Plastic pollution recycling: A case study of first marine protected area of Pakistan (Astola Island)

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Abstract

Astola Island is the first marine protected area of Pakistan acknowledged 2017, June 15. It is a rich biodiversity hotspot, Ramsar site inhabiting endangered species like Green turtle, Hawksbill turtle, and Arabian Humpback whale. A saw-scaled *Russell's viper* is endemic to Island. Marine ecology of Astola Island is affected by plastic pollution resulting in coral destruction, ocean acidification, global warming, fishing nets blockage, water pollution, and coastal erosion. Zeolite catalyst synthesized from environmentally friendly way by coal fly ash to degrade collected plastic waste from Island into useful products in pyrolysis reactor. The synthesized catalyst functionalized further with three type of organosilane(1) Octyltriethoxysilane(OS),(2)Phenyltriethoxysilane(PS),(3)Vinyltriethoxysilane(VS).Zeolite functionalize with octyltriethoxy silane (ZO) shows the highest performance in plastic pyrolysis, resulting in lower degradation temperature, low residue and more product formation may be due to having long chain hydrocarbon and acidic sites. Plastic recycling is the promising solution to tackle plastic blooming issue. Which is negatively impacting all the compartments of ecosystem especially marine environment.

Keywords Astola Island; Plastic pollution; Zeolite catalyst; Recycling

1. Introduction

In developing countries, plastic pollution is of prime concern that affects all compartments of the environment, especially water. Plastic litter varies in composition and quantity in seawaters, beaches and deep seas (Kalogerakis et al., 2017). The environmental and human impacts of plastic waste are indicative of nonchalant behavior of human towards nature. Pakistan has coastline of 1050 km, out of which 800 km falling in the Balochistan province and 250 km in Sindh. Significance of establishing of the marine protected areas (MPA's) in Pakistan at different levels for conservation of ecosystem, cultural value and scientific reference site is contributing to the sustainable tourism, recreational activities and local community's employment (Siddiqui et al. 2008; Waqas, 2011).

Astola Island is the first marine protected area of Pakistan acknowledged on June 15, 2017. This is also known as Jazeera Haft Taller (Island of seven hills). It covers an area of $6.7km^2$ in width, 240 feet high above sea level and buffer zone of 401.47 km^2. It is a rich biodiversity hotspot, inhabiting endangered species like Green turtle, Hawksbill turtle, and Arabian Humpback whale.A saw-scaled *Russell's viper* is endemic to Island. Marine ecology of Astola Island is affected by plastic pollution resulting in coral destruction, ocean acidification, global warming, fishing nets blockage, water pollution, illegal fishing and coastal erosion. Astola is uninhabited offshore largest island due to high tides and roughness of the sea (Pakistan, M. F. F. (2018). Astola Island–First Marine Protected Area in Pakistan; Ramseur sites information services. (2019, May 1) Retrieved from https://rsis.ramsar.org/?language=en). Astola Island – First Marine Protected Area in Pakistan.MFF Pakistan, Pakistan. 92 pp.).

Plastic degradation fragments and filaments enter the   food web in the ocean threatening marine species health and major ecological catastrophes that endangers vulnerable species. Plastic have different shape, color and size ingested mistakenly by animals (Isangedighi et al., 2018) cause serious problem in migration, lower level of reproduction, endocrine abnormalities, internal injuries and even death (Maia et al 2019) .Sandy beaches is the most accumulated area of plastic litter, plastic destructed not only coastal area but also rises sea level (Fuentes et al., 2010; Elms et al., 2016). Nesting activities make difficult due to presence of plastic in marine environment (Gundog et al., 2019).

Macro plastic converted to unseen form of plastic pollutants which have been detected in 1970's is named as microplastic.Microplastic reported in the sediments of Yangtze Estuary, South China Sea, yellow sea and Bohai Sea (Wang et al., 2019). Micro plastic are heterogeneous group of materials exhibit distinct physiochemical properties related to sources of emissions. Biological effects of micro plastic influenced by many factors like size, composition and polymeric additives.

The traditional method for plastic degradation was incineration, but not environmentally friendly. Due to carbon dioxide emission released in the air but pyrolysis is the most promising technique for plastic waste management (Constantinescu et al., 2019). Plastic waste energy is the new paradigm for plastic related problems, so that plastics can be a potential new cheap energy source of important chemicals which are recyclable. Thermal degradation produces low hydrocarbons fuels and other chemicals by inert atmosphere by pyrolysis of plastic waste in the temperature ranging from 500^0C to $800\ ^0C$. This technique leads to a wide product distribution and highly energy efficient.

