Green corrosion inhibitors. A review

Arkadiusz Gruca*, Magdalena Greczek-Stachura

Pedagogical University of Cracow, Faculty of Geography and Biology, Institute of Biology, Cracow, Poland; *Arkadiusz.gruca@up.krakow.pl

Corrosion is a significant issue in wide range of fields, including but not limited to: oil and gas industry, water and land transportation, and sewage systems. Destruction of materials exposed to environment is closely related to corrosion. Pipelines and other metal elements exposed to freshwater, seawater, sewage, soil or harsh environmental conditions are especially susceptible to corrosion. Repairing damage caused by corrosion process costs billions of dollars a year. One of the main corrosion prevention methods is to use corrosion inhibitors. Chemical agents and biocides used as corrosion inhibitors are often highly toxic and pose a serious threat to human health and natural environment. Eco-friendly, low cost, and non-toxic alternative is to use natural, green corrosion inhibitors, such as fruits, fruits waste, seeds or leaves extracts, chitosan etc. These natural substances are a reach source of antioxidants, flavonoids, alkaloids, carbohydrates and biocides. Studies show that the use of natural extracts is highly cost-effective and practical technique in the fight against corrosion. Commercial use of green corrosion inhibitors could contribute to substantial savings in infrastructure maintenance costs. This study aims to exemplify natural surfactants that could be used as non-toxic, cheap and effective corrosion inhibitors.

Key words: corrosion, eco-friendly, extract, inhibitor, plant, surfactant.

1. INTRODUCTION

Corrosion is defined as a conversion of refined materials: metal, concrete etc. into more chemically stable forms, such as nitrates, sulfides or oxides. Destruction of materials exposed to environment is closely related to corrosion [1]. According to NACE International global costs of corrosion are estimated to be US$ 2.5 trillion which roughly equals to 3.4% of the GDP (global Gross Domestic Product). Savings equal to about 25% of this astronomical sum could be realized by using available corrosion control practices [2].

One of the main corrosion prevention methods is to use corrosion inhibitors. Many of the inhibitors, including alkyl trimethyl-ammonium chloride and alkyl hydroxyethyl dimethylammonium chloride are, however, very toxic to human health and natural environment [3–6].

Non-toxic, eco-friendly, and low cost alternative is to use natural, green inhibitors, such as fruits, fruits waste, seeds or leaves extracts, chitosan etc. [7–13]. Studies show that the use of natural extracts is highly cost-effective and practical technique in the fight against corrosion. Some of the plant extracts were even proven to inhibit microbial induced corrosion [11, 12]. This study aims to exemplify natural surfactants that can be used as corrosion inhibitors.

2. CORROSION AS A GLOBAL PROBLEM

The impact of corrosion on the global economy cannot be underestimated. Economic sector analysis reveals that corrosion generates highest costs in services (ranging from 40% of total corrosion costs in Arab Countries to 79% of total corrosion costs in United States) followed by industry (20% in the United States to 55% in Arab Countries), and agriculture (1% in the United States to 17% in India) [2]. Due to abundance of forms and prevalence, corrosion cannot be eliminated completely. However, with proper corrosion management practices, savings amounting to 30% of annual corrosion costs could be made [2, 14].

Considerable, corrosion related, maintenance costs in a range of economic sectors result in higher prices of goods and services. 80% of upkeep generated by gas and liquid transmission pipelines is a result of corrosion. Cost of maintaining other infrastructure also cannot be overlooked. Annual direct costs of repairing bridge damage caused by corrosion in US estimates at US$ 8.3 billion. Indirect costs, such as lost productivity and traffic delays were estimated to be 10 times higher than direct corrosion costs. Water, land and air transportation is also suffering from high costs generated by corrosion. In United States alone, combined cost of corrosion in transportation industry is as high as US$ 30 billion annually [2, 14].

These data clearly reveals that corrosion prevention is necessary and can lead to savings amounting to billions of dollars every year.

