

Cow Urine Effectiveness in Control of Microbially Induced Corrosion on Oil Transmission Pipelines

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Abstract: This study investigated the effectiveness of the use of cow urine in the control of microbially induced corrosion in oil transmission pipelines. Hydrogenase test was carried out and used to detect the presence of micro-organisms that cause corrosion in the pipeline samples. The cow urine biocide was subjected to urinalysis test after which it was characterized. The biocides were then subjected to experimentation to ascertain how effective they can be in reducing microbial corrosion using coupons filled with bacterial cultured agar. Weight loss and the corrosion rate of the samples were determined at weekly intervals throughout the duration of the experiment. The results show that cow urine coupon witnessed the least weight loss amounting to 0.9 g throughout the duration of the experiment. The other biocides formaldehyde, polyamine, diamine and biguanide have weight loss of 6.6, 5.8, 6.81 and 1.2 g, respectively. The 5 polynomial equations were formulated for weight loss for each of the biocides. R^2 goodness-of-fit statistical technique was employed in the analysis for future predictions from the model and the R^2 values obtained in each case is close to 1 which indicates a good measure that future outcomes are very likely to be predicted well by the obtained polynomial equations. Results also show that cow urine has an average corrosion rate of $0.0686 \text{ mm year}^{-1}$, as against the formaldehyde, polyamine, diamine and biguanide which have on the average 1.687, 1.7817, 1.8004 and $0.2225 \text{ mm year}^{-1}$ corrosion rates, respectively. Hence, it can be concluded that cow urine is the most potent biocide followed by biguanide out of the rest treated in this study for microbial corrosion.

Key words: Cow urine, microbial corrosion, corrosion rate, biocide, Nigeria

INTRODUCTION

Cow urine is a natural antiseptic and is extremely effective in treating all kinds of infection, especially those of the kidney and liver. It is able to cleanse the system of toxins and act, as an antidote that protects the body from various types of poison. The component analysis of cow urine shows that it contains nitrogen, sulphur, phosphate, sodium, manganese, carbolic acid, iron, silicon, chlorine, magnesium, melci, citric, titric, succenic, calcium salt, vitamin A-E, minerals, lactose, enzymes, creatinine, hormones and gold acids all needed in small amounts by human body. The body contains many micronutrients that give us strength and these micronutrients are flushed out anytime researchers urinate. Cow urine meets the deficiency of these micro-nutrients in the body. It maintains the balance of these substances in our body. Cow urine is basically an excellent germicide that kills variety of germs, therefore many diseases that are caused by germ are destroyed through cow urine therapy. If it is taken on daily basis, it improves immunity in such a way that resists almost every disease. Some

constituents of cow urine have biocidal properties like phenol. Phenol is bactericidal to gram-positive and negative bacteria, therefore the presence of phenol may be instrumental for its potent antimicrobial nature (Linton and Dick, 1990).

A scientific experiment was undertaken to elucidate the antimicrobial activities of cow urine and its distillate, this activity was tested by agar well diffusion methods for the following strains of microbes like *Escherichia coli*, *Staphylococcus epidermitis*, *Bacillus subtilis*, *Klebsiella pneumonia* and *Proteus vulgaris*. Ofloxacin was used, as a standard for the study and the zone of inhibition was measured. The result shows that cow urine and its distillate inhibited effectively against free radicals and microbes and comparatively, fresh cow urine has exhibited better antimicrobial activity and was comparable with that of the standard Ofloxacin (Mackie *et al.*, 1989).

Microbially induced corrosion is a major issue for the petroleum industries. It is not fundamentally different from any other type of electrochemical corrosion. It is simply that the chemical or physical condition giving rise

to the environment is produced by the metabolic by-product of the micro-organisms. It should be noted that micro-organisms often excrete surfactants leading to fuel emulsifications and thus the probability of microbial penetration into a hydrophobic phase of the fuel increases (Waites *et al.*, 2001). The activities of these micro organisms leads to the formation of peroxides, pitches and acids in fuels, as well as to an increase in viscosity and to a decrease of thermal stability and volatility of the fuel (Chesnau, 2000). In addition, the activities of micro organism on oil pipelines also promote an increase of suspended solids contents in the fuel in form of sludge, corrosion debris and metal particles of the pipeline. Even very small quantities of solid particles present in a fuel are sufficient to cause filtration problems (Ferreira *et al.*, 2006).