Catalytic degradation of plastic significantly reduces the temperature required to polymer cracking. Liquids fuels and gas which are highly desired chemical products requires proper selection of the catalytic system (Covarrubias et al., 2010). There are several catalysts used for plastic degradation. Marine environment threatened by anthropogenic activities, need of hour is to understand concerned people perceptions of plastics and their environmental impacts if we want to reduce the input of plastic into the ocean (Henderson et al ., 2020).

Zeolites are crystalline micro porous alumina silicate materials which are stable over a wide range of temperature. Zeolite synthesized from both naturally (e.g. Coal fly ash) and synthetically from pure chemicals. The coal fly ash precursor for zeolite synthesis is environmentally friendly and has major components like Alumina (Al) and silica (Si) (Cuzma et al., 2020). Zeolites are stable up to 650^0C -1000^0C mostly containing high silica-to- alumina ratios. It exhibits acidity comparatively higher than previous silica-alumina catalyst. Zeolites have both Bronsted and Lewis acid sites. These acidic sites present on zeolite affected by nature, type, density, strength distribution, location and geometric distribution of acidic sites. Synthesis of zeolite by coal fly ash is environmentally friendly way.

Organosilane was used for the surface modification of zeolites (Li et al., 2015).Zeolite modifies or grafted with octyltriethoxy silane (OTEOS) by variable amount because of maximum active sites accessibilty.It also increases hydrophobicity of zeolites. These modify zeolites have several applications (Novak et al., 2020).

Pyrolysis is obtained through different catalytic processes like thermal, hydrocarbon and catalytic. Thermal catalysis has a drawback as; it produces more carbon range products. But compared to thermal, catalytic degradation decreased reaction temperature and also increase product yield (Zee et al., 2020; Rajendran, 2020). ZSM-5 zeolite catalyst in the plastic waste pyrolysis plays an important on the color of oil, oil yield and also on capability to decompose the polymer (Magnet et al., 2020). Pyrolysis with the help of catalyst in the range of temperature of 300°C -650°C helps to improve bio-oil hydrocarbon range because of zeolite molecular structure and their strong acid sites (Hoi and Claim et al., 2020).

Pyrolysis is convenient technique than gasification and high-pressure liquefaction because economically cheap and the manipulation of parameters during process is easy (Hassan et al., 2020).

Pyrolysis put up to the circular economy, waste plastic converted thermo chemically into degradation products using polyethylene and polypropylene feedstock's (Canopoli et al., 2020).Production of biodiesel was achieved by renewable resources. In diesel engines used as additive, replace petrol-diesel, reduce gaseous pollutants, increase economy, waste management of biomass and also this leads to acquiring sustainability (Bhan et al ., 2020).Plastic recycling has become very lucrative activity aims to achieved sustainable development through providing benefits to the current and future generations, economic prosperity and social equity (Gall et al., 2020).

2. Methods and Materials

The study area was visualized through ArcGIS (10.7.1) to select the sampling sites. Sampling was carried out in March, 2020 and weather conditions were mostly sunny Samples were collected on five different beaches including Ormara, Jabbal Juddi, Jabbal zareen, Pasni creek beach and Astola Island (first marine protected area).The geographical coordinates of sampling site was recorded through global positioning system (GPS). The areas were chosen due to accumulation of plastic waste and garbage.

