

## Urea removal from aqueous solutions—a review

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**Abstract** The abundance of urea in the natural environment is dictated by the fact that it is one of the major products of mammalian protein metabolism. Due to the extensive use of urea in many branches of industry, it is produced in large quantities. Urea enters into the environment not only with wastewater from the production plants but also by leaching from the fields, agro-breeding farms, and the effluents from the plants using it as a raw material. There are many methods of urea removal, but most of them are still being developed or are very new. The

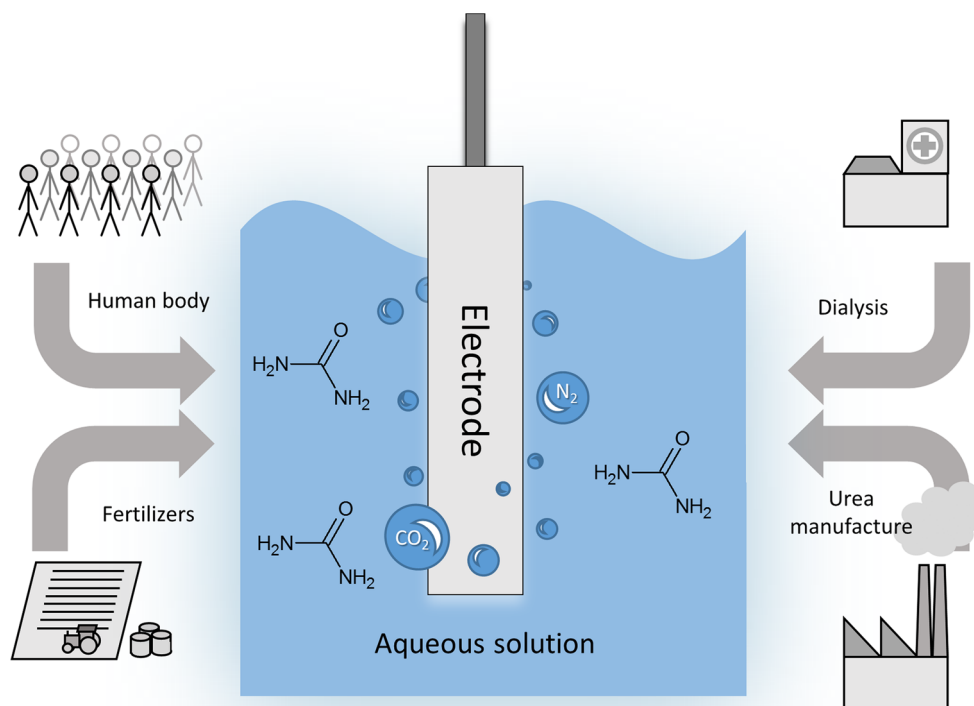
methods themselves differ in terms of physicochemical nature and technological ingenuity. Many wastewater treatment methods include processes such as hydrolysis, enzymatic hydrolysis, decomposition in the biological bed, decomposition by strong oxidants, adsorption, catalytic decomposition, and electrochemical oxidation. In this work, methods of urea removal from aqueous solutions have been reviewed. Particular attention was paid to electrochemical methods.

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## Graphical Abstract



**Keywords** Urea · Urine · Electro-catalytic oxidation of urea · Electrochemical methods · Waste treatment

## 1 Background

Urea is considered a key molecule in the history of modern chemistry, because it unlocked access to synthetic organic chemistry as it is known today [1]. Chemically pure urea is a colorless and odorless solid. It is also an important molecule for all living organisms, because it takes part in many biological processes and metabolic pathways (e.g., decomposition of proteins). The human body produces 20–30 g of urea per day [2]. Urea is a weak base; however, it is stronger than most amides and can be hydrolyzed in the presence of acids, bases, and ureases [1].

Pure urea can be regarded as a nitrogen fertilizer. When in aqueous solutions with ammonium nitrate or magnesium sulfate, it can be applied as a foliar fertilizer. It forms complexes with hydrogen peroxide (used in medicine as an antiseptic), which allows for longer storage times. Urea derivatives are used in pharmaceuticals production and as bioactive compounds in cosmetics and dermatology as well as herbicides and insecticides [2]. Urea is an excellent reducing agent in the selective catalytic reduction (SCR) reaction of nitrogen oxides ( $\text{NO}_x$ ) from exhaust gases in internal combustion engines, especially heavy-duty diesel engines [3].

