EFFECTS OF PIGEON EXCRETA ON COPPER AND ITS ALLOYS USED IN HISTORICAL MONUMENTS

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A thesis submitted in partial fulfilment of the requirements for the award of the degree of Master of Science in Zoology with special paper Ecology and Environment.

Submitted to

Central Department of Zoology

Institute of Science and Technology

Tribhuvan University

Kirtipur, Kathmandu Nepal

April, 2021

DECLARATION

I hereby declare that the work presented in this thesis "**Effects of Pigeon Excreta on Copper and Its Alloys Used in Historical Monuments**" has been done by myself and has not been submitted elsewhere for the award of any degree. All sources of information have been specifically acknowledged by reference to the authors or institutions.

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RECOMMENDATION

This is to recommend that the thesis entitled **"AVIAN DIVERSITY ALONG URBANIZATION GRADIENT OF BUTWAL SUB-METROPOLITAN CITY, NEPAL"** has been carried out by Bibek Aryal for the partial fulfillment of Master's Degree of Science in Zoology with special paper ecology and environment. This is his/her original work and has been carried out under my supervision. To the best of my knowledge, this thesis work has not been submitted for any other degree in any institutions.

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LETTER OF APPROVAL

On the recommendation of supervisor "Assistant Professor Laxman Khanal" this thesis submitted by Saroj Shrestha entitled "**Effects of Pigeon Excreta on Copper and Its Alloys Used in Historical Monuments**" is approved for the examination in partial fulfillment of the requirements for Master's degree of Science in Zoology with special paper Ecology and Environment.

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CERTIFICATE OF ACCEPTANCE

This thesis work submitted by Saroj Shrestha entitled "**Effects of Pigeon Excreta on Copper and Its Alloys Used in Historical Monuments**" has been approved as a partial fulfillment for the requirements of Master's degree of Science in Zoology with special paper Ecology and Environment.

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LIST OF ABBREVIATIONS

Abbreviated form	Details of abbreviations
UM	Unit of measurement
bs	Brass
cu	Copper
br	Bronze
DW	Distilled water

Abstract

Pigeons have been a common disturbance in numerous cultural sites of the Kathmandu Valley. Besides health, economic and aesthetic issues caused by the pigeon excreta, it also involves damaging the materials including the metals like copper and its alloys used in Nepalese architecture. The primary goal of this study was to discover the impacts of pigeon excreta on the metal monuments of cultural importance in Kathmandu Valley. The pigeon excreta were collected from three world heritage sites of the Kathmandu Valley- Kathmandu Durbar Square, Bhaktapur Durbar Square and Patan Durbar Square. Supplementary metals of copper and its alloy mainly bronze and brass of similar composition as used in the monuments were collected from the surrounding area of Patan. The metal samples were cut, cleaned and immersed in excreta samples by tying them with thread suspended with a stick and covering the beaker with foil over 122 days' duration. The metals were regularly cleaned and weighed to find the change in weight over short, medium and longer period. Effects of the pigeon excreta on the metals were analysed based on staining, and corrosion loss compared to initial weight. There was considerable corrosion loss in copper and its alloy samples, but a major decrease was seen in copper pieces that were kept in the fresh pigeon excreta. Statistical analysis revealed a significant corrosion loss in copper but not in bronze and brass samples. It supports the stronger negative impact of bird excreta on copper compared to its alloy. Therefore, the use of copper-alloys instead of pure Copper in monuments that are being reconstructed could minimize the adverse effects of pigeon excreta. The findings of this research provide important insight into the preservation of cultural heritage sites.

1 INTRODUCTION

1.1 Background

Outdoor buildings and heritages are exposed to physical, chemical, and biological damages that has degraded the aesthetic and material integrity of the structure (Bernardi et al. 2009). Pigeon dropping contains high acidic material which attacks the metal objects accelerating the corrosion and damage (Vasiliu & Buruiana 2010). Because of the high chemical reactivity of pigeon excreta accelerated by the presence of moisture content, a higher concentration of salts like sodium and magnesium, the build-up and leaching of these substances into concrete and building structures are having a negative impact on the construction materials and the health of the infrastructures (Huang & Lavenburg 2011).

Pigeons have become well adapted to live in a modern city and are becoming a nuisance to the urban areas. Especially in the region of Kathmandu valley due to the presence of different cultural heritage sites like temples, stupas, monasteries, and people freely providing foods to them, pigeons have created a type of conflict in the surrounding area of cultural sites. The theory of ideal free distribution states that the selection of a bird habitat is influenced by factors such as potential predators, food density, and cover. (Fretwell & Dewitt 1969). The availability of building ledges overhangs low level of predators, easy food availability with high protein content has helped in creating an ideal place for a pigeon to live (Spennemann & Watson 2018)

Besides health, economic and beauty issues caused by the pigeon excreta it also helps in damaging the materials used in cultural sites. The metal monuments are exposed to physical, chemical, and biological threats. It has damaged the beauty appeal and integrity of the metals too (Bernardi et al. 2009, Stukenholtz et al. 2019). Due to the need and importance of cultural heritage sites and different monuments found there, there have been many studies in understanding the different hazards that can damage them and measures for its prevention. The environmental effects on the stone surface have been studied in the past (Ali et al. 2015) but the direct and indirect effect of the pigeon excreta on the metal has not been properly done and there is a gap in research regarding this topic.

Copper alloys are used for the making of the pinnacle, statues, idols, roof of many cultural sites of Nepal. It is very malleable and ductile as metal. Pigeons can damage the copper structure in many ways like by visual staining the surfaces, chemical damage by acids and soluble salts, nutrient deposition aiding in biodegradation through different microorganisms (Spennemann & Watson 2018). Many pigeons in multiple flocks residing in and around the heritage sites of Kathmandu valley cast off their excreta on the stone and metals of the sites which deteriorate their beauties.

There is mixed opinion on the pigeon droppings as the agent for the damage to the building materials (Bernardi et al. 2009). This study is necessary to determine the degradation caused due to pigeon excreta on the exposed metal building materials which are of great importance involving economic and cultural loss. To address this issue of pigeon excreta as the damaging agent on metal this study is conducted. There is various literatures asserting a link between pigeon excreta and the damage to the building materials and this study finds the influence of the pigeon excreta responsible for the damage to copper and its alloys i.e., bronze and brass in an experimental study.

1.2 Research objectives

General objective of this study was to determine the effects of pigeon excreta on culturally significant monuments in Kathmandu valley.

Specific objectives are:

- To determine the corossion loss of the metals used in monuments construction under the influence of pigeon excreta.
- To compare the differential effects of pigeon excreta in different metals and alloys of monuments at various exposure durations.

1.3 Rationale of the study

Kathmandu has many cultural heritage sites and the infestation of pigeons has created many problems in the metal monuments. Apart from losing the beauties, metal surfaces of the monuments are deteriorated by the acidic contents of pigeon excreta. This study is needed to know the way how pigeon excreta deteriorates the metal surfacedifferential effects of the excreta on different alloys, variation in the metal deterioration at temporal exposure etc.