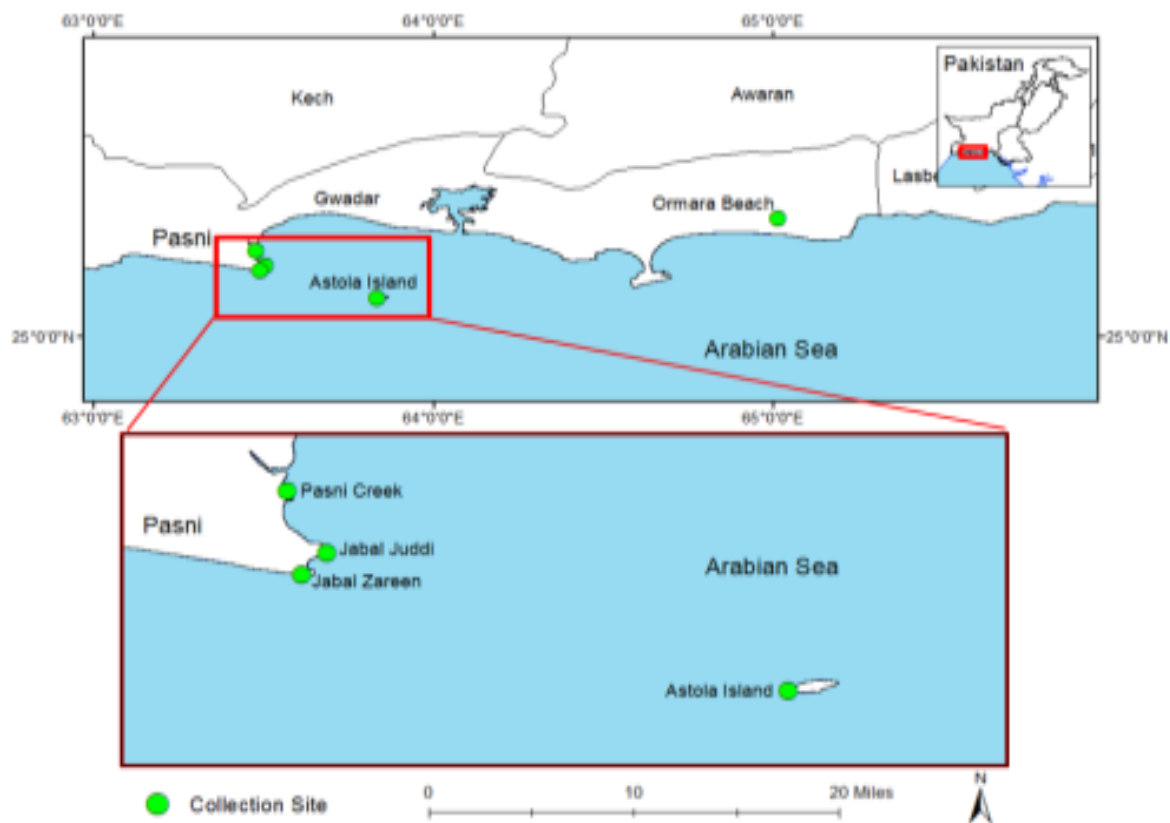



Figure (2) .Showing map of collection points of sediments and water samples.

Coal fly ash was provided by National Cleaner Production (NCPC) Rawalpindi Pakistan, Sodium Meta silicate (BDHL), Aluminum isoprop-oxide (Sigma Aldrich), tri ethoxy octyl silane, phenyl tri ethoxy silane, trimethoxy vinyl silane, potassium hydroxide, sodium hydroxide purchased from Merck. All the chemicals were of analytical grade and used without further purification. Representative plastic samples were prepared by cuttings of plastic 2cm^2 of area.

2.1. Synthesis of zeolite using hydrothermal method

Zeolite is synthesized sodium Meta silicate by using hydrothermal method reported by Chauhan et al., (2012). For this purposes, 8.9g of sodium Meta silicate was mixed with 2g NaOH anhydrous form and grounded into fine powder mixture using a pestle and mortar. The dried mixture was transferred into a crucible and placed in a furnace at 500°C for 2

hours. The resultant solid mixture and grounded again into fine powder and mixed with 100 ml of deionized water and small quantity of aluminum isopropoxide added and stirred at 600 rpm. The suspended slurry mixture was then placed for autoclave (120mmHg; 2 hours). The solid was filtered and washed until pH 8 was attained. Then, dried in oven at 100 °C for 12 hours.

2.2. Functionalization with organosilane

Organosilane was used for the surface modification of zeolites (Li et al., 2015).Functionalization with silane derivatives containing octal group was carried out by refluxing a mixture of zeolite 2g and trimethoxyoctylsiane (2ml) in toluene (70 mL) for 5 hours. After Centrifugation the solid was washed with toluene. Silane containing- phenyl group was carried out by refluxing a mixture zeolite (2 g) and tri ethoxy phenyl silane (2 ml) in toluene (70 mL) for 5 hours followed by centrifugation and washing of zeolite powder with toluene. Zeolite 2g was immersed in toluene (70 mL) containing tri ethoxy vinyl silane (2ml). Then five minutes suspension was shaken at room temperature. The solid was collected by centrifugation and finally dried at 90°C for 5 hours. (Hassan et al., 2013).Synthesized zeolites were codes as Z (Without silane), ZP, ZV, and ZO.

