Facile removal of Fluoride Ions from water using Triethylamine Modified Polyethylene Adsorbent

Gerald Mbugua[1], Isaac Mwangi[1], Ruth Wanjau[1], Moses Abednego Ollengo[2], Esther Wanja Nthiga[2], Jane Catherine Ngila[3]

[1] Department of Chemistry, Kenyatta University, P.O. Box 43844, Nairobi, Kenya
[2] Department of Chemistry, Dedan Kimathi University of Technology, Private bag, Nyeri, Kenya
[3]Department of Chemistry, University of Johannesburg, Doornfontein Campus, Doornfontein, South Africa
*Corresponding Author E-mail:

ABSTRACT:

Highly fluoridated water is hazardous to human and animal health and effects are not limited to dental and skeletal fluorosis, diarrhea and impaired brain development. Traditional water treatment methods have limitations such as high production cost, ineffectiveness and are not reusable. In this work, the use of waste polyethylene materials derived from municipal solid waste as a green water treatment technique that affords low price, value addition and ecological friendly technology has been presented. The polyethylene wastes were dispersed in vegetable oil and modified using triethylamine. Modification was confirmed by Fourier transform infrared spectrometry (FTIR) and scanning electron microscopy (SEM). The effect of pH, initial fluoride concentration, contact time and adsorbent dose were investigated and optimized. adsorption was found to prescribe to Langmuir adsorption with an adsorption capacity of 10. 30 mgg-1. The removal process was found to be optimal at pH 6.0. This study showed that triethylamine modified polyethylene adsorbent has a potential application for removal of fluoride from contaminated waters.

KEYWORDS: Complexation capacity, triethylamine, vegetable oil, kinetic isotherm.

INTRODUCTION:

Plastics are very light, cheap, and dangerous materials. They are generally used only once and are then thrown away as they are easily made. The fact that plastics are light and non- biodegradable, they litter and gather in the environment and are transported from source areas to the ocean (Hammer *et al.*. 2012). The throwing away of plastic based materials into the environment has become an increasingly serious form of environmental pollution in recent years (Yu *et al.*. 2019). These materials last for long and are persistent especially in developing countries like Kenya (Krueger *et al.*. 2015).

Many challenges are experienced regarding plastic waste management which degrades the beauty of the environment including littering towns, rural areas, shores and even oceans in many developing countries.

Image 1: Gioto dumping site in Nakuru County- Kenya
Source: Author

These materials may also be eaten by animals during grazing thus providing a way by which poisonous polychlorinated biphenyls enter into the animal body (Chua *et al.*, 2014). As much as plastic is harmful and degrade the environment when unwanted after its first utility as seen in image 1.

Since the release of polyethylene into the market, addition of functional groups on their surface is a concern to both academic and industrial communities (Hu *et al*. 2018). Some approaches which change the surface of plastics are engaged to alter this polymer surface, which include use of chemicals, heat, mechanical or plasma usage (Navaneetha Pandiyaraj *et al.*. 2008).The material has quaternary ammonium compounds which represent a group of polymers that have special properties along its backbone (Bshena *et al.*. 2011). In this study, improvement of polyethylene waste was done..

MATERIALS AND METHODOLOGY:

Modification of the polyethylene material:

Five hundred milliters of vegetable oil was heated to boiling in a three neck flask. To this, clean dry plastic wastes cut to small pieces were added. A 10 mL strongly basic hydrogen peroxide was then added drop wise. The mixture was allowed to boil for 15 minutes for complete epoxidation process. Epoxidated plastic material was refluxed for six hours in an isomantle. The hot epoxidated plastic sample was allowed to cool and then ground to fine powder. Ground epoxy was activated at 100˚C for 72 hours. Activated solid sample was ground into fine powder to increase surface area for fluoride adsorption.

Batch experiments:

Removal studies were carried out on a Lab-line mechanical reciprocating shaker model (DKZ-1NO.1007827) using plastic screw cap bottles. Batch experiments were done to investigate the effects of pH, initial fluoride concentration, adsorbent dose and contact time. Fluoride ions removed per unit mass were calculated using the equations 1 and 2 respectively (Mbugua *et al*.. 2017).