Many researches have already been carried out on the effect of bird excreta on different surface including stones, bridges, outdoor statues. But study on effects of pigeon excreta on metal surface is required to know about its negative impact on cultural monuments. Since pigeons have become a major pest in the urban area of Kathmandu and their activities are mostly seen in the heritage sites this study will give the degree of effect of pigeon excreta on metals used in heritage sites and the extent of deterioration it can cause in the future. This can be implicated for making a further decision for preserving metal monuments and different steps to be applied for decreasing its effect.This research will benefit in fulfilling the knowledge gap regarding the pigeon excreta and the amount of damage it can cause in our copper monuments.

2 LITERATURE REVIEW

2.1 Copper and its alloys used in monumental architecture

Copper and its alloys especially bronze and brass are very good metals for the construction of statues and cultural monuments (Knotkova & Kreislova 2007). Different metals tend to combine with other chemical elements and corrode easily by combining with oxygen and water (Loto et al. 2014). The long-term exposure to copper alloy is affected by the atmospheric environment. The areas affected in copper include changes in mechanical properties like strength and ductility. After approx. 20 years length changes by 10 % and tensile strength decrease by 5%. Copper is mostly used as an alloy and when combined with tin bronze is formed and with the addition of zinc brass alloy is formed. The addition of zinc and tin to an alloy increases its breaking strength and hardness. (Knotkova & Kreislova 2007).The most common technique used in Kathmandu for monument construction was an old technique called “retardataire”, but it has also been confirmed that the “lost wax” technique was also known to the Newar craftsmen of Kathmandu (Ray 1973, Bonapace & Sestini 2003). They used gilt metal alloys composed of five or eight metals i.e. Pancha Dhatu (Ali et al. 2015) and Astha Dhatu, respectively, consisting of metals like copper, bronze, brass, zinc, lead, iron, gold and silver (Bonapace & Sestini 2003).

2.2 Corrosion loss in monuments review by pigeon excreta

Pigeons’ digestive tract is different than mammals as they have a cloaca, and their defecation is combined in one dropping. The white area represents uric acid, which is found in urine, while the dark area represents defecated excreta. (Balogh et al. 2019). The study on the long term and short-term effects of the pigeon excreta on the metals are not much satisfactory. The experimental studies have shown that bird excrement has a deleterious impact on metals such as copper, bronze, zinc, and other alloys used in monuments Adam & Grübl 2004, Bernardi et al. 2009, Vasiliu & Buruiana 2010, Spennemann & Watson 2018, Balogh et al. 2019). The damage is mostly seen in the form of metal corrosion (Vasiliu & Buruiana 2010, Balogh et al. 2019), structural and textural damage (Ramezanzadeh et al. 2009) and tarnishing of the metal (Bernardi et al. 2009) all leading to the damage in visual appearances and corrosion loss of the metal.

The major cause for the damage seems to be due to the presence of organic salt material, uric acid, the microbial and fungal growth, and there's an acidic chemical reaction, where the rate of reaction is increased with the presence of humidity (Gómez-Heras et al. 2004, Bernardi et al. 2009, Vasiliu & Buruiana 2010). The presence of uric acid has been considered the prime factor for the degradation of the building materials (Pudelkiewicz et al. 1968, Bernardi et al. 2009, Vasiliu & Buruiana 2010, Spennemann et al. 2017) but (Ginez et al. 2018) found uric acid to have no relation to the damage to the bronze metal. Studies signify the relation of the pigeon excreta with the degradation in the building materials where the acidity of excreta increases with the urban food diet compared to the natural diet of the birds (Spennemann et al. 2017, Spennemann & Watson 2017). Ramezanzadeh et al. (2009) illustrated how the catalytic influence of the enzyme structure of bird droppings causes harm, linked to hydrolytic processes. Vasiliu & Buruiana (2010), (Balogh et al. 2019) found that on the surface of copper and its alloy, a natural protective coating is formed (Catelli et al. 2018) which reacts with the bird excreta in time even if it seems to protect in the initial phase of the bird droppings. Bernardi et al. (2009) water played a significant role in accelerating the corrosion of metal. The presence of a highly favourable substrate in the pigeon excreta favours the fungal, algal and bacterial growth helping to enrich the nutrient content in the excreta that facilitate certain microbes to produce acid and increase of acidity of the excreta thus causing chemical erosion and staining of the building materials which is of greater concern and their long term effect is a truth that cannot be denied (Del Monte & Sabbioni 1986, Spennemann et al. 2017, Spennemann & Watson 2018).

(Channon 2004) tested the impact of the excreta sample on the limestone, marble and concrete and after a year of exposure on the rooftop, it resulted in the deep surface loss with staining. Ramezanzadeh et al. (2009) in Iran found that the effect of bird excreta had an irreversible effect on visual appearance before and after the introduction of the bird dropping. Ali et al. (2015) at the historical site Al-Namrud in the north of Iraq found that the bird dropping seems to be an active factor for damage. Vasiliu & Buruiana (2010) confirmed the significant chemical reactions were triggered by bird droppings on metals leading to damage. Balogh et al. (2019) it is evident that bird droppings clearly have a chemical reaction with metals. There is the potential chemical damage that is caused by the bird dropping which is significant when it comes to the value of cultural heritages and construction materials made up of copper and its alloys (Bernardi et al. 2009). Pigeon excreta had a negative influence on the copper metal alloys and confirmed significant damage in statue and monuments considering cultural heritage (Vasiliu & Buruiana 2010).Major past studies used fresh as well as old dry excreta in the form of coating, paste and drop and immersion to see the damage it causes to the metals but mostly the immersive liquid form of the bird excreta was advised to perform the laboratory experiment in the enclosed environment (Spennemann & Watson 2018, Balogh et al. 2019).

The major cause for the damage seems to be due to the presence of uric acid and its acidic chemical reaction, where the rate of reaction is increased with the presence of humidity, the microbial and fungal growth also seems to be the cause and the presence of organic salt material. They cause damage in the form of corrosion, corrosion loss, cracking, damage in visual appearances. The review showed an increase in the rate of degradation with the presence of microbial growth, use of chamber and humid conditions.

3 MATERIALS AND METHODS

3.1 Study area

The cultural sites- Kathmandu Durbar Square, Bhaktapur Durbar Square and Patan Durbar Square was selected for fresh excreta sample (Fig 1). The durbar squares date back to the Licchavi period in the third century, though they have been extensively renovated and little substantial from that time period survives. Extensive constructions and development took place during the Malla Dynasty. But these sites were heavily devastated by the 2015 earthquake.