2.5. Characterization:

The method consists of hydrothermal method to obtain zeolite directly. Different techniques (FTIR, EDX, TGA, Bomb Calorimeter) were used to characterize the zeolite catalyst.FTIR spectrophotometer (Bruker IFS 113 V) was used to identify the main functional groups of catalyst and oil obtained from pyrolysis of plastic. EDX was used to determine the elemental composition (Si, Al, O, and C) of zeolite catalyst. TGA was applied in the experiments to investigate the decomposition of PE, PP, PET and PS with or without catalyst. TGA characterize catalyst by evaluating their activity in terms of the change of degradation temperature. The instrument used was TG209F3 from Netzsch Company. Bomb calorimeter (ASTM D4858) was used to determine the caloric value of oil obtained from plastic waste.

3. Results and Discussion

3.1Fourier transformation infrared spectroscopy (FTIR):

3.1.1FTIR of Zeolite catalyst:

Functional group zeolites were determined by FTIR analysis (Mittal et al., 2020). FTIR of the zeolite was done in the laboratory using KBr pellets at room temperature after background correction. The FTIR spectra of zeolite catalyst are in the range of 4,000 to 400 cm^{-1}.FTIR analysis of zeolites shows absorption band in the 3424 cm^{-1} region which attributed (Si-OH) terminal silanol group (Abdullah et al., 2020).Asymmetric stretch of Si-0 vibration occurred at 1049 cm or 800 cm^{-1}.the band near 470 cm^{-1} shows bending mode of Si-O-Si (Osackyet et al ., 2020).

3.1.2 FTIR of oil obtained from plastic waste:

Functional group of each collected fuel was determined by FTIR analysis. Sodium chloride cells were used to perform the analysis (Kumar and Singh, 2013) and sample were diluted in methanol. After distillation this fuel is used as alternative of diesel (zhao et al ., 2020).C-H group stretch around(3000-2800cm^{-1})were more intense bands and angular deformation occued at (1464cm-1-1379cm^{-1}).Carbonyl absorption band (1750 -1735 cm^{-1}) and aliphatic ester absorption band (1300-100 cm^{-1}) shows the presence of biodisel in the samples.Low intensity bands (675-900 cm^{-1}) are aromatic compounds (Nespeca et al ., 2018)

Table No. (1) FTIR assignment of pyrolysis oil

Wave number(cm^{-1})	Type of vibration	Name of functional group
3626.29-35.832	O-H strong broad	Alcohol,Amide,phenol,
2351.30-20.98	Aliphatic C-H stretching	Alkane
1651.12	C=C stretching	Alkene/phenylring substitution overtone
1415.80	C-H bending	Alkane
1392.65-1325.14	C-H scissorimg and bending	Alkane
1290.42-1240.27	C-N stretch	Aromatic Amines
1016.52	C-N stretch	Aliphatic amines
1178.65	C-O stretching	Alchol,carboxylic acid,ester
707.90	C-H rock	Alkane
929.72	==C-H bending	Alkene

3.2. Energy dispersive x-ray (Edx) analysis:

Eight zeolite catalyts concentrations were measured by suggests that of energy dispersive x-ray analysis (Si, Al, O, Ca, K ,C, Na), the Si/Al ratios within the vary of 47(Si) /10(Al) .This results showed that very same weight percentage share as antecedently studied Si/Al quantitative relation 46 Si /10Al (Wang et al., 2011).

Table No. (2): Elemental composition of zeolites (Weight percent)

Sample Code	Al	Si	Ca	O	Na	K	C
Z	16.49	23.55	33.99	35.48	7.14	10.03	6.52
ZP	11.10	47.29	21.39	33.94	3.25	1.79	6.86
ZV	20.87	23.83	43.87	31.53	9.06	27.48	12.69

3.3. Degradation of plastic waste by using pyrolysis reactor:
Pyrolysis reactor setup according to method proposed (Awusu et al., 2018).