3. 3. GREEN CORROSION INHIBITORS

3.1. Carbohydrates

Carbohydrate substances are biodegradable, biologically and chemically stable, and non-toxic polymers, which are abundant in nature. Carbohydrates like cellulose, pectin, chitosan and konjac glucomannan (KGM) can be acquired from natural sources which are easily renewable. Recently, thanks to their affinity and good adsorption ability on metal surface, polysaccharides are gaining much attention, as potential corrosion inhibitors for metallic materials [15].

Konjac glucomannan (KGM), commercially used as a thickener and emulsifier in food industry is comprised of β-1, 4 linked D-mannose and D-glucose residues with probable ratio of 1:6:1 [16]. KGM has potential for being effective corrosion inhibitor; however, amount of its hydroxyl groups has to be reduced in order to improve solubility of KGM in acid solution [17]. Zhang et al. have modified KGM with L-arginine and L-histidine and thus enhanced its water solubility and increased amount of active sites for better metal adsorption. Water-soluble konjac glucomannan L-arginine ester (KGMA) and konjac glucomannan L-histidine ester (KGMH) were then tested as corrosion inhibitors for mild steel in 0.5 M HCl solution. Tests have revealed that both KGMA and KGMH are effective inhibitors for corrosion of mild steel. Adsorption of both inhibitors on the metal surface was spontaneous and followed Langmuir isotherm. Their effectiveness was concentration dependant and KGMH turned out to be more potent as inhibitor than KGMA [17].

Chitosan, structurally the N-deacetylated product of chitin, is a polysaccharide composed of β-D-glucosamine and N-acetyl-β-D-glucosamine unit with a 1, 4-linkage [18]. Thanks to ease of extraction from the shells of crustaceans, such as shrimps, lobsters, and crabs in sea food waste, about one billion tons of chitosan are
produced every year [19, 20]. Thanks to the presence of hydroxyl and amino groups, chitosan displays anticorrosive properties. Utilization of chitosan as a corrosion inhibitor at industrial level could largely contribute to preservation of natural environment. Chitosan was found to inhibit corrosion of API 5L X60 pipeline steel, in saline solution saturated by CO₂, to some extent in comparison to commercial inhibitor [21]. However, for enhanced inhibition efficiency, usage of chitosan in combination with other substances is necessary [22]. A synergistic inhibition effect could be achieved by addition of iodide ions, well known for their ability to improve corrosion inhibitory effects of organic compounds [23, 24]. Studies have shown that, for mild steel in 1 M sulfamic acid medium, inhibition efficiency of 90.3% can be achieved with a blend comprising of chitosan 200 ppm and KI 5 ppm [13]. O-fumaryl-chitosan (OFC), derivative of fumaric acid and chitosan was also proven to be an effective corrosion inhibitor. Inhibition efficiency of 94.1% was achieved for mild steel, with 500 ppm concentration of OFC. Inhibitive properties of OFC are associated with its ability to create protective adsorption film on the surface of metal [25].

Another promising range of natural corrosion inhibitors are hydroxypropyl methylcellulose (HPMC) derivatives [26]. HPMC, a flexible [27] biopolymer with high film forming ability [28] is widely used in the medical field and food industry [29-32]. Thanks to its decomposability and biocompatibility, it is also employed as a corrosion inhibitor [33-36]. However, as a result of its solubility in water, HPMC is ill suited for high humidity and water environments. Because of that, insoluble HPMC derivatives, created by addition of acetate, succinate, and phthalates, are being employed. Hydroxypropyl methylcellulose phthalate (HPMCP) and hydroxypropyl methylcellulose acetate succinate (HPMCAS) were proven to inhibit corrosion in strong acid environment [26]. Corrosion inhibition ability of HPMCP and HPMCAS was positively correlated with their film thickness. HPMC, thanks to its low moisture content and hydrophobic surface provides better corrosion protection than HPMCAS [26].