Figure 1. Sites of the pigeon excreta collection within the Kathmandu Valley

3.2 Study design

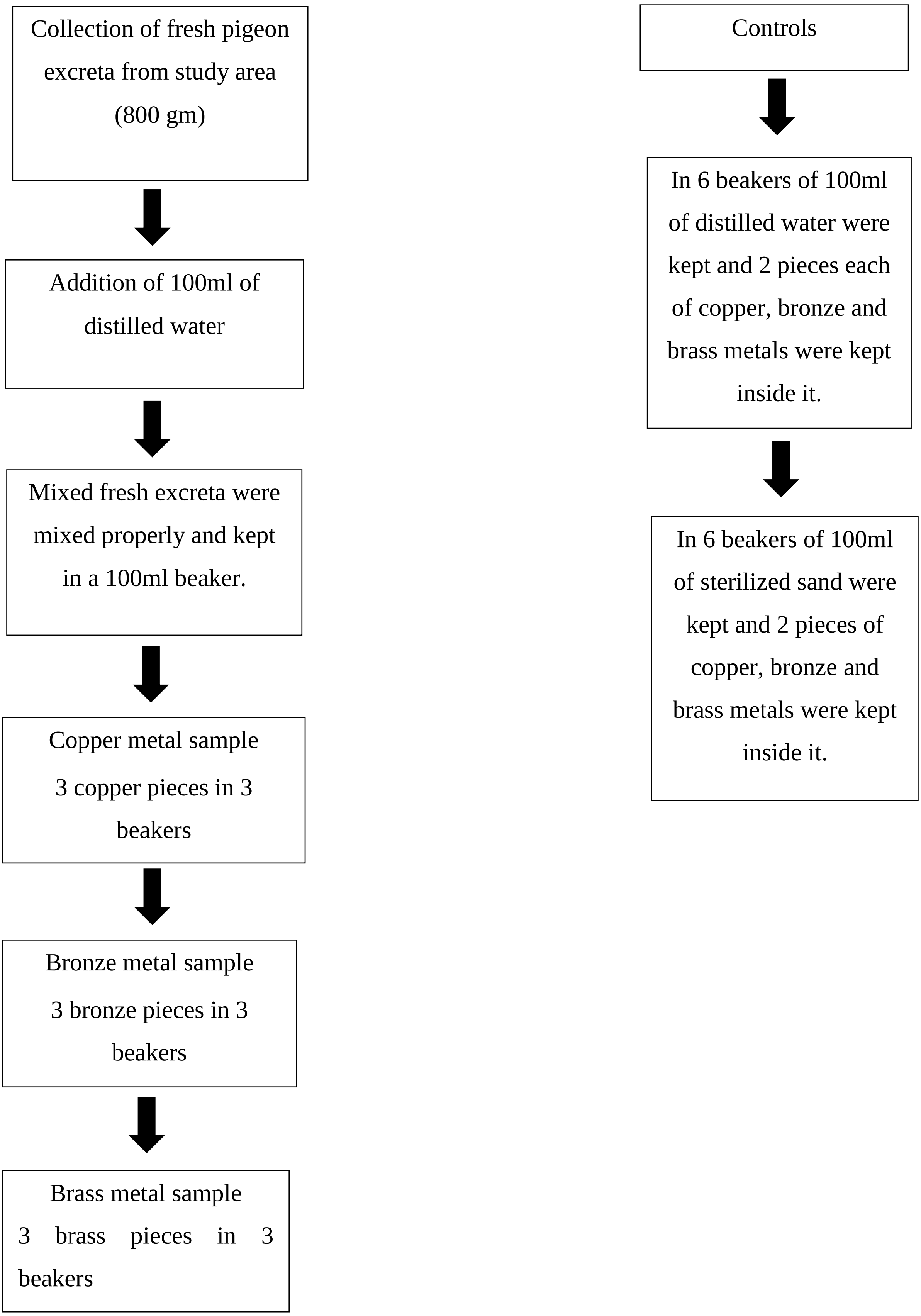


Figure 2. A schematic flow chart showing the experimental design

3.3 Materials

3.3.1 Apparatus used.

i. Plastic bags
ii. Spatula
iii. Gloves
iv. Mask
v. Beakers (100ml)
vi. Digital balance (RadwagWagiElectroniczne, Model: AS 220.R2, S/N: 482379)

3.3.2 Chemicals used.

i. Distilled water
ii. Alcohol
iii. Acetone etc

3.4 Excreta collection

Three cultural sites- Kathmandu Durbar Square, Bhaktapur Durbar Square and Patan Durbar Square were selected for fresh and wet excreta sample. A preliminary survey was conducted to find out the optimal areas where the number of pigeons was more. After the selection of the collection spot the birds were observed for feeding behaviour and in the interval of 30 minutes, the fresh excreta sample was collected on several spots on each site. Feeding ground was selected for the maximum chance of obtaining the pigeon's excreta sample. A plastic spatula was used to scrape out the sample and for storing closed plastic container was used (Bernardi et al. 2009). The sample collection was done for 2 weeks from 9am to 4pm. All together 800 gm of fresh excreta was obtained. Fresh excreta was used in this study to obtain the accurate result as suggested by (Balogh et al. 2019).

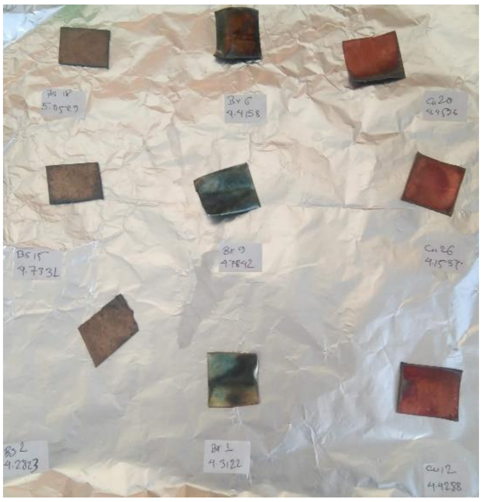
3.5 Experimental design

The laboratory-based work was performed in the lab of the Central Department of Zoology from 5 October 2020 to 1 February 2021 T.U. The fresh excreta were homogenized in 100 ml distilled water and 100 ml of prepared sample was kept in 9 beakers. Supplementary metals of copper and its alloy of similar composition as used in the monuments were collected from the surrounding area of Patan where the craftsmen still made the monuments with the ancient technique. The metal sheets were cut and made into many small pieces of equal dimension. They were cleaned with acetone and alcohol properly and external contaminations were removed (Loto et al. 2014).