Research has shown that around 20-30% of corrosion deposits are related to the activities of micro-organism. The activities of these organisms affect the integrity, safety and reliability of petroleum pipeline operations. The organism causes problems from production strings to transmission pipelines and through refinery, storage and even in end user vehicle fuel tanks and fuel filters. This pipeline corrosion causing-organism slows down production, causes product quality loss, health hazards in polluted areas through spillage and a great cost burden to oil industries (Chung *et al.*, 2000). Current technologies used to control this microbial contamination includes the use of chemical biocides and mechanical scrapping of biofilms formed in the pipeline with pigs. These chemical biocides are ineffective, expensive, dangerous and toxic to humans and the environment (Kaur *et al.*, 2009). In particular, chemical biocides are ineffective against sessile bacteria protected in a complex community known as resistant biofilms.

As the biocides passes the systems, it will react with the bacteria, organic matter, other solids and pipe wall materials, the concentration of the active agent will therefore decrease with increasing distance through the system. Different biocides shows this reduction to different degrees but the system demands for biocides must be considered to ensure that an effective dose remains throughout the pigging operation in the pipeline for at least 50-70% for a long distance transmission pipelines (Rosser, 1994). This batch treatment using conventional biocide by the industries is not effective because some bacteria protected by biofilms survive the chemical treatment and re-grow thereby enhancing their immunity on the biocides. Applications of various chemicals compounds to crude oil and its transport media results in pollution of the environment due to the

slow decomposition of the xenobiotics, many of which possess mutagenic and carcinogenic properties (Zhigletsova *et al.*, 2000).

The identification and application of the most effective biocides and inhibitors of microbial activities on oil pipelines are also been pursued but uptill now, none has been discovered that met the requirements of an effective biocide (Bonch-Osmolovskaya *et al.*, 2003). Significant research all over the world is constantly been done in an attempt to develop new and more effective biocide for microbial contamination on oil pipelines. For example, >500 million dollars are spent annually in Western Europe for this purpose (Neale, 2003).

According to the current policy in the oil producing and refining field, the developed biocide should meet the following requirements:

- High biocidal activity and wide spectrum in action
- Long term action
- Good solubility in water and hydrocarbons
- Effective activity at low concentration without fuel deterioration
- Chemical and thermal stability
- Corrosion inertness with regards to oil facilities
- Ecological safety
- Must be from cheap and accessible raw materials (Gaylarde *et al.*, 1999)

As a result of the inability of the current measures used by the petroleum industries to combat corrosion effectively and efficiently, this research proposes the use of cow urine as a panacea for controlling microbially induced corrosion on oil transmission pipelines.

MATERIALS AND METHODS

The urine of a female indigenous jersey cow was used in this study. It was collected from animal husbandry in Agbor, Nigeria. The cow was physically healthy, as at the time the urine was collected and the detailed history of the cow was obtained from the owner regarding the age, milk yield, feeding practice and previous illness. The urine sample was collected using a urine collection container cup that is leak-resistant and amber colored to protect light sensitive analytes in the urine, as recommended by NCCLS guidelines.

Collection of the cow urine and characterization: The first morning urine of the cow was used for the study, since the urine is more concentrated as a result of the length of time it remained in the bladder, so it contains relatively

Table 1: Properties of the cow urine

Property	Results
Percentage of water	94.6%
Colour	Deep amber
Urine Specific Gravity (USG)	1.005
Epithelial cells	0-1/h.p.f
Urobilinogen	Normal
Bilirubin	Negative
Ascorbic acid	Negative
Ketones	Negative
pH	6.3
Leukocytes	Negative
Red blood cell	Numerous/h.p.f
Uric acid	1 g 100 mL ⁻¹
Urea	2 g 100 mL ⁻¹
Glucose	Negative
Creatinine	Positive
Phenol	Positive

higher levels of cellular elements analyses. The urine was collected by gently stroking the cow just under her vulva, this motion sends a signal to the brain to urinate. The first few dribbles of the urine from the cow were not taken because it is most likely to be contaminated with vaginal mucous. What was used was the urine from the full stream. A hand gloves was worn, as at the time of stroking under its vulva, gloves are more slippery than bare hands so they provide better stimulation.

Finally, the samples were taken to the laboratory for urinalysis test. The urinalysis test result with regards to the properties of the cow urine used for the study is shown in Table 1. The result revealed that the cow was healthy has no sign of abnormality like jaundice, as at the time the urine was collected. The water content of the urine is within the normal range and the color of the urine and the pH show that the concentration is of appreciable value in the acidic region.