All catalysts decreased the initial degradation temperature which is more expressive for the catalyst ZO that is 180^0C and total reaction time was 63 minutes. The more product formation with ZP catalyst that was 80ml (oil).

Rate of conversion **(%)** =<u>Initial mass of plastic – Mass of plastic left in the reactor</u> x100
<div align="center">Initial mass of plastic.</div>

It was found that chemical action on plastic waste within the temperature varies 175^0C - 500^0C depending on

- Temperature,
- Quantity of catalyst
- Reaction time.

Because of chemical action degradation of plastic waste upon heating, to get 5 kg wax, 10 kg charcoal, 5 kg of gas and maximum 80 ml liquid product.

Table No (3) .This shows pyrolysis of plastic with different catalyst minimum to maximum reaction time

Feed stock (grams)	Catalyst	First drop obtained (temperature)	Last drop obtained (temperature)	Reaction Time	Volume of liquid obtained(mL)
PE,PP.,PS,PET	Without	385°C	500°C	1 hour 15 minutes	2 mL
..	Z	200°C	275°C	75 minutes	10 mL
..	ZP	190°C	260°C	70 minutes	80 mL
..	ZV	195°C	255°C	60 minutes	20 mL
..	ZO	180°C	243°C	63 minutes	2 mL

3.4.Analysis of pyrolysis fuel:

Two type of analysis generally one is physical and other is chemical analysis.

3.5. Physical analysis of pyrolysis oil:

- Color of the oil
- Viscosity of oil
- Calorific value of oil

3.5.1.Yield of oil:

To calculate yield of oil two formulas were used (Tiwari et al ., 2007; Ahmed et al ., 2017)

Yield of oil=   Mass of the obtained oil   x 100

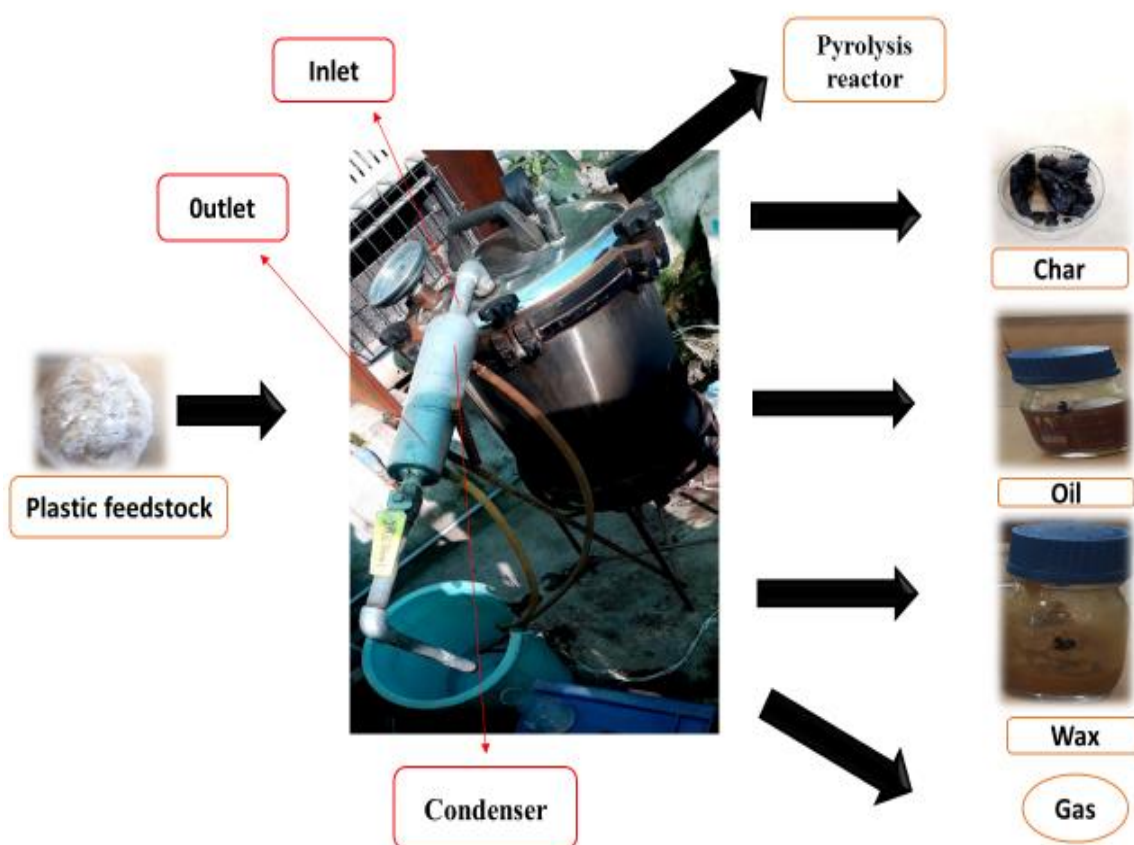
                    Initial weight of plastic waste sample

Oil recovery was measured by using formula according to Elmo and Rapsing (2016).

