EVALUATION OF EGG SHELL AS A COAGULANT AID IN DYE REMOVAL FROM AQUEOUS SYSTEM

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Abstract: The evaluation of powdered egg shell (ES) as coagulant aid to alum [$Al_2(SO_4)_3$], a primary coagulant in the treatment of basic dye, Methylene blue (MB) contaminated aqueous system was investigated. The ability of alum and the Egg Shell (ES), separately, to decolourise the methylene blue contaminated water was investigated by method of continuous variation of the alum and ES dosages. The ability of the ES to serve as a coagulant aid was also assessed. The coagulation and flocculation process variables (pH, dosage effect, initial dye concentration) were also optimized by method of continuous variation. The results obtained when alum alone was used as primary coagulant showed that alum alone has precipitating effect on the removal of MB from aqueous solution, with over 86% of the MB removed. On the other hand, when ES alone was used, the precipitating effect was very low. However, the combination of alum, as primary coagulant, and ES as coagulant aid enhanced the amount of MB removed with over 98% removal achieved. The effect of pH on the removal of MB was not noticeable but the percentage of MB removed was appreciable at all the pH studied. This result indicates that egg shell could be successfully used as a coagulant aid to alum in the treatment of dye contaminated wastewater.

Keywords: Alum, coagulation, egg-shell, flocculation, methylene blue, wastewater

Introduction

Wastewater from textiles, cosmetics, printing, dying, food processing, and paper-making industries is polluted by dyes. Wastewaters containing dyes are very difficult to treat; the dyes are recalcitrant molecules (particularly azo dyes), resistant to aerobic digestion, and are stable to oxidizing agents (Nigam *et al*., 2000). Discharge of these coloured effluents presents a major environmental problem because of their toxic and carcinogenic effects on living beings (Acemioglu, 2004). Azo and nitro compounds have been reported to be reduced in sediments of aquatic bodies giving rise to potentially carcinogenic amines (Chen, 2006). Many dyes are made from known carcinogens like benzidine and are also known to accumulate, thus posing a serious threat (Baughman and Perenich, 1988). Many dyes are also known to get reduced to toxic substances inside living organisms (Weber and Wolfe, 1987). The carcinogenicity of azo dyes, which constitute a significant proportion of textile dyes, is well known (Weisburger, 2002; Umbuzeiro *et al*., 2005). Color is the first contaminants to be recognized in any wastewater and its gives an indication that such water has been polluted (Azhar *et al*., 2005). This affects its aesthetic merit, impedes light penetration and may be toxic to aquatic lives.

Therefore many methods such as adsorption, chemical coagulation, ion exchange, electrolysis, and biological treatments (Gupta *et al*., 2004; Adelagun *et al.*, 2014), have been developed for removing dye pollutions from wastewater before being discharged into the environment. Coagulation is one of the cheapest processes for treatment of various organic effluents (Pradeep *et al*., 2011). Coagulation and flocculation processes are used to separate the suspended solids portion from the water. Most solids suspended in water possess a negative charge and since they have the same type of surface charge, they repel each other when they come close together. Therefore, they will remain in suspension rather than clump together and settle out of the water. Coagulation and flocculation occur in successive steps intended to overcome the forces destabilizing the suspended particles, allowing particle collision and growth of floc (Tridib and Bhudeb, 2006). Inorganic coagulants such as aluminum and iron salts are the most commonly used. When added to the water, they furnish highly charged ions to particles. Common coagulant chemicals used are alum, ferric sulfate, ferric chloride, ferrous sulfate, and sodium aluminate (Fatoki and Ogunfowokan, 2002; Azhar *et al*., 2005; Garcia, 2005; Badmus *et al*., 2007). Coagulation efficiency on the other hand is enhanced by adding appropriate coagulant aid. Coagulant aids are generally used to reduce flocculation time and when the raw water turbidity is very low, add density to slow-settling flocs and add toughness to the flocs so that they will not break up during the mixing and settling processes. Common coagulant aids include bentonite, calcium carbonate, sodium silicate, anionic polymer, nonionic polymer.