Experimentation of cow urine with other biocides:

The 4 chemical biocides were chosen in addition to cow urine, so as to determine how effective the cow urine will be comparatively in curbing the activities of these micro-organism on the oil infrastructure. These biocides are formaldehyde, diamines, polyamines and biguanides. The biocides were injected in the 5 anaerobic pipes ranging from the concentration 5-580 mg L⁻¹. In all the treatment given at weekly intervals, the mixture was circulated in a closed loop at 30°C for 13 weeks representing the standard duration used in the treatment of microbial induced corrosion within the petroleum industries.

Hydrogenase kit test was used to detect the presence of micro-organism causing corrosion in the sample pipes. Thereafter, the 5 anaerobic pipes containing the biocides were labeled P₁₋₅, accordingly the agar medium in P₁ received 5 mg L⁻¹ of Formaldehyde, agar medium

Table 2: Weight loss of the coupons at varying concentrations/weeks of the biocides

Coupons weight loss (g) for various biocides						
Weeks	Concentration (mg L ⁻¹)	Formaldehyde	Polyamine	Diamine	Cow urine	Biguanide
1st	5	0.02	0.40	0.10	0.00	0.03
2nd	30	0.88	0.90	0.50	0.00	0.04
3rd	80	2.87	2.70	0.90	0.01	0.10
4th	130	3.55	2.90	3.80	0.02	0.12
5th	180	3.60	3.60	3.80	0.02	0.70
6th	230	3.60	3.80	3.81	0.02	0.74
7th	280	3.80	4.30	6.40	0.03	0.74
8th	330	3.81	5.40	6.40	0.03	0.74
9th	380	3.82	5.56	6.70	0.20	0.75
10th	430	6.40	5.59	6.70	0.67	0.75
11th	480	6.40	5.80	6.80	0.67	0.80
12th	530	6.50	5.80	6.81	0.70	0.84
13th	580	6.60	5.80	6.81	0.90	1.20

in P₂ received 5 mg L⁻¹ of Polyamines that in P₃ received 5 mg L⁻¹ of Diamines, the medium in P₄ received 5 mg L⁻¹ of cow urine, the medium in P₅ received 5 mg L⁻¹ of Biaguanides. After the 1st week, the test coupons were washed, dried, weighed and recorded. The concentration was then increased to 30 mg L⁻¹ and after the 2nd week, the observation in the various pipes was equally recorded. Subsequently, it was increased by 50 mg L⁻¹ and at each instance, measurements was done until it reached the 13 weeks duration in which the concentration has been increased to 580 mg L⁻¹. The results of the weight loss are shown in Table 2.

RESULTS AND DISCUSSION

Table 2 revealed that the total weight loss in the coupon treated with cow urine is 0.9 g, during the period under study which can be assumed negligible compared to the losses in other coupons treated with the other biocides. Even the coupon treated with biguanides which shows a little resemblance to that of cow urine in terms of antimicrobial capabilities as could be seen from Table 3 has a higher loss of about 1.20 g. Figure 1 depicted the losses for the biocides better.

Table 3 shows the values of the correlation coefficient (R), coefficient of determination (R²) and the polynomial equations for the weight loss of the 5 coupons treated with the various biocides. The R² values for each of the biocides were close to 1 which indicates a good measure that future outcomes are likely to be predicted well by the developed models. Specifically from the models developed, the degree of correlation for formaldehyde, polyamine, diamine, cow urine and biaguanide are 93.8, 98.9, 97.3, 95.7 and 91.8%. This means that the models results can come out true to reality up to the above percentages when applied.

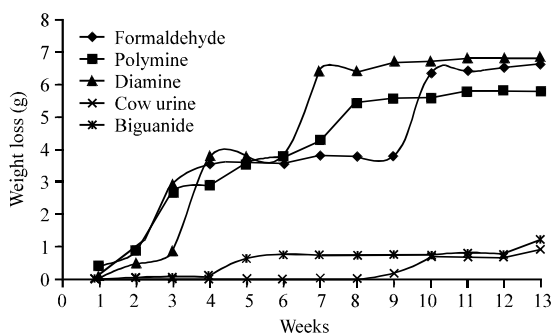


Fig. 1: Weight loss of the biocides for the 13 week duration

Table 3: Values of R, R² and models of biocides for weight loss

Biocides	R	R ²	Trendline equation for weight loss
Formaldehyde	0.938	0.88	$y = -0.014x^2 + 0.696x + 0.000$
Polyamine	0.989	0.979	$y = -0.043x^2 + 1.062x - 0.662$
Diamine	0.973	0.947	$y = -0.065x^2 + 1.541x - 2.055$
Cow urine	0.957	0.916	$y = 0.011x^2 - 0.078x + 0.1050$
Biaguanide	0.918	0.843	$y = -0.005x^2 + 0.156x - 0.200$

