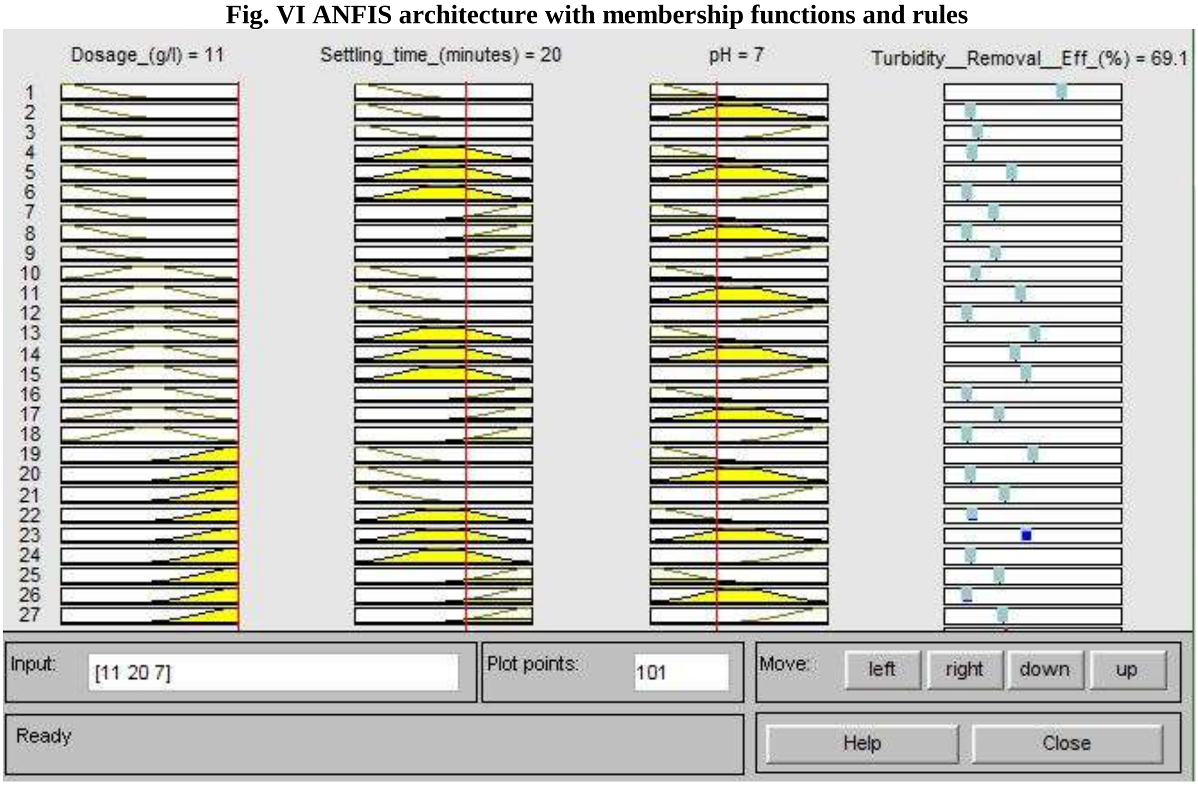

Fig. VII Predetermined fuzzy logic rules of ANFIS system realized by Matlab

Predetermined fuzzy logic

The rule viewer of turbidity removal efficiency of the model system obtained using ANFIS is presented by fig. VI. There are 27 rules in the structure and each row represents one rule. The three columns corresponds to the input variables selected for the analysis namely; dosage, settling time and pH and the last column represents the turbidity removal efficiency selected as output variable.

The ability of ANFIS to adequately predict the system performance during the training from the

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set of experimental data is presented by fig. VII. Twenty data points of table 1 were used for the training, after twenty epochs, an error of approximately 0.456 was obtained. This value compared to that of ANN shows that ANFIS is a better tool for the prediction and modelling of system's responses since it combines the capability of artificial intelligence (AI) and fuzzy logic (FIS). From the plot it is clear that the system can adequately be employed in modelling of the Coag-flocculation process. However, proper selection of the number of epoch and membership functions is pivotal to the reduction of error associated with the predictive ability of the ANFIS.