Pectin (Fig. 1), a structural heteropolysaccharide and a component of terrestrial plant cell walls is mainly extracted from citrus fruits. It is used commercially as a gelling agent and stabilizer in food industry. Pectin also finds use as a medicament in gastrointestinal disorders and lowers blood cholesterol level [37]. The desirable properties of pectin include: low production costs, biodegradability, polyfunctionality, nanotoxicity, and flexible structural network. Pectin has been reported to inhibit corrosion of aluminium in HCl solution [38]. Pectin-grafted polyacrylamide (Pec-g-PAAm) and pectin-grafted poly-acrylic acid (Pec-g-PAA) were also proven to inhibit corrosion in the neutral medium with corrosion inhibition efficiency of about 85% [39]. Other reports state, that pectin inhibits X60 pipeline steel corrosion in acidic environment, its inhibition efficiency is positively associated with concentration and temperature, and reaches 98.2% at 60°C and pectin concentration of 1000 ppm [40].

Cellulose (Fig. 2), an organic compound with the formula (C₆H₁₀O₅)n is the most abundant organic polymer on Earth [41]. As a structural component of the primary cell wall of green plants, many forms of algae and the oomycetes it is readily available and easily extracted from wood pulp and cotton. Main uses of cellulose include production of paper, paperboard and confection into wide variety of derivative products such as cellophane and rayon [41]. Hydroxyethylcellulose (HEC) is water soluble polymer derived from cellulose, commercially used in food, pharmaceutical, cosmetic, paper and other industries [42]. It also found use as a relatively cheap and eco friendly corrosion inhibitor. Studies have shown that HEC inhibits corrosion of mild steel and aluminium in HCl solution [43]. Corrosion inhibition properties of HEC on 1018 c-steel in NaCl solution were also tested. Obtained results have shown that HEC is mixed-type inhibitor which inhibition efficiency reaches 96.6% at substance concentration of 403 ppm. Corrosion inhibitive properties of HEC decreased with rise of the temperature [44].

Many plant species are known to exhibit desirable properties and have been utilized by humans since antiquity [45]. Extracts from plant bark, roots, leaves, seeds, heartwood and fruits are readily available, renewable and environmentally friendly source for useful substances. A range of naturally synthesized chemical compounds can be extracted by simple and low cost methods. Many of said extracts have been reported to exhibit corrosion inhibitive properties for mild steel and aluminium [46-49].

The longan (Dimocarpus longan), member of the family Sapindaceae, is a tree that produces fruits very popular in China. Inedible seeds and peels of longan are commonly treated as a waste and thrown away. However, studies have shown, that water extracts of longan peels (WELs) and seeds contain high levels of phenolic antioxidants, such as gallic acid, ellagic acid, (+)-epicatechin and 4-O-methylgallic [50]. All four of the above mentioned substances have aromatic rings and oxygen atoms commonly regarded as adsorption sites [51]. Some of this sites display corrosion inhibiting properties [52-54]. WEL was proven to inhibit corrosion of mild steel in 0.5 M HCl solution, when added to the tested medium, with excellent efficiency and was marked as mixed-type inhibitor that has high application potential as eco friendly corrosion inhibitor [55].

Plantago ovata, member of the family Plantaginaceae, commonly known as blond plantain or desert Indianwheat is a medical plant native to southern and eastern Asia. Mucilage extract from epidermis of dried Plantago ovata seeds is commonly used in pharmaceutical industry due to its properties which include non-irritating nature, low production costs and lack of toxicity [56, 57]. Main ingredient of the mucilage is arabinosyl (galaturonic acid) rhamnosylxylan (AX) [58], which acts as corrosion inhibitor for carbon steel. Studies have proven that mucilage extract of Plantago ovata inhibits corrosion of carbon steel in 1 M HCl solution with good
efficiency when added to the solution [59]. Analyses have shown that AX molecules adsorbed on the metal surface by mixed-type adsorption and created barrier layer on the carbon steel surface protecting it from aggressive HCI medium. Inhibition efficiency of AX reached 94.4% at a concentration of 1000 ppm in temperature of 60°C [60].