Determination of the corrosion rate of the biocides: The corrosion rate is given by:

$$CR = \frac{K(\Delta W)}{AT\rho}$$

Where:

CR = The penetration (corrosion) rate (mm year⁻¹)

ΔW = Weight loss (g)

A = Exposed surface area of coupon (cm²)

ρ = Density of the material (g cm⁻³)

T = Time of exposure (h)

K = Constant for unit conversion = 8.76×10^4

Each of the coupons used had a cuboid geometric shape and are of equal size, hence the exposed surface area (A) of each of them is given, thus:

$$A = 2(LB + LW + BW) = 2(7.62 \times 0.16) + (7.62 \times 1.27) + (0.16 \times 1.27), A = 22.2 \text{ cm}^2$$

Where:

L = Length of the coupon

B = The breadth of the coupon

W = The width of the coupon

Similarly $\rho = 7.86 \text{ g cm}^{-3}$, since it is a mild steel. A sample of calculation of the corrosion rate of the first coupon exposed to formaldehyde for the first week which has 168 hours is as follows:

$$CR = \frac{K(\Delta W)}{AT\rho} = \frac{87600 \times 0.02}{22.2 \times 168 \times 7.86} = 0.0598 \text{ mm year}^{-1}$$

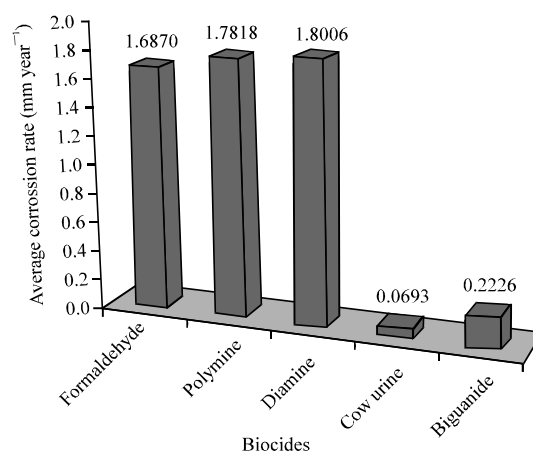


Fig. 2: Average corrosion rate of the biocides on the coupons

Table 4: Corrosion rate for various biocides

Coupons weight loss in (g) for various biocides						
	Concentration	Formal-			Cow	
Weeks	(mg L ⁻¹)	dehyde	Polyamine	Diamine	urine	Biguanide
1st	5	0.0598	1.1953	0.2988	0.0000	0.0896
2nd	30	1.3149	1.3447	0.7471	0.0000	0.0598
3rd	80	2.8588	2.6895	0.8965	0.0100	0.0996
4th	130	2.6521	2.1665	2.8389	0.0149	0.0896
5th	180	2.1516	2.1516	2.2711	0.0120	0.4184
6th	230	1.7930	1.8926	1.8976	0.0100	0.3686
7th	280	1.6222	1.8357	2.7322	0.0128	0.3159
8th	330	1.4232	2.0171	2.3906	0.0112	0.2764
9th	380	1.2684	1.8461	2.2246	0.0664	0.2490
10th	430	1.9125	1.6705	2.0022	0.2002	0.2241
11th	480	1.7386	1.5756	1.8473	0.1820	0.2173
12th	530	1.6187	1.4443	1.6959	0.1743	0.2092
13th	580	1.5171	1.3332	1.5654	0.2069	0.2758
Average		1.6870	1.7818	1.8006	0.0693	0.2226

The results of the corrosion rate for the entire 13 weeks of the experimental duration for the various biocides are tabulated in Table 4 and the average corrosion rate is shown in Fig. 2. From the foregoing, it is clearly shown that the average corrosion rate of cow urine is the lowest of the 5 biocides considered in this experiment. It can be noted from the results that the rate of formaldehyde, polyamine, diamine, cow urine and biguanide are 0.1675, 0.1770, 0.1788, 0.0069 and 0.0221 mm year⁻¹, respectively.

CONCLUSION

This study has established the effectiveness of the use of cow urine in the prevention of microbial corrosion. Though, the other biocides used for this study have antimicrobial abilities in killing the microbes, it can be seen from results obtained that cow urine has better antimicrobial capabilities. The rate of metal loss is less in the coupon with cow urine treatment than in any of the

biocides used. Similarly, average corrosion rate of cow urine is the lowest. In fact, it is about 24 times better than formaldehyde, about 26 times better than polyamine and diamine. The coupon treated with biguanides shows a little resemblance to that of cow urine yet it is about 3 times better than it. Hence, the magnitude of cow urine effectiveness in combating microbial induced corrosion is very high.

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