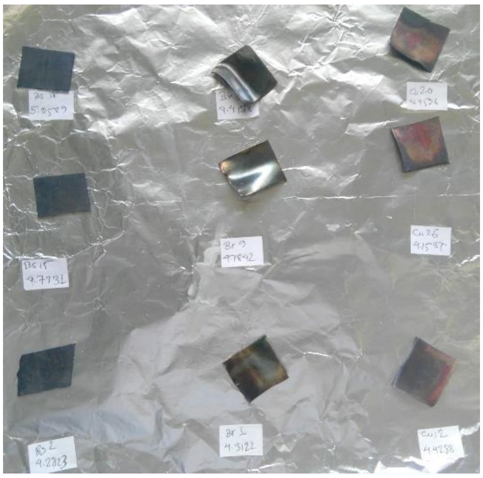
The metal samples were immersed in excreta sample as suggested by (Balogh et al. 2019) by placing the metals and tied with thread on a bamboo stick at the top so that the metal doesn’t get attach to the glass. The beakers were closed with aluminium foil at the top and left at room temperature. At certain exposure time duration, the metal samples were taken out and cleaned properly with distilled water, acetone, and alcohol. The samples were then air-dried and measurement in concealed weighing machine was conducted. Before and after analysis of the metal was done at a different time interval, in cases like staining, corrosion loss in metal and corrosion. For proper analysis controls as distilled water and sterile fine sand were also kept at room temperature and the metal samples were also kept in a similar experimental setting. The experiment was replicated with other samples of metals in fresh excreta and in controls too, so that proper result was obtained from the observation. The original weight of the metals was recorded, and the loss of the weight was calculated using measuring the weight at a different time interval of 3 days, 7 days, and 10 days as short duration changes 17 days, 24 days, and 42 days as medium duration changes and 66 days, 94 days, and 122 days as long-term duration changes in the metal samples.

Photograph 1. Beaker with pigeon excreta sample

Photograph 2. Short-term colour change in metal sample immersed in fresh pigeon excreta.



Photograph 3. Medium-term colour change in metal sample immersed in fresh pigeon excreta.



Photograph 4. Long term colour change in metal sample immersed in fresh pigeon excreta.

3.6 Weight measurement

At a different interval of time, the metal samples from the excreta and the control medium were taken out individually from the beaker with a help of a tweezers and at first cleaned by dipping it in distilled water followed by rinsing with acetone and removing any substrate lying on the metal sample (Bonapace & Sestini 2003, Bernardi et al. 2009).The samples were then cleaned with 70% alcohol and finally left to air dry at the aluminium foil with the proper labelling. The beaker was again closed to avoid any contamination. Same procedure was applied for every metal sample and then after drying they were taken for weighing. Any moisture from the metals was removed by cleaning the metal samples with tissue paper and after calibrating the weighing machine the weight was measured and noted down. Same procedure was done for every metal sample and then they were re-immersed in their original beaker by tying them with thread and hanging on a stick and finally enclosed by foil and then placed at room temperature. Same process was followed for all the measurement.

3.7 Data management and analysis

All the metal samples and the beakers were properly labelled. Initial weight and the final weight after the exposure duration were properly noted and kept in an excel sheet. After the completion of the final experimentation, the data were sorted and the corrosion loss in measurement was calculated and the loss percentage in each measurement was also calculated and properly tabulated as in (Table 1). Corrosion loss in percentage versus the exposure time duration graph was prepared for the excreta, sterile fine sand, and distilled water metal samples. ANOVA (Kruskal-Wallis one-way) was used for comparing the final weight difference of the metal samples in a different medium of experimentation (Loto et al. 2014).

4 RESULTS

4.1 Pattern of corrosion loss in experimental metals

The results obtained for the change in the weight of different copper and its alloy sample immersed inside the pigeon fresh excreta and control medium with different exposure time duration is given in Table 1. The loss in the weight of metal sample was observed in all medium but larger corrosion loss in percentage was observed in sample that was kept inside the excreta. Maximum loss was seen in copper sample that was kept in fresh excreta sample with 0.21% weight difference compared to the initial weight and minimum loss was seen in copper sample as well that was placed in the distilled water with 0.0019%. Brass and bronze samples showed little change in the weight when kept inside the control medium but showed more loss in excreta samples, but the change was minimum when compared to the loss observed in the copper samples that was placed in the excreta. The copper metal in the control medium showed much more resistance to the corrosion and least loss compared to the bronze and brass samples.

Table 1. Corrosion loss in the metal samples in fresh excreta and control medium over 122 days

Sample	UM	Mass									
Excreta		0 days	3 days	7 days	10 days	17 days	24 days	42 days	66 days	94 days	122 days
bs18	[g]	5.0529	5.0512	5.0511	5.0511	5.0511	5.0511	5.0509	5.0509	5.0509	5.0509
	%	100	99.9664	99.9644	99.9644	99.9644	99.9644	99.9605	99.9605	99.9605	99.9605
br6	[g]	4.4158	4.4142	4.4142	4.4138	4.4138	4.4138	4.4134	4.4133	4.413	4.4129
	%	100	99.9638	99.9638	99.9548	99.9548	99.9548	99.9457	99.9434	99.9366	99.9344
cu20	[g]	4.4596	4.4587	4.458	4.4574	4.4572	4.4572	4.4554	4.4534	4.4515	4.4507
	%	100	99.9799	99.9642	99.9507	99.9462	99.9462	99.9059	99.861	99.8184	99.8005
bs15	[g]	4.7331	4.7313	4.7313	4.7313	4.7313	4.7313	4.7313	4.7313	4.7312	4.7312
	%	100	99.962	99.962	99.962	99.962	99.962	99.962	99.962	99.9599	99.9599
br9	[g]	4.7842	4.7839	4.7838	4.7837	4.7837	4.7837	4.7831	4.7829	4.7823	4.7823
	%	100	99.9938	99.9917	99.9896	99.9896	99.9896	99.9771	99.9729	99.9593	99.9591
cu26	[g]	4.017	4.0157	4.0153	4.0147	4.0144	4.0136	4.0129	4.0112	4.0096	4.0091
	%	100	99.9677	99.9577	99.9428	99.9353	99.9154	99.898	99.8557	99.8158	99.8034
bs2	[g]	4.2823	4.2805	4.2804	4.2804	4.2804	4.2804	4.2804	4.2804	4.2804	4.2804
	%	100	99.958	99.9557	99.9557	99.9557	99.9557	99.9557	99.9557	99.9557	99.9557
br1	[g]	4.3122	4.3119	4.3119	4.3119	4.3118	4.3118	4.3114	4.3111	4.3109	4.3109
	%	100	99.9931	99.9931	99.9931	99.9908	99.9908	99.9815	99.9745	99.9699	99.9699