In recent time, in other to compensate the high cost of inorganic coagulants and problems associated with residual metals after water and wastewater treatment (Sayed *et al*., 2004), naturally derived substances have been developed as coagulants and coagulant aids in water and wastewater treatment. The need to improve on the economy on water and wastewater operations and environmental friendly coagulants has geared scientists to search for more biocoagulants (materials of biological origin). A lot of these substances have been reported while efforts are still directed at obtaining more. These include turkey's feathers, pre-cooked puffed cereals, ground corn cobs (Sayed *et al*., 2004), periwinkle shells (James and Okolo, 2006; Badmus *et al*., 2007), fly ash, red mud (Shaobin *et al*., 2005), sugarcane baggase (Azhar *et al.*, 2005), tannin (Ozacar and Sengil, 2003a, 2003b), chitosan and modified chitosan biopolymer (Pan *et al*., 1999, Huang *et al*., 2000; Bratskaya *et al*., 2002; Strand *et al.*, 2003; Roussy *et al*., 2005), plantain peelings ash extract (Oladoja and Aliu, 2008), snail shell (Oladoja and Aliu, 2009).

Recent advances in biotechnology have shown that egg shell is no longer regarded as a waste but rather as a feedstock for producing several products. Thus, efficient recycling of egg shell requires extensive research and development work towards exploring newer applications and maximizing the use of existing technologies for a sustainable and environmentally sound management. The present study is aimed at the use of alum as primary coagulant and egg shell as a coagulant aid in the decolourisation of methylene blue (methylthioninium chloride) (Fig. 1) contaminated water.

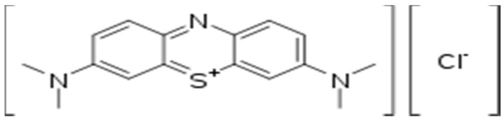

Fig. 1: Structure of methylene blue

Materials and Method

Preparation of powdery egg shell

The egg shell (purchased from local farms and restaurants in Wukari, Taraba State) was first washed with tap water then rinsed thoroughly with deionized water, dried in the oven and ground in a wooden mortar and pestle. The ground egg shell was finally made into powder using laboratory grinding machine and sieved with a laboratory sieve of mesh size 50 microns and stored in an air-tight container.

Preparation of coagulant (alum) solution

A stock solution of 500 mg/L of commercial alum [$Al_2(SO_4)_3$] was prepared while working solutions of various concentrations (5 - 100 mg/l) were prepared from the stock solution by serial dilution.

Preparation of dye solution

A stock solution of 500 mg/L of Methylene Blue (MB) was prepared while working solutions of various concentrations (5 -100 mg/L) were prepared from the stock solution by serial dilution.

Determination of effect of initial alum concentration

Five (5) mL of the dye solution (MB) of 50 mg/L was added to 50 mL beaker containing 50 mL of varying concentration of alum (5–100 mg/L). Each mixture was stirred vigorously for two min at 240 rpm and followed by gentle stirring at 80 rpm for 20 min using a magnetic stirrer. Settling time of 30 min was allowed and 30 mL of the supernatant was drawn from the mixture with a syringe. Uniform level of drawing was maintained throughout the experiment. Residual MB concentrations was analysed using UV-spectrophotometer at a wavelength of 497 nm. The alum dose that gave the least residual MB concentration was noted and the corresponding coagulant dose was taken as the optimum alum dose in each case.

Determination of effect of initial dye concentration

Five (5) mL of alum of (50 mg/L) was added to 50 mL beaker containing 50 mL of varying concentration (5–100 mg/L) of the dye solution, MB. Same procedure was followed as described above. The MB dose that gave the least residual alum concentration was noted and the corresponding coagulant dose was taken as the optimum dye dose in each case.

Determination of effect of egg shell dose

Powdered egg shell (ES) was used as coagulant aid in the present study. However, its ability to coagulate the MB molecules singly was tested. 5 mL of 50 mg/L MB was added to 50 mL beaker containing varying amount of egg shell (1, 2, 3, 4, 5, 6, 7 g). Same procedure was followed as described above and the egg shell dose that gave the minimum residual dye concentration in each case was regarded as the optimum egg shell dose.

Determination of optimum alum/egg shell dose

The effects of alum/egg shell combination were studied at fixed alum (25 mL of 50 mg/L) and varying egg shell (ES) doses (1, 2, 3, 4, 5, 6, 7 g) and 25 ml of 50 mg/L of the dye solution, MB. Same procedure was followed as described above. The combination that gave the least residual dye concentration was taken as the optimum alum/ES combination.