Other species of the family Plantaginaceae, such as many members of the genus Veronica display desirable biological properties, including anti-inflammatory, antibacterial and antioxidant activities [73-75]. Some of the Veronica species were traditionally used in folk medicine [76]. Extracts from Veronica genus plants are known to contain high amounts of iridoid, flavonoid and phenylethanoid metabolites [77-79]. Butanolic extract of the aerial parts of Veronica rosea was proven to inhibit corrosion of copper in 1.0 M HNO3 solution [80]. Studies have shown that V. rosea extract is a mixed type inhibitor and that its adsorption on the surface of the metal is spontaneous. Inhibition efficiency rose with the increase of extract concentration and reached 87.4% at 300 ppm [80].

Mentha pulegium, more widely known as pennyroyal, pennyrie, or squaw mint is a species of flowering plant in the Lamiaceae family. Pennyroyal shares chemical properties with Mentha spicata (spearmint), and finds use as a culinary and medicine herb. It has also been used as a folk remedy [61]. Mentha pulegium plant extracts (MPEs) are known as a source of flavonoids, alkaloids and essential oils rich in oxygen monoterpenec hydrocarbons, such as menthone or menthol [62, 63]. These substances may exhibit good corrosion inhibiting properties. Studies have shown that addition of MPE inhibits corrosion of steel in 1M HCl solution with over 86% efficiency at MPE extract concentration of 33%. Mentha pulegium extract acts through mixed type of corrosion inhibition mechanism [63]. These findings suggest that MPE has a potential to become the base for new eco-friendly corrosion inhibitor.

Ginkgo biloba, last living species in the division Ginkgophyta, is a widely cultivated tree native to China [64]. First introduced to Europe in 18th century, it was eventually spread all over the world. G. biloba is known as a source of food and finds use in traditional medicine. Ginkgo biloba extracts are known to contain terpenoids and flavonoids, and have shown antioxidant activities [65-67]. Studies have proven that water extract from Ginkgo biloba leaves, at a concentration of 1,000 mg/L, inhibits corrosion of Q235A steel with 83.2% efficiency in 1M HCl medium at 60°C [68]. Extract has also shown to be a good antimicrobial agent and thus could potentially be used as a microbial induced corrosion inhibitor. Other concentrations of water and alcohol G. Biloba extracts were also tested, but turned out to be less effective [68].

Loquat (Eriobotrya japonica), member of the family Rosaceae is a species of flowering plant native to China. It is also common in Korea, Japan, hilly regions of India, Potohar and foothill regions of Pakistan [69-71]. Thanks to high pectin, sugar and acid content, Eriobotrya japonica finds use in food industry, traditional Chinese medicine and wine-making. Acid loquat leaves extract (LLE) was tested as corrosion inhibitor for mild steel in 0.5 M HCl solution [72]. Studies have shown that LLE inhibits cathodic corrosion processes. Inhibition efficiency increased with rising LLE concentration, but decreased with rising temperature. At a highest point inhibition efficiency of LLE reached 96.8%. Corrosion inhibition effect was caused by a combination of different LLE components [72]. Thanks to synergistic inhibition effect of main extract components, LLE shows promise as a subject of further corrosion research.