cu12	[g]	4.4288	4.4273	4.427	4.4263	4.4257	4.4257	4.4245	4.4224	4.4203	4.4194
	%	100	99.9662	99.9594	99.9436	99.9301	99.9301	99.903	99.8555	99.8081	99.7878
Dew											
bs24	[g]	4.4415	4.4415	4.4415	4.4415	4.4415	4.4415	4.4415	4.4411	4.4408	4.4407
	%	100	100	100	100	100	100	100	99.991	99.9843	99.982
br24	[g]	4.1049	4.1049	4.1049	4.1049	4.1049	4.1049	4.1049	4.1047	4.1041	4.1038
	%	100	100	100	100	100	100	100	99.9952	99.9806	99.9733
cu6	[g]	5.1778	5.1778	5.1778	5.1778	5.1778	5.1778	5.1778	5.1778	5.1777	5.1777
	%	100	100	100	100	100	100	100	100	99.9981	99.9981
bs8	[g]	3.713	3.713	3.713	3.7129	3.7129	3.7125	3.7124	3.7121	3.7119	3.7118
	%	100	100	100	99.9974	99.9974	99.9866	99.9839	99.9758	99.9704	99.9677
br13	[g]	3.8035	3.8035	3.8035	3.8035	3.8035	3.8035	3.8035	3.8033	3.8026	3.8025
	%	100	100	100	100	100	100	100	99.9948	99.9764	99.9738
cu16	[g]	4.6862	4.6862	4.6862	4.6861	4.6861	4.6861	4.6861	4.6861	4.6857	4.6857
	%	100	100	100	99.9979	99.9979	99.9979	99.9979	99.9979	99.9894	99.9894
Sterile sand											
bs7	[g]	5.0067	5.0067	5.0067	5.0067	5.0067	5.0067	5.0067	5.0064	5.0063	5.0062
	%	100	100	100	100	100	100	100	99.9941	99.9921	99.9901
br2	[g]	4.7614	4.7614	4.7614	4.7614	4.7614	4.7614	4.7613	4.7613	4.7611	4.7611
	%	100	100	100	100	100	100	99.9979	99.9979	99.9937	99.9937
cu23	[g]	4.1095	4.1095	4.1095	4.1095	4.1095	4.1094	4.1093	4.1091	4.109	4.1089
	%	100	100	100	100	100	99.9976	99.9952	99.9903	99.9879	99.9854
bs1	[g]	5.1192	5.1192	5.1184	5.1184	5.1184	5.1184	5.1182	5.1178	5.1178	5.1177
	%	100	100	99.9844	99.9844	99.9844	99.9844	99.9805	99.9727	99.9727	99.9707
br16	[g]	4.4739	4.4739	4.4739	4.4739	4.4739	4.4739	4.4738	4.4736	4.4735	4.4735
	%	100	100	100	100	100	100	99.9978	99.9933	99.9911	99.9911
cu11	[g]	4.6668	4.6668	4.6668	4.6668	4.6668	4.6668	4.6668	4.6668	4.6667	4.6667
	%	100	100	100	100	100	100	100	100	99.9979	99.9979

4.2 Corrosion loss pattern with time

The corresponding corrosion loss vs the exposure time is shown in Figure3. It shows that maximum corrosion was seen in copper but for the alloy brass and bronze, less corrosion loss was observed compared to the copper. Sharp corrosion loss was seen during the initial time duration of experimentation compared to the later stage of the exposure duration, but the copper sample showed a regular decrease in the medium exposure duration and again a sharp decline in the longer time duration as shown in (Figure3).

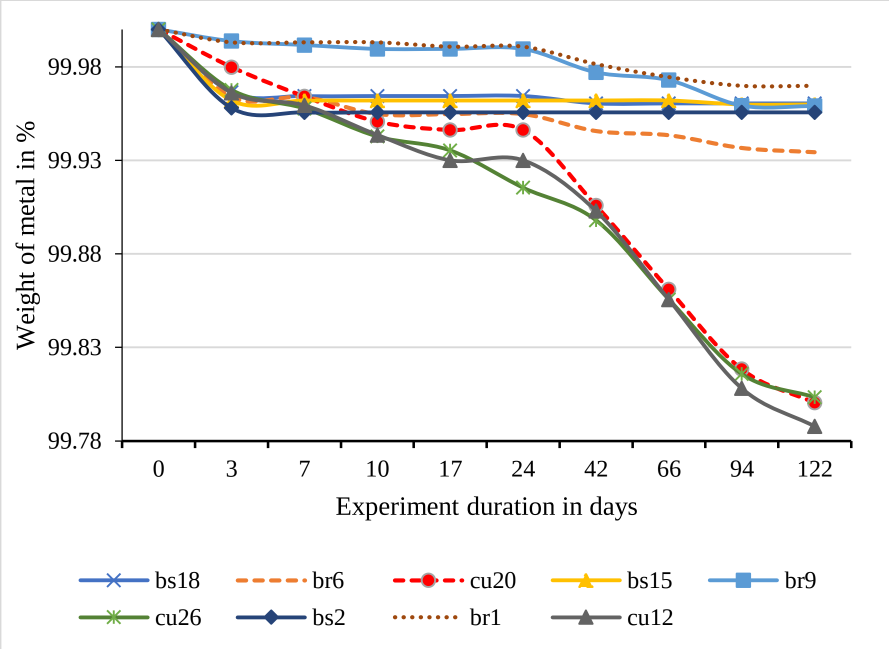


Figure 3. Variation in the weight retained by copper and its alloys in fresh pigeon excreta with exposure time in days

In the control medium of sterile fine soil, there was not much change in the weight of metal samples but, compared to bronze and brass, copper showed less weight retention in the soil control as shown in Figure 4.

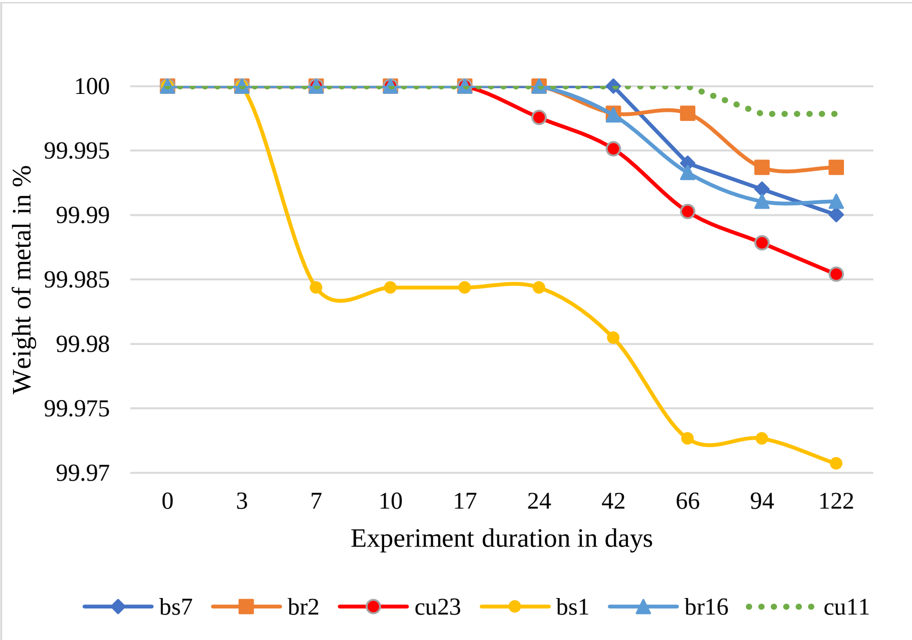


Figure 4. Variation in the weight retained by copper and its alloys in control sterile soil sample with exposure time in days

Similarly, the change in distilled water sample was also comparatively less but, bronze showed the most corrosion loss among the sample as shown in Figure 5.