Determination of pH effect for methylene blue removal

Coagulation and flocculation is a unit process that is highly pH dependent. In order to optimize the effect of pH on the removal of MB from aqua system using alum coagulant; the pH of MB contaminated water was adjusted to 2, 3, 4, 5 and 6 using HCl and NaOH as appropriate. Same procedure was followed as described above.

Results and Discussion

Effect of initial alum concentration

An overview of the result obtained when alum alone was applied as primary coagulant in dye removal from aqueous system is presented in Fig. 2 Increase in the initial alum concentration resulted in a corresponding reduction in the intensity in the colour of the samples. The visible change in the colour and increase in the amount of MB removed showed that alum is an efficient coagulant in dye removal. At the initial alum concentration 5 mg/L, the amount of methylene blue removed was 52%, which increased to 86% with increased in alum concentration of 100 mg/L. Alum efficiency in the present studies can be attributed to the fact that alum dissolves in water to produce series of products with positive charges. Edzwald *et al.* (1990) reported the possibilities of Al^{3+}, $[Al(OH)]^{2+}$, $[Al(OH)_4]^-$ and $Al(OH)_3$ during aluminum coagulation. The cations, produced by the alum ionization in aqueous medium, destabilized the MB particles by neutralizing their negative charges. Neutralization of the negative charges resulted in the formation of flocs which was observed. From the result, optimum alum concentration for removal was 50 mg/L.

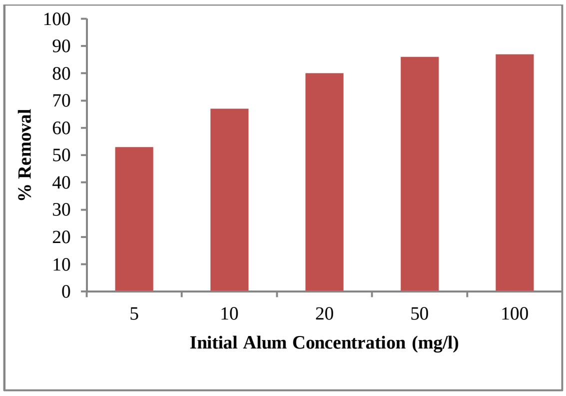

Fig. 2: Effect of initial alum concentration

Effect of initial dye concentration

Effect of initial dye solutions of various concentrations (5-100 mg/L) was investigated on the coagulation process by alum showed that the removal of dye increases with the increase in concentration (Fig. 3) achieving a maximum removal of 81% at 50 mg/l. This implies that alum could be used to treat dye contaminated wastewater of different concentration. Optimum dye concentration of 50 mg/L was taken.

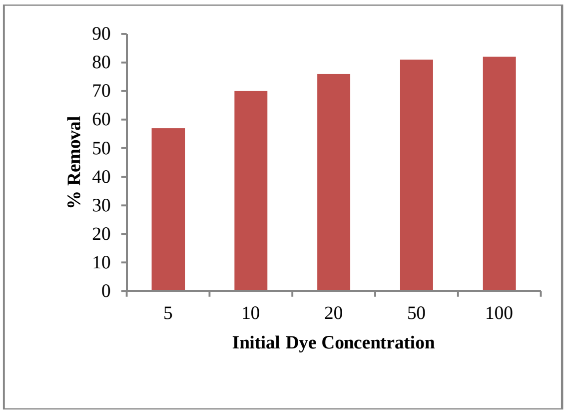

Fig. 3: Effect of initial dye concentration

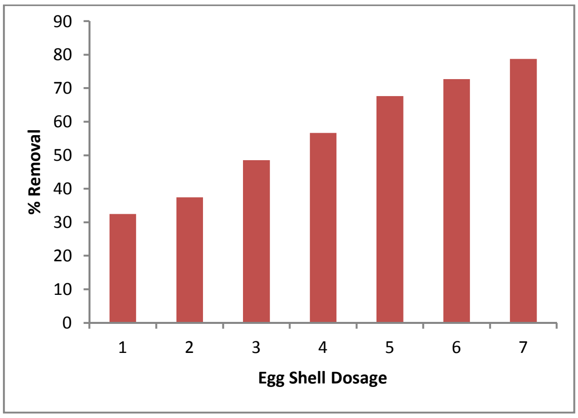

Fig.4: Effect of egg shell dosage

Effect of egg shell dosage

The result obtained from this study, expressed as a percentage are presented in Fig. 4. The percentage of the dye removed increased with increase in the ES dosage for each dye concentration. In the present studies, the addition of egg shell to the various dye solutions produced water with low-residual dye concentrations. This increase is attributed to increase in the driving force of overcoming all mass transfer resistance between adsorbent moieties and the adsorbate.