Oil recovery= Volume of oil recovered (ml) x100

                    Weight of sample material (Kg)

3.5.2. Color of the fuel:

The colors were identified visually, light yellow to orange in color due to different polymer composition.

(Figure. (1) Pyrolysis reactor in which mixture of plastic converted into useful products)

3.5.3. Viscosity of oil:

Viscosity of oil produced from plastic was measured by using Ostwald Viscometer. The viscometer was filled with the oil up to mark .after the suction was done to pull it to the upper reserivor.The suction was removed and the oil was allowed to go back to the lower reservoir. During this movement from upper to lower mark on each reservoir, the time was measured using stopwatch. Water was used as a reference material for the viscometer as its density is well- known and calculated relative viscosity of the oil by using Oswald equation.

Table No (4): Viscosity of oil at two different temperatures

Serial number	Fuel type	Viscosity at 60 ^{0}C (cSt)	Viscosity at 100ºC (cSt)
1	Feedstock+catalyts	2.2	2.1

Fuel densities are much similar due to the same nature of feedstock consists of Polyethylene both low and high density, polypropylene and polyethylene terephthalate.

3.5.4. Calorific value of fuel:

Calorific value is the heat energy produced by the oil upon combustion under constant conditions. The calorific value was used by bomb calorimeter in National Cleaner Production Center (NCPC) Morgah, Rawalpindi. The test method used for determining the calorific value was ASTM D4858. The calorific value of oil was 45.9 MJ/Kg was determined.

3.6. Thermo gravimetric analysis (TGA):

Thermal Decomposition Analysis about half dozen mg of HDPE and PP was heated by a non-isothermal temperature program, from 30^{0}C temperature to 800 ^{0}C at twenty ^{0}C/min of heating rate underneath sixty mL/min of atomic number 7 atmosphere, using a TGA (Pyris Diamond, Perkin-Elmer, Waltham, MA, USA).For the chemical change TG analysis, 6 mg of catalyst was mixed with plastics and the same temperature program was applied. TGA studies showed that without catalyst more residues left but with the addition of zeolite catalyst having different organo silane modifications are fewer residues and more product formation.

Table No (5): Thermal gravimetric analysis (TGA) of Zeolites and plastic degradation

Sample code	Step 1 Loss(% Wt)	Step2 Loss(% Wt)	Step3 Loss(% Wt)	Step4 Loss(% Wt)	Total Loss (% Wt)	Residue (% Wt)
Z	83.93 0-142.2ºC	74.48 335.4 ºC	34.90 488.8ºC	29.52 799.1ºC	29.37	70.63
ZP	88.44 0-153.4 ºC	82.73 337.9 ºC	65.18 452.7 ºC	74.56 584.6 ºC	41.15	58.85
ZV	9.77 0-184.2 ºC	89.87 330.1 ºC	46.86 477.0 ºC	43.64-52.08 626.9-702.8 ºC	41.12	58.88
ZO	85.58 0-133.6 ºC	77.42 326.2 ºC	58.59 478.7 ºC	41.64-52.08 626.9 ºC	59.1	40.9

Zeolite without functionalization exhibited a lower degradation rate compared to others, so ZO showed higher catalytic activity may be associated with the greater number of strong acidic sites.

4. Conclusion

The synthesized catalyst ZO showed the highest performance in plastic pyrolysis, resulting in lower degradation temperature, low residue and more product formation might be due to having long chain hydrocarbon and acidic sites. This is the first study to focus on plastic pollution in Astola Island. Recycling of plastic is the most promising solution to conserve biodiversity of all ecosystems especially marine environment. This research recommends proper waste management plan implementation in Astola Island because there is no management plan yet.

Declaration of interest

There is no declaration of interest.

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