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Where C_0 and C_e are the initial and equilibrium concentration (mgl^{-1}) of fluoride ions in solution respectively, V is the volume of solution (in liters) and W (g) is the mass of the solid material.

RESULTS AND DISCUSSION:

Characterization of solid sample:

FTIR for unmodified and modified sample:

The FTIR spectra of liquid vegetable oil dispersed polyethylene bags, epoxidated samples, activated, fluorine treated adsorbent and regenerated adsorbent were characterized using FTIR (8400 Shimadzu model) and the resulting spectra are presented in Fig.1.

Disappearance of the peaks at 1741.6 cm^{-1}, 1074.7 cm^{-1}, 609.5 cm^{-1}, 538.1 cm^{-1}, 486.0 cm^{-1} and 846.7 cm^{-1} in epoxy was observed upon activation with amines. This was as a result of - NH attachment on the surface of the epoxide that occurred during curing reaction. The resulting functional group which is permanently charged, is capable of interacting with the with the negatively charged fluoride ion to form a strong bond (Mwangi *et al*.. 2019).

Fig 1: Modified polyethylene material (Temperature= 373 K, 500 mL liquid vegetable oil, 10 mL basic hydrogen peroxide, 10mLbtriethylamine and 72 hours).

Image 2: Scanning electron microscope images for unmodified and modified polyethylene sample.

Scanning Electron Microscopy:

The SEM images of the surface morphology of the unmodified and modified polyethylene material as shown in image 2

Scanning Electron microscopy images for unmodified appeared rough with few cracks while in modified material, the surface appeared rough with few large pores. Appearance of pores on the surface could increase the adsorption capacity of the product the three images showed a clear illustration that amine groups had interacted with the epoxide.

Optimization experiments:

Effect of pH:

Monitoring the pH of an sorbate is important in adjusting sorption process as reported (Pérez-Marín *et al..* 2007). In this study, a 50 mL fluoride solution was put in 100 mL plastic bottle. The pH of solution was adjusted using 0.1 M Nitric acid and 0.1 M sodium hydroxide solutions. The results were presented in Fig 2.

Fig 2: Effect of pH on the removal of fluoride ions by triethylamine modified plastic material (Initial solution concentration = 10 mgl-1, temperature = 298 K, amount of adsorbent = 0.1 g and contact time = 30 minutes, agitation speed = 150 rpm).

It was observed that at higher pH values, the amount of fluoride ions removed from water was low. Decrease in fluoride removal at higher pH may be due to gradual increase in number of negatively charged hydroxide ions on the adsorbent surface causing electrostatic repulsion of fluoride ions (Kim *et al..* 2015). This corroborates the high surface charge characteristic observed in SEM images. The sharp decrease in fluoride removal efficiency was probably due to the competition between hydroxide and fluoride ions for adsorption sites and the increase in diffusion resistance of fluoride caused by abundant hydroxide ions. The OH^- ions could have displaced fluoride ions from the solid decreasing the efficiency of the modified material (Iriel *et al..* 2018). At lower pH values, removal of fluoride increased significantly. This could be due to increase in the positively charged H^+ ion on the surface of the adsorbent from which reacts with fluoride ions to form hydrofluoric acid that leads to a greater decrease of fluoride ions in solution. To increase efficiency of the modified polyethylene adsorbentin this study, the pH of solution was maintained 6.0.

Effect of initial fluoride ions concentration on removal of fluoride ions:

Concentration of fluoride ions on the percentage removal of fluoride was studied at different initial fluoride concentrations by keeping other parameters constant. The effect of initial concentration on removal of fluoride was shown in Fig3.

Fig 3: Effect of varying the initial concentration of fluoride solution from 0.5 to 20 mgl-1on percentage removal of fluoride ions by triethylamine modified plastic material (pH= 6.0, dosage = 0.1 g, temperature = 298 K, contact time = 30 minutes, agitation speed = 150 rpm).