Effect of egg shell dosage as coagulant aid

In order to evaluate the ability of ES to act as coagulant aid, the optimum dose of primary coagulant (alum) was used with the ES shell dosage varied (1, 2, 3, 4, 5, 6 and 7 g). The different combination ratios were used to carry out the coagulation process at the neutral pH of the MB solutions. The results obtained (Table 1) showed the efficacy of ES to improve the efficiency of alum as the primary coagulant. The percentage of MB dye removed from different initial concentrations increased from 60% to 98% as the concentration of MB was increased from 5–100 mg/L.

The performance of alum/egg shell combination was found to increase with increase in concentration of the MB dye. Alum molecules undergo hydrolysis reactions in water to give cationic, neutral and anionic complexes depending on the extent of substitution of H_2O with OH^-. A complex containing several molecules of aluminium may even be formed with OH^- as a bridging group by a process called flocculation. These several alum products are capable of forming stable flocs by "sweep floc" and/or destablisation of MB particles. Adsorption could even take place simultaneously due to polymeric nature of egg shell. All this would account for the optimum clarification of the MB dye solutions. The amount of MB removed from the solution was higher with the combination of ES and alum than when alum was used alone. This implies that ES used as a coagulant aid improved efficiency of MB removal. This is attributed to the presence of elemental composition of the ES, $CaCO_3$, which releases Ca^{2+} thus precipitating the MB from solute.

Table 1: Determination of optimum alum/egg shell dose

Concentration (mg/l)	% Removal
1	60.3794
2	66.6805
3	78.5861
4	85.6148
5	90.6826
6	94.7313
7	98.7608

Table 2: Determination of pH effect on MB removal

pH	% Removal
2	86.99461
3	89.99431
4	90.99402
5	92.99343
6	97.65000

Effect of pH for the removal of MB from aqueous solution

Coagulation and flocculation is a unit process that is highly pH dependent. The pH influences polymeric metal species which are formed when the metal coagulants are dissolved in water (Stumm and Morgan, 1996). The influence of pH on chemical coagulant, as posited by Randtke (1988) is a balance of two competitive forces: between H^+ and metal hydrolysis products for organic ligands and between hydroxide ion and organic anions for metal hydrolysis products. If the pH is too low, the protons outcompete the metal hydrolysis products for organic ligands and poor removal occurs because some of the organic acids are precipitated. At a higher pH, the OH^- ion competes with organic compounds for metal adsorption sites and the precipitation of metal hydroxide occurs by co-precipitation.

Evaluation of the effects of pH on the removal of MB from aqua system by alum coagulation of MB dye was conducted at the optimum alum/ES combination. The percentages of MB dye removed in all cases were appreciably high at all the pH values studied (Table 2). This shows that flocs were appreciably stable even at varying pH range. Similar stability of aluminium derivates coagulant (polyaluminium chloride) has been reported (Pernitsky and Edzwald, 2003). When the experiment was conducted at the natural pH of the MB (pH 6.7), the values of the percentage MB removed was not less than 99% in almost all the concentrations studied. Hence we can infer that pH has little or no effects on the removal of MB dye molecules from solution and that the possible structural change occasioned by the change in pH did not affect the interaction between the dye molecule and the egg shell used for the coagulation.

Conclusion

The effects of alum as primary coagulant and ES as coagulant aid in the removal of MB from aqueous system were studied in the present work. The effects of alum and ES dosages, alum/ES combination ratio and pH were optimized by method of continuous variation. Alum, when used alone was found to be effective in the decolourisation of MB and the effects increased with increase in alum dosage. The ability of alum to decolourise MB dye can be attributed to the formation of positively charged ion in aqueous system which will then interact with the negatively charged MB molecules. Thus precipitation occurred. The ability of ES when used alone to remove MB was very low. However, the process was enhanced when alum was used as primary coagulant in combination with ES as coagulant aid with over 98% removal achieved. The optimization of pH showed little or no variation in the amount of MB removed from solution. However, the amount of MB removed was appreciably high at all the pH studied. This project through its effective demonstration has successfully evaluated powdered egg shell as coagulant aid to alum a primary coagulant in the treatment of dye contaminated water. It is therefore recommended that use of egg shell as a coagulant aid in dye removal from aqueous system.

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