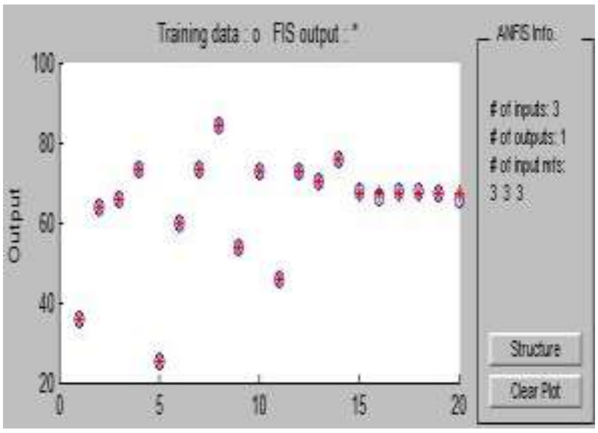

Fig. VIII Comparison of ANFIS output and test data

To adequately analyze the predictive ability of the ANFIS, 20 empirically obtained output data set was tested at 20 epochs using the error back propagation optimization technique. Fig. VIII shows the plot of ANFIS predicted output against the experimentally obtained output data set. From the plot it is clear that ANFIS can adequately be employed in the modelling of the process. Between 1 to 14 epochs the system performance seems to be erratic and unstable due to variation in the input variables, however this error was completely minimized between 15 to 20 epochs.

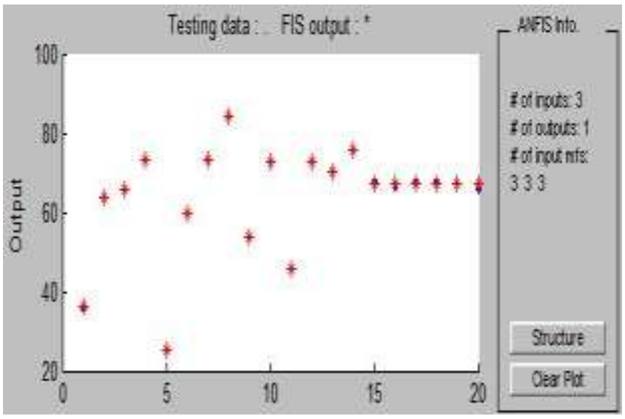

Fig. IX Comparison of ANFIS output and test data

The experimentally obtained data were also checked to determine the magnitude of the error associated with the predictive ability of ANFIS. Fig. IX demonstrates the plot of experimentally obtained output data to the ANFIS output data during the checking period. In this plot, the system checks the data over 20 epochs to obtain the error associated with the process and minimize it as low as possible.

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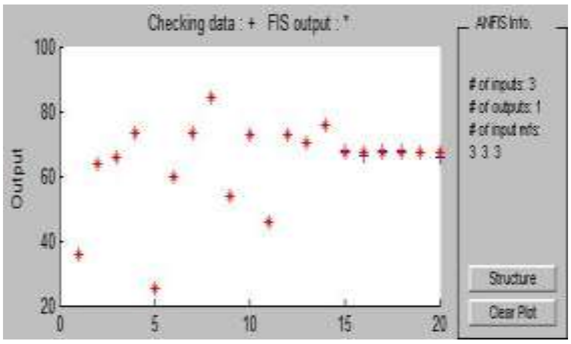

Fig. X Comparison of ANFIS output and test data

In order to minimize the error associated with the process as low as possible, the training was performed over 50 epochs as shown by fig. X. From the plot the error associated with the process at the early stage of the training was unstable. The system however tries to subdue the perturbation and the error was minimized to obtain a stable system, which enabled accurate prediction of the process response. The end error obtained during the process was 0.46523.