Lychee (Litchi chinensis), a tropical fruit tree native to Fujian and Guangdong provinces of China is a tall, evergreen tree that bears small fleshy fruits. Being very popular in Asia, lychees are extensively grown in China, Vietnam, India and Thailand [52]. Lychee peels and seeds are commonly discarded as inedible. However, extract of the Litchi chinensis peel and seed was found to contain cyaniding-3-glucoside, (-)-epicatechin and (-)-epigallocatechin, regarded as strong antioxidants. These substances possess potent electron-donating and chelating capacity with iron, which gives lychee waste extract ability to inhibit corrosion of metal [81, 82]. Ethanol extract of lychee peels and seeds (EELPS) was proven to inhibit mild steel corrosion in 0.5 M HCl solution; its inhibition efficiency reached 97.95% at a 600 mg/L extract concentration. Analyses have shown that EELPS adsorbs onto the metal surface by donating π electron and lone pair electron to vacant orbital of iron which blocks corrosion process [83]. EELPS, being extracted from otherwise unusable food waste, could prove to be a great, eco-friendly and non-toxic alternative to traditional corrosion inhibitors.

Piper nigrum, a flowering vine in the family Piperaceae is a source of black pepper, well known spice widely used all over the world. Black pepper vine, native to Kerala in south-western India is extensively cultivated in tropical regions [84]. Dried ground pepper has been used as a seasoning and traditional medicine since antiquity. Main ingredient of black pepper, alkaloid piperine has been screened for its corrosion inhibition abilities [85]. Studies have shown that black pepper extract inhibits corrosion of mild steel in 1 M sulphuric acid medium. Inhibition efficiency of Piper nigrum extract was as high as 90% at a 20ppm extract concentration. Authors state that piperine is main anticorrosive agent, but other substances, such as starch, proteins and terpenoids may have synergistic effect with piperine [88]. Described results picture black pepper extract as a potent anti corrosive agent that could be used as eco-friendly and cheap alternative to traditional corrosion inhibitors.

4. SUMMARY

Various eco-friendly, non-toxic and alternative corrosion inhibitors were described in this study. A lot of them show high promise and could potentially replace currently used inhibitive substances. Inhibition efficiency of natural anticorrosive agents (Fig. 3) turns out to be comparable to commonly used chemicals.

Natural corrosion inhibitors extracted from various plant parts and plant waste might contribute to high maintenance cost savings in a range of economic sectors. Introduction of natural inhibitors could also help to protect natural environment.

Despite recent advancements, more research is still required to refine technological processes, formulas and extract compositions used in creation of natural inhibitors, in order to adapt them for commercial use.

REFERENCES


Thereafter, we can continue with the rest of the text chunk, ensuring that it is properly formatted and readable.
Przegląd ekologicznych inhibitorów korozji

Arkadiusz Gruca*, Magdalena Greczek-Stachura

* Uniwersytet Pedagogiczny im. KEN w Krakowie, Wydział Geograficzno-Biologiczny, Instytut Biologii; arkadiusz.gruca@up.krakow.pl

Słowa kluczowe: ekologia, ekstrakty roślinne, inhibitor, korozja.

1. CEL I ZAKRES PRACY
Niszczenie materiałów wystawianych na działanie warunków środowiskowych jest ściśle związane z procesem korozji. Jedną z głównych metod zapobiegania temu procesowi jest stosowanie inhibitorów. Wiele powszechnie używanych substancji charakteryzuje dużą toksyczność dla człowieka oraz dla środowiska. Dobrą alternatywą dla takich środków są naturalne inhibitory korozji ekstrahowane z różnych części roślin. Badania dowodzą, że naturalne ekstrakty roślinne skutecznie hamują korozję, a niektóre wykazują właściwości biobójcze, pomocne w walce z biokorozją. Celem pracy jest przedstawienie naturalnych ekstraktów, które mogą zostać wykorzystane w zapobieganiu korozji.

2. KOROZJA JAKO PROBLEM ŚWIATOWY
Zapobieganie negatywnym skutkom korozji ma niebagatelną wpływ na światową gospodarkę. Co roku na zapobieganie korozji i naprawę skutków tego procesu przeznacza się w przybliżeniu 3,4% dochodu światowego brutto, czyli około 2,5 biliona dolarów amerykańskich. Około 25% tej kwoty może zostać zaoszczędzone dzięki zastosowaniu odpowiednich procedur kontroli i zapobiegania korozji.