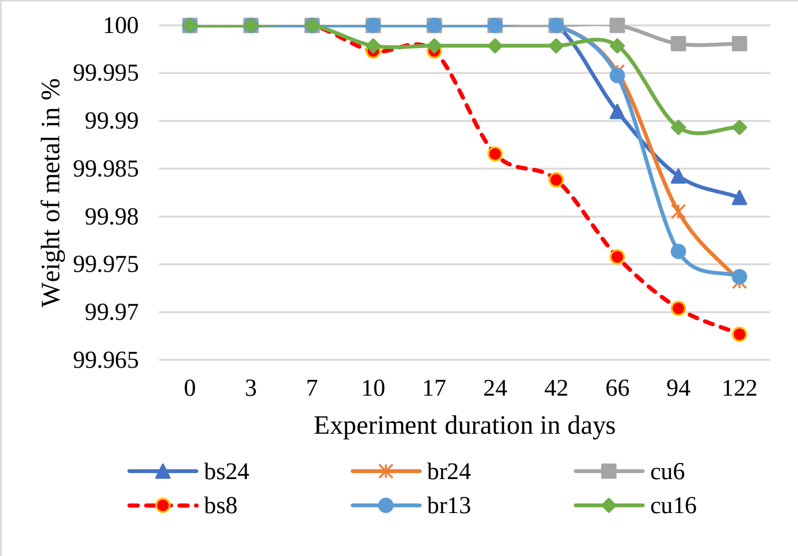


Figure 5. Variation in the weight retained by copper and its alloys in control distilled water with exposure time in days

In the short term versus the medium- and long-term exposure of metal samples in the excreta, it showed that there was less weight retention in the first initial day of 3rd day and the weight retention slowly decreased up to 10th day (Figure 6). The loss was maximum in the Copper compared to bronze and brass. Maximum loss of 0.057% was seen in copper, 0.045% in bronze and brass with 0.044% loss compared to initial weight of the metal samples.

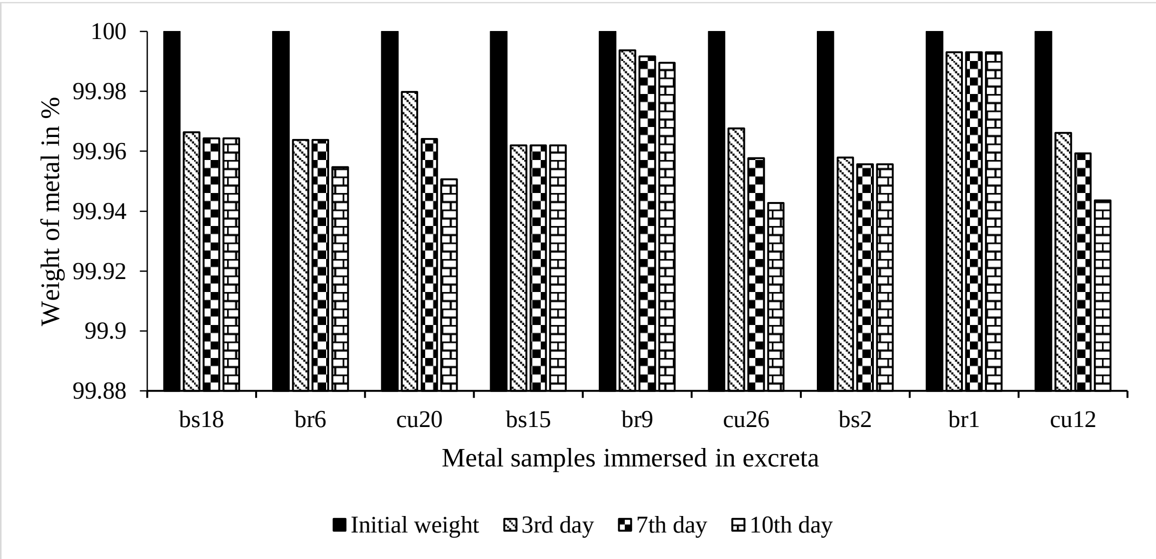


Figure 6. Variation in the weight retained by copper and its alloys in excreta for short duration

In the medium duration the weight retention of all the samples after 42 days was good compared to the shorter duration (Figure 7). Copper had the maximum loss of only 0.044% where as in bronze 0.012% loss and brass with 0.0039% loss compared to the initial weight of tenth day.

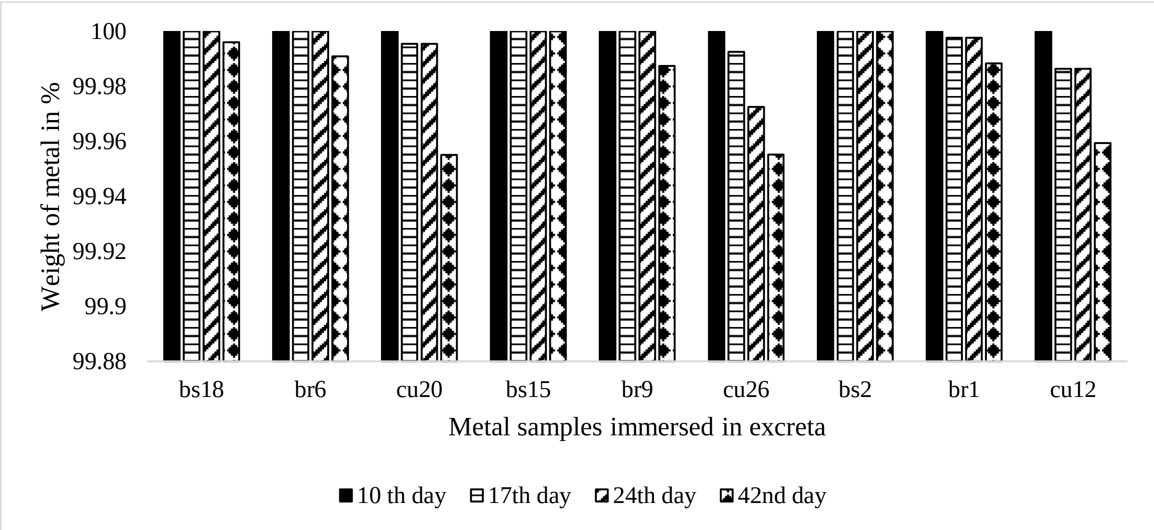


Figure 7. Variation in the weight retained by copper and its alloys in excreta for medium duration

In the longer duration of exposure up to 122-day, maximum loss was observed in the metal samples (Figure 8). Copper showed maximum loss of 0.094%, bronze 0.017% and brass with 0.002% loss compared to the initial weight of 42nd day.