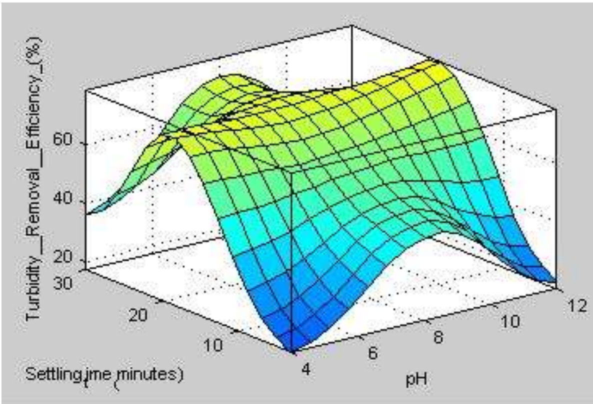

Fig. XI ANFIS Surface Plot of Efficiency versus settling time (minutes) and pH

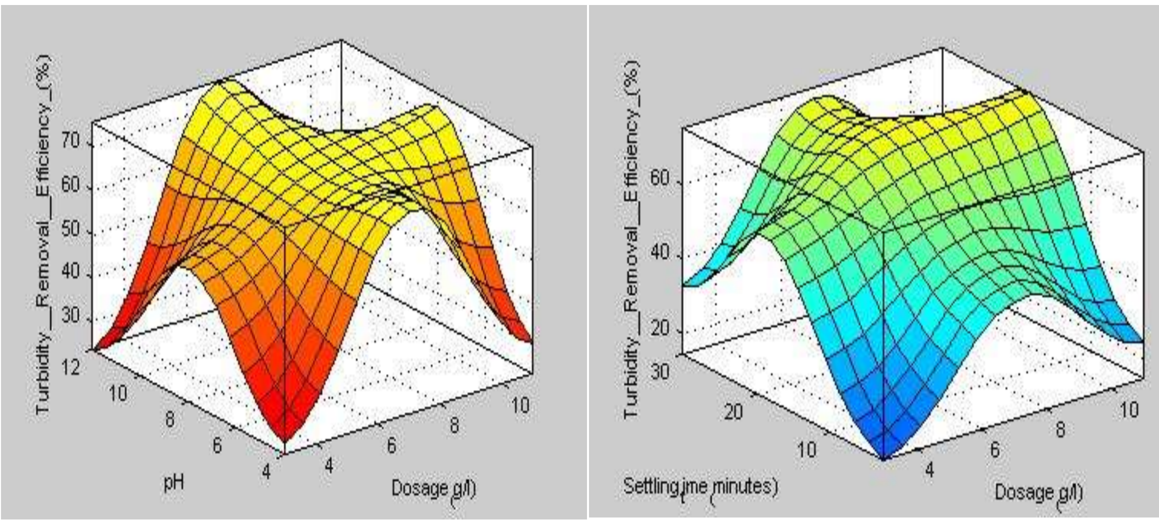

Fig. XII ANFIS Surface Plot of Efficiency versus Dosage (g/l) and pH

Fig. XI is the ANFIS surface plot of efficiency against settling time and pH. The side peaks of the plot comparatively show the effect of the two factors on the efficiency of the process. From the plot it is observed that pH has relatively lower effect compared to settling time in the reduction of turbidity of the effluent. It is also noteworthy to say that increase in both pH and settling time has positive effect on the efficiency of the formulation in the reduction of turbidity. This favourable increase in efficiency due to pH could be attributed to the effect of calcium hydroxide as water softener and its ionization tendency in the effluent.

The comparative effect of dosage and pH on Coag-flocculation efficiency is presented by fig XII. A vivid look at the plot suggests a relatively lower effect of pH in the reduction of turbidity of the effluent. It is also observed that increase in the dosage of the formulation and pH of the effluent was positive in the reduction of the effluent turbidity.

IV CONCLUSION

In this study, experimentation has been done to simulate the coagulation of suspended oil droplets from synthetic crude oil polluted-surface water using a blend of chitosan, bentonite and sawdust. Also an effort has been made to model the coagulation process using the fuzzy inference system. The surface plots obtained and the graphic viewers generated can be successfully used to predict the process response at any given condition of dosage, settling time and pH within the experimental limits studied.

SOME OF THE HIGHLIGHTS FROM THE ABOVE RESULTS

a) Adaptive Neuro Fuzzy Inference system (ANFIS) is capable of predicting the efficacy of the formulation.
b) The formulation of bentonite, chitosan, and sawdust are good combination for effective remediation of crude oil polluted wastewater.

REFERENCE

[1]. J. Li, S. Jiao, L. Zhong, J. Pana, Q. Maa, Optimizing coagulation and flocculation process for kaolinite suspension with chitosan Colloids and Surfaces A: Physicochem. Eng. Aspects 428 (2013) 100– 110.

[2]. L. Rizzo, G. Lofrano, M. Grassi, V. Belgiorno, Pre-treatment of olive mill wastewater by chitosan coagulation and advanced oxidation processes, Sep. Purif. Technol. 63 (2008) 648–653.

[3]. R. Divakaran, V.N.S. Pillai, Flocculation of kaolinite suspensions in water by chitosan, Water Res. 35 (2001) 3904–3908.

[4]. F. Renaut, B. Sancey, P.-M. Badot, G. Crini, Chitosan for coagulation/flocculation processes – an eco-friendly approach, Eur. Polym. J. 45 (2009) 1337–1348.