Znaczące obciążenia finansowe związane z korozją, występujące w wielu sektoren gospodarczych, wpływają na wysokie ceny dóbr i usług. Największe koszty utrzymania generują infrastruktury komunalne i komunikacyjne. W przypadku tej drugiej, koszty pośrednie są nawet 10 razy większe od bezpośrednich i wynikają z opóźnień w transporcie i strat produktywności. Statystyka pokazuje, że zapobieganie korozji jest konieczne i może prowadzić do znacznich oszczędności w gospodarce globalnej.

3. EKOLOGICZNE INHIBITORY KOROZJI
Węglowodany to nietoksyczne, biodegradowalne, stabilne biologicznie i chemicznie, naturalne polimery licznie występujące w przyrodzie. Komercyjnie są pozyskiwane z łatwo dostępnych źródeł. W przeważającym stopniu działają jako inhibitory typu antyoksydacyjne i wysokie powinowactwo wobec powierzchni metalu. Właściwości antyoksydacyjne, znikoma toksyczność, a proces ich pozyskiwania jest prosty i nie wymaga użycia wielu szkodliwych substancyj, miejsce utrzymania infrastruktury. Wprowadzenie do powszechnego użytku naturalnych ekstraktów w hamowaniu procesu korozji, ze względu na temat negatywnych skutków użytkowania niektórych środków chemicznych oraz narastającej degradacji środowiska powrót do stosowania substancji naturalnych pozyskiwanych w sposób nieinwazyjny jest obecnie obiecuje kierunkiem. Wiele z powszechnie występujących substancji nieならばce chuje się właściwościami antyoksydacyjnymi, znikomą toksycznością, a proces ich pozyskiwania jest prosty i nie wymaga użycia wielu szkodliwych mechanizmów. Cechy te wskazują na duży potencjał zastosowania naturalnych ekstraktów w hamowaniu procesu korozji.

Wyniki analiz ekstraktów pozyskanych z gatunków roślin takich jak Plantago opata, Veronica rosea, Mentha pulegium, Ginkgo biloba, Eriobotrya japonica, Litchi chinensis, czy Piper nigrum pokazują, że substancje pochodzenia roślinnego mogą efektywnie hamować procesy korozji. Szczególnie obiecujący z punktu widzenia późniejszego zastosowania jest ekstrakt z pieprzu czarnego (Piper nigrum), którego efektywność w hamowaniu procesu korozji wynosi 90% przy stężeniu zaledwie 20 ppm. Głównymi substancjami aktywnymi zawartymi w ekstrakach wymienionych gatunków są flavonoidy, fenylotanoidy, alkaloidy, terpenoidy kwasy organiczne i węglowodory aromatyczne. Substancje te wykazują właściwości antyoksydacyjne i wysokie powinowactwo wobec powierzchni metalu. W przeważającym stopniu działają jako inhibitory typu międzyciem. W przypadku gatunków o nieznanej lub słabiej zbadanej antyoksydacyjnej, wyniki analiz zawierają informacje o potencjale zastosowania substancji w różnych sektorach gospodarki.

4. PODSUMOWANIE
W pracy omówiono ekologiczne i nietoksyczne inhibitory korozji, które mogą być alternatywą dla obecnie stosowanych rozwiązań. Wiele z omówionych substancji wykazało efektywność w hamowaniu procesu korozji, a ich pochodzenie roślinne pozwala na ich przyszłość w przemyśle i budownictwie, w której korzystanie jest wysoce przydatne dla ochrony środowiska.

Dzięki wykorzystaniu naturalnych ekstraktów w hamowaniu procesu korozji, a ich pochodzenie roślinne, można oszczędzać na produkcji substancji chemicznych, a proces ich pozyskiwania jest prosty i nie wymaga użycia wielu szkodliwych substancji. Wyniki analiz pokazują, że substancje pochodzenia roślinnego mają duży potencjał zastosowania w przemyśle i budownictwie.