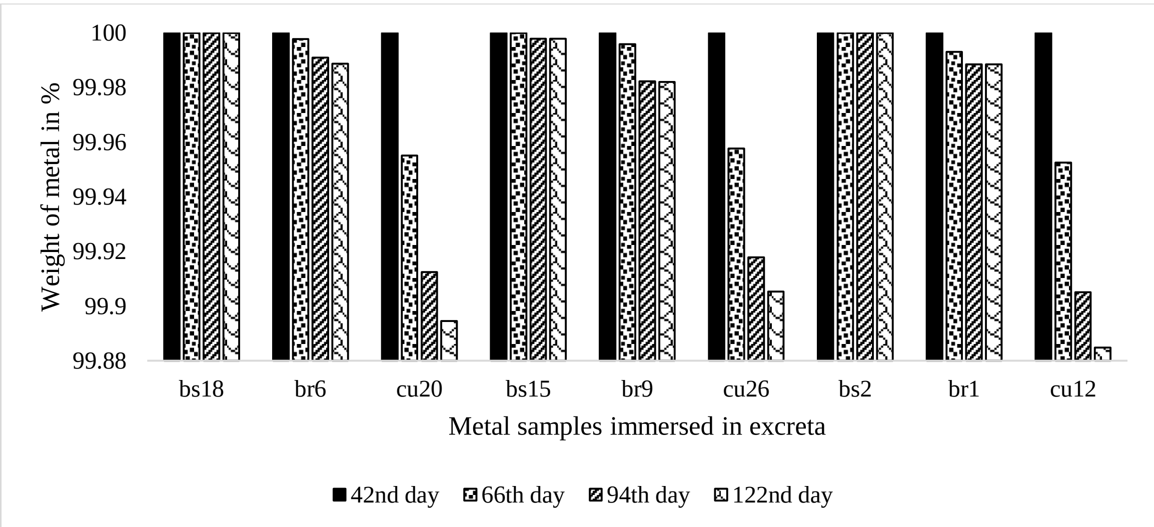


Figure 8. Variation in the weight retained by copper and its alloys in excreta for long duration

There is the maximum loss of the metal in the initial shorter duration and longer duration than compared to the medium duration when metals were immersed in pigeon excreta.

ANOVA (Kruskal-Wallis one-way) was used for comparing the final weight difference of the metal samples in a different medium of experimentation.

Table 2. Summary of ANOVA for final corrosion loss corrosion loss measurement compared to initial weight in percent.

S. N	ANOVA tests for final corrosion loss corrosion loss	Test for equal means	Sum of square (SS)	DF	Mean square (MS)	f	Significance (f)
1	All-metal samples	Between groups	0.0000655026	2	0.0000327513	6.179	3.55
		Within groups	0.0000954049	18	0.00000530027		
		Total	0.000160907	20	0.01129		
2	Copper samples	Between groups	0.000121203	2	0.0000606013	176.7	6.944
		Within groups	0.00000137167	4	0.000000342917		
		Total	0.000122574	6	0.02869		
3	Brass samples	Between groups	0.00000149333	2	0.000000746667	5.091	6.944
		Within groups	0.000000586667	4	0.000000146667		
		Total	0.00000208	6	0.1429		
4	Bronze sample	Between groups	0.00000362973	2	0.00000181487	5.571	6.944
		Within groups	0.00000130307	4	0.000000325767		
		Total	0.0000049328	6	0.1056		

Based on the results obtained from (Table 1), ANOVA analysis was performed comparing the final corrosion loss corrosion loss percentage change in the metal sample. It can be concluded with 95% confidence that in the test for equal means for final corrosion loss corrosion loss in all-metal sample there was rejection of null hypothesis as (f) 6.179>3.55, there was difference in corrosion loss of metal sample in different excreta and control medium. Similarly, Test for equal means for final corrosion loss for copper sample showed statistical difference in corrosion loss of copper metal in different medium as 176.7>6.944.But for final corrosion loss in brass and bronze sample, null hypothesis was accepted as 5.091<6.944 and5.571<6.944, there was no difference in corrosion loss of brass and bronze in different medium.

The overall corrosion was seen in every sample of metals but there was a significant difference in the corrosion loss in copper samples placed in excreta compared to other control media. So, a considerable amount of effect was seen due to pigeon excreta.

5 DISCUSSION

Difference in the corrosion loss of copper metal and its alloys was performed in this study with different exposure time duration. The samples were immersed inside the pigeon excreta as well as inside distilled water and sterile fine sand as a control in the enclosed beaker. Corrosion loss was observed in all the sample but the major difference in the corrosion loss was observed in the metal samples that were immersed inside the excreta.

5.1 Pattern of corrosion loss in experimental metals under the influence of pigeon excreta

The maximum loss of 0.21 % in the copper sample was seen in our study compared to 0.028 % (Vasiliu & Buruiana 2010). 0.065 % compared to 0.001 % in bronze and 0.044% compared to 0.002% corrosion loss in brass was also seen in the experiment done by (Vasiliu & Buruiana 2010) where the change in mass percentage was maximum in copper over a period of 60 days. The difference in the higher percentage loss in every sample was due to the use of fresh excreta sample compared to the dry pigeon excreta used, better experimental condition (enclosed beaker vs open exposure) and longer exposure time for the experimentation. It is only the past study that performed the immersion of copper metal and its alloys (bronze and brass) sample corrosion loss measurement in bird excreta. Other experimental setup involving the bird excreta and metal sample included studies like (Adam & Grübl 2004, Vasiliu & Buruiana 2010, Spennemann & Watson 2018, Balogh et al. 2019) that provided some pieces of evidence regarding the negative influence of excreta on the metals that were used in the monuments like copper, bronze, zinc, brass and other alloys. Their experimentation used pigeon excreta as a paste rather than the immersion in a closed vessel so, the corrosion loss could not be properly compared but the structural, textural damage, damage in visual appearances and corrosion loss in the metal samples were too observed on those studies.

The fungal growth was observed in our study which was also seen in other studies involving similar studies like (Del Monte & Sabbioni 1986, Spennemann et al. 2017, Spennemann & Watson 2018, Balogh et al. 2019) where those growths helped in enriching the nutrient in the excreta that facilitated the production of microbes which finally increased the acidity of the medium and contributed in the more corrosion loss. Similar damage of staining and corrosion loss like that to the metal sample was also observed in other experimented samples like limestone, marble, concrete, wooden structures, automotive clear coat and steel too (Bassi & Chiatante 1976, Adam & Grübl 2004, Huang & Lavenburg 2011, Ramezanzadeh et al. 2011, Ali et al. 2015, Ginez et al. 2018, Spennemann & Watson 2018).The reviewed articles based on the experimental studies have provided pieces of evidence regarding the negative effect of bird excreta on the building materials like limestone (Gómez-Heras et al. 2004, Huang & Lavenburg 2011, Dyer 2017) the damage is mostly seen as the staining on the materials discolouration and corrosion. Ramezanzadeh et al. (2009) found that the simulated bird droppings on the protective coating of the automotive had an unrepairable effect on the appearances due to the etching mechanism of the excreta with the coating material.