[5]. B. Bolto, J. Gregory, Organic polyelectrolytes in water treatment, Water Res. 41 (2007) 2301–2324.

[6]. E. Guibal, J. Roussy, Coagulation and flocculation of dye-containing solutions using a biopolymer (chitosan), React. Funct. Polym. 67 (2007) 33–42.

[7]. A. Szygula, E. Guibal, M. Ruiz, A.M. Sastre, The removal of sulphonated azo-dyes by coagulation with chitosan, Colloids Surf. A 330 (2008) 219–226.

[8]. M. Ashmore, J. Hearn, Flocculation of model latex particles by chitosans of varying degrees of acetylation, Langmuir 16 (2000) 4906–4911.

[9]. M. Ashmore, J. Hearn, F. Karpowicz, Flocculation of latex particles of varying surface charge densities by chitosans, Langmuir 17 (2001) 1069–1073.

[10]. S.P. Strand, T. Nordengen, K. Ostgaard, Efficiency of chitosans applied for flocculation of different bacteria, Water Res. 36 (2002) 4745–4752.

[11]. A.L. Ahmad, N.H. Mat Yasin, C.J.C. Derek, J.K. Lim, Optimization of microalgae coagulation process using chitosan, Chem. Eng. Sci. 173 (2011) 879–882.

[12]. S. Bratskaya, V. Avramenko, S. Schwarz, I. Philippova, Enhanced flocculation of oil-in-water emulsions by hydrophobically modified chitosan derivatives, Colloids Surf. A 275 (2006) 168–176.

[13]. V.D. Savant, J.A. Torres, Chitosan-based coagulation agents for treatment of cheddar cheese whey, Biotechnol. Prog. 16 (2000) 1091–1097.

[14]. C. Huang, Y. Chen, Coagulation of colloidal particles in water by chitosan, J. Chem. Technol. Biotechnol. 66 (1996) 227–232.

[15]. C. Huang, S. Chen, J.R. Pan, Optimal condition for modification of chitosan: a biopolymer for coagulation of colloidal particles, Water Res. 34 (2000) 1057–1062.

[16]. J. Roussy, M.V. Vooren, B.A. Dempsey, E. Guibal, Influence of chitosan characteristics on the coagulation and the flocculation of bentonite suspensions, Water Res. 39 (2005) 3247–3258.

[17]. J. Roussy, M.V. Vooren, E. Guibal, Chitosan for the coagulation and flocculation of mineral colloids, J. Dispersion Sci. Technol. 25 (2005) 663–677.
[18]. J. Ruhsing, C. Huang, S. Chen, Y.-C. Chung, Evaluation of a modified chitosan biopolymer for coagulation of colloidal particles, Colloids Surf. A 147 (1999) 359–364.
[19]. J.P. Wang, Y.Z. Chen, X.W. Ge, H.Q. Yu, Optimization of coagulation- flocculation process for a paper-recycling wastewater treatment using response surface methodology, Colloids Surf. A 302 (2007) 204–210.
[20]. A. Domard, pH and c.d. measurements on a fully deacetylated chitosan: application to CuII-polymer interactions, Int. J. Biol. Macromol. 9 (1987) 98–104.
[21]. B. Lindberg, J. Lonngren, S. Seversson, Specific degradation of polysaccharides, Adv. Carbohydr. Chem. Biochem. 31 (1975) 185–240.
[22]. M.H. Ottøy, K.M. Vårum, O. Smidsrød, Compositional heterogeneity of heterogeneously deacetylated chitosans, Carbohydr. Polym. 29 (1996) 17–24.
[23]. W. Wang, S. Bo, S. Li, W. Qin, Determination of the Mark-Houwink equation for chitosan with different degrees of deacetylation, Int. J. Biol. Macromol. 13 (1991) 281–285.
[24]. K.V. Harish Prashanth, F.S. Kittur, R.N. Tharanathan, Solid state structure of chitosan prepared under different N-deacetylating conditions, Carbohydr. Polym. 50 (2002) 27–33.
[25]. J. Xu, S.P. McCarthy, R.A. Gross, D.L. Kaplan, Chitosan film acylation and effects on biodegradability, Macromolecules 29 (1996) 3436–3440.
[26]. A. Ozkan, M. Yekeler, Coagulation and flocculation characteristics of celestite with different inorganic salts and polymers, Chem. Eng. Process. 43 (2001) 873–879.