The results show that when fluoride initial concentration was increased, the adsorption capacity of fluoride ions removal of fluoride ions increased as shown in Fig 7 because of higher concentration gradient acting as a driving force overcame mass transfer resistance between bulk solution and adsorbent surface (Srivastava *et al..* 2006). At higher concentration (.>10 mgl^{-1}) the efficiency of the material declines, this could be because at a fixed adsorbent dose, the total available adsorption sites are few and this becomes saturated at higher concentrations (Bhaumik and Mondal 2016)**.**

Effect of contact time:

The speed of fluoride ions uptake is related to the efficiency of the adsorption sites to hold the ion, as well as the electro negativity of the halide, thus controlling the residence time of the ions between sorbate and the adsorbent (Demirbas *et al..* 2004). This led to the investigation of the effect of contact time by varying the equilibrium time from 0 to 60 minutes while keeping all the other conditions constant. The results obtained were presented in Fig 4.

Fig 4: Effect of contact time on the removal of fluoride ions using modified plastic material (initial solution concentration = 10 mgl-1, temperature = 298 K, dosage = 0.1 g, pH= 6.0, agitation speed = 150 rpm).

The general observation was that there was an initial rapid rate within the first 30 minutes followed by a subsequent slower rate. This was probably due to the availability of high number of complexation sites on the surface of the material at the initial stage. Upon saturation of the binding sites, the amount of fluoride complexed at a given time decreased due to limited complexation sites (Hiremath and Theodore 2016). Between 20 to 30 minutes, the removal of fluoride decreased slightly, this could have been contributed by a steep concentration gradient between the solution and the adsorbent, making the fluoride ion to migrate back to the sorbate until equilibrium is established.

Effect of dosage:

The removal efficiency of an adsorbent increases with increase in adsorbent dose (Mbugua *et al..* 2014). This is due to available adsorption sites increase by increasing the adsorbent dosage. In this study, effect of dosage on fluoride ions removal, initial solution concentration of 10 mg L^{-1}, 30 minutes contact time, temperature of 298 K and agitation speed of 150 rpm and the results were as shown in Fig 5.

Fig 5: Effect of dosage (initial solution concentration = 10 mgl^{-1}, pH= 6.0, temperature = 298 K, contact time = 30 minutes, agitation speed = 150 rpm).

The results show an increase in complexation capacity as the dosage was increased from 0.01g to 0.1g. This was due to the large number of binding sites resulting from increased adsorbent dosage and availability of more effective surface area of the adsorbent. Similar results were also obtained by Suneetha *et al*.. (2015) in removal of fluoride from polluted waters using active carbon derived from barks of vitexnegundo plants.

Adsorption capacity:

To determine the efficiency of modified polyethylene material adsorption isotherms models were used to provide the nature and physico-chemical interactions involved in the adsorption. In this study, Langmuir and Freundlich isotherm models were used to determine the maximum removal capacity of modified plastic adsorbent (Foo and Hameed, 2010). The study was done by varying the initial concentration of fluoride solution from 4 to 50 mgl^{-1} in a water bath shaker for 30 minute and the results presented in Table 1.

Table 1: Langmuir and Freundlich constants

Adsorbent	**Langmuir constants***			**Freundlich constants***		
Modified plastic material	**Qmax (mgg^{-1})**	**K_L (L/mg)**	**R^2**	**(Kf) (mgg^{-1})**	**1/n**	**R^2**
	10.30 mgg^{-1}	0.0348	0.8638	7.86	0.6745	0.4836

*Langmuir and Freundlich adsorption isotherm constants Initial concentration 4 to 50 mgl^{-1}, dosage = 0.1 g, pH = 6.0, Temperature = 298 K, agitation speed = 150 rpm).

From the table, it was observed that the data fitted well in the Langmuir adsorption isotherm with a removal capacity of 10.30 mgg^{-1} and a correlation coefficient R^2 of 0.8638 compared to that of Freundlich isotherm model which gave a lower value. The 1/n value obtained was 0.6745 and Kf value was 7.86 mgg^{-1}a lower value of 1/n indicated that the adsorption process was favorable to a homogenous surface. Therefore, there is a clear indication that adsorption of fluoride ions using modified polyethylene material follows a monolayer adsorption process on homogeneous surface.

CONCLUSIONS:

This study successfully modified plastic wastes through modification with triethylamine. The modified adsorbent confirmed removal of 10.30 mgg^{-1} in less than 30 minutes at pH 6.0 indicating that plastic wastes can be modified and used as an alternative cheap adsorbent for treating water of with high fluoride content.

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