The presence of various soluble inorganic and organic salts such as halite, sylvite, potassium calcium sulphate, aphthitalite, apatite group minerals, weddellite, and gypsum is mostly responsible for the effects(Gómez-Heras et al. 2004). The presence of uric acid has also been considered the prime factor for the degradation of the building materials (Pudelkiewicz et al. 1968, Bernardi et al. 2009, Vasiliu & Buruiana 2010, Spennemann et al. 2017) but (Ginez et al. 2018) found uric acid to have no relation to the damage to the bronze metal. Studies signify the relation of the pigeon excreta with the degradation in the building materials where the acidity of excreta increased with the urban food diet compared to the natural diet of the birds (Spennemann et al. 2017, Spennemann & Watson 2017). Ramezanzadeh et al. (2009) illustrated that hydrolytic reactions caused by the catalytic impact of the enzyme structure of the bird droppings directly contributed to the damage on automobile coating. Vasiliu & Buruiana (2010) found that the natural protection layer formed on the surface of copper and its alloys reacts with the uric acid in time even if it seemed to protect in the initial phase of the bird droppings. The presence of the fungal, algal and bacterial growth helping to enrich the nutrient content in the excreta that facilitate the increase of acidity and staining of the building materials is of greater concern and their long-term effect is a truth that couldn't be denied (Del Monte & Sabbioni 1986, Spennemann et al. 2017, Spennemann & Watson 2018).

5.2 Corrosion loss pattern with time and the metal that is most affected by pigeon excreta.

Our study showed a great amount of corrosion loss in the early shorter duration stage and longer duration compared to the medium duration stage of the experimentation where all the samples in the excreta showed much loss which was contrasting from the result obtained from (Vasiliu & Buruiana 2010) here the metal samples kept in excreta showed no much change in the weight in the initial exposure duration. The medium and the later longer exposure duration, corrosion loss pattern was similar in trend but the value of the percentage lost was larger in our study. It might be due to longer exposure duration and the use of fresh excreta sample. The study on the long term and short-term effects of the pigeon excreta on the metals are not much satisfactory as only a few works have been performed. The visual impact of the excreta on the metal was similar to the study (Balogh et al. 2019) where darker brown colour was seen in copper and bronze, which was also backed up by the laboratory test (Adam & Grübl 2004, Bernardi et al. 2009) where bird excreta showed tarnish in the metal surface of copper and bronze.

Reviewing the experimental setup of various papers, there were some shortcomings in the collection of the excreta sample where the samples were collected randomly without considering the species (Bernardi et al. 2009) as multiple species of birds may have excreted and there was also no indication of the diet of the birds. Experiments were conducted in the 100 percent humid condition (Adam & Grübl 2004, Bernardi et al. 2009) which does not occur in real-life conditions always and other environmental factors like temperature, light, bacterial growth, were not taken into consideration and no replication of the experiment was done (Adam & Grübl 2004, Bernardi et al. 2009). The materials that were used in the experimentation were of different sizes, shapes, and weight (Vasiliu & Buruiana 2010). The metals were also not cleaned before submerging them in the excreta sample (Vasiliu & Buruiana 2010) as the impurities in the metals attached might influence the result of corrosion and the experiment involved open exposure to air, there was no consideration for the evaporation loss in the excreta sample. Spennemann & Watson (2018) reviewed and provided some extra precautions and measures by which further experimentation could be performed to gain better knowledge of the impact of bird excreta on the building materials. Major past studies used fresh (Adam & Grübl

2004, Bernardi et al. 2009, Huang & Lavenburg 2011) as well as old dry excreta (Bassi & Chiatante 1976, Vasiliu & Buruiana 2010, Ramezanzadeh et al. 2011, Ali et al. 2015) in the form of paste and immersion to see the damage it causes to the metals but mostly the immersive liquid form of the bird excreta was advised to perform the laboratory experiment in the enclosed environment (Spennemann & Watson 2018, Balogh et al. 2019).

For better result, the experiment should be conducted with identified fresh faecal sample of pigeon species only, where the samples and materials should be kept in the enclosed box with a built-in misting device to control humidity and controlling temperature with more control reagents and more replication of the experimentation for a longer duration of the time.

6 CONCLUSION AND RECOMMENDATIONS

6.1 Conclusions

The corrosion loss measurement in the copper metal and its alloys due to pigeon excreta was done using the experimentation method in immersed condition. Copper metal was found to be more susceptible to damage by the pigeon excreta exposure than compared to its alloy bronze and brass. The metal discoloration gave a good visual characterization of the impact in copper alloys. ANOVA confirmed the statistical difference among difference in the final corrosion loss among the metal samples at different medium. Pigeon excreta is found to be the cause of corrosion and damage in copper alloys. This answers the mixed opinion on the question of bird excreta harming different metal monuments.

6.2 Recommendations

Regular cleaning of the wet pigeon excreta and stopping the perching of pigeon is a simple approach to reduce corrosion effect on the historical monuments. So, it is suggested to follow the bird deterrent technique to reduce the impact of pigeon excreta on the metal monuments. For future work on this topic, it is advised to have a larger beaker and more excreta sample to be kept in an enclosed vessel for a longer period.

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APPENDICES

Pigeon excreta

Pigeon excreta on metal structure

Pigeon excreta over Bronze Garuda statue

Pigeon flock on Kathmandu Durbar Square

Pigeon excreta on bell

Weighing machine

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ललितपुर

प.सं. २०७६।७७
च.नं. ३५

फोन नं.:०१५५२२०२१
मिति : २०७६।०१।०१२

विषय :- pigeon excreta संकलन सम्बन्धमा ।

श्री सरोज श्रेष्ठ,
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प्रस्तुत विषयमा त्रि.बि.प्राणी शास्त्र केन्द्रीय विभागको पत्र मार्फत तपाईले पुरातत्व बिभागमा दिनु भएको निबेदन अनुसार तपाइलाई पाटन दरबार क्षेत्रमा सम्बन्धीत अनुसन्धान गर्ने स्थलगत रुपमा नै अध्ययन प्रयोजनको लागि केही pigen excreta संकलन गर्ने अनुमति प्रदान गरिएको व्यहोरा जानकारी गराइन्छ । साथै तपाइको अध्ययनको एक प्रति यस कार्यालयमा समेत उपलब्ध गराउन हुन जानकारी गराईन्छ ।

बोधार्थ:-
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सन्दिप खनाल
कार्यालय प्रमुख