Due to the extensive use of urea, it is produced in large quantities. Industrial synthesis of urea involves ammonia reacting with carbon dioxide at high pressure. The modern urea production technologies are the Stamicarbon process (involves  $\text{CO}_2$  stripping), the Snamprogetti process (involves  $\text{NH}_3$  stripping), the ACES process, and the IDR process [4, 5]. However, the waste generated during urea production is problematic. The largest quantities of waste are produced in the concentration process in the evaporators. During this process, the vaporization of water entrains droplets of urea solution, which can then pass into the condensate [6]. Additionally, the amount of wastewater increases during auxiliary operations such as the washing of the prilling towers and pumps transporting the solution along with a urea crystal suspension. Some wastewater can also be generated during the centrifugation process of the urea crystals [6]. Urea enters into the environment not only with wastewater from production plants but also by leaching from fields and agro-breeding farms, in effluents from plants using it as a raw material, and as a final product of mammalian protein metabolism.

The latter is the main reason of the abundance of urea in the natural environment. Terrestrial vertebrates produce it in the urea cycle, in which one nitrogen atom of urea is captured from a  $\text{NH}_4^+$  ion, while the other comes from aspartate. The carbon atom present in urea comes from  $\text{CO}_2$ . Mammals produce urea in the liver, after which it is

transported by the blood to the kidneys and excreted with urine. The concentration of urea in the blood of an adult human is approximately 1–10 mM [7].

The accumulation of urea and other products of metabolism can occur in humans in the case renal failure. The most popular method of treatment for uremia is dialysis [8]. However, the regeneration of spent dialysate is expensive due to the presence of urea. For this purpose, adsorption on activated carbon can be applied, although this method has a low removal efficiency. A suitable alternative might be enzymatic hydrolysis. In this method, the high cost of enzymes and the need for the removal of toxic ammonia from the resulting solution must be taken into account [2].

There are many methods of urea removal, but most of them are still being developed or are very new. Urea can be removed from aqueous solutions by a variety of methods that differ in terms of their physicochemical nature and technological ingenuity. Many wastewater treatment methods include processes such as hydrolysis, enzymatic hydrolysis, decomposition in the biological bed, decomposition by strong oxidants, adsorption, catalytic decomposition, and electrochemical oxidation [1].

In this work, different methods of urea removal from aqueous solutions have been reviewed. This paper aims to present and describe methods for urea decomposition. Particular attention was paid to electrochemical urea removal methods. The issue is interesting because electrochemical treatment of urea-containing aqueous wastes can be utilized in dialysis, wastewater plants, and in fuel cells.

## 2 Methods of urea removal

### 2.1 Hydrolysis of urea

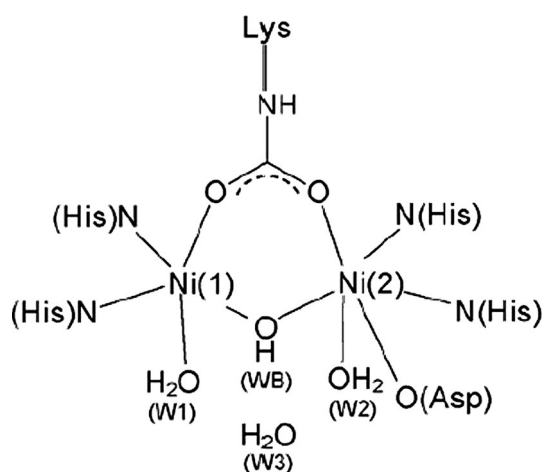
During hydrolysis, an aqueous solution containing urea comes in contact with high-pressure steam. This process proceeds at high temperatures and under large pressures. After hydrolysis, the products of the decomposition (ammonia and carbon dioxide) are separated. This process can be realized in several variations including at different temperatures, pressures, and residence times [1].

One way to perform the hydrolysis of urea is to heat the wastewater to 200–220 °C under a pressure of 2–3 MPa over 0.5 h. Next, the heated wastewater is cooled by the feeder wastewater for hydrolysis. Then, the wastewater is fed to a flash separator, where the gaseous phase is condensed and recycled for urea production and the liquid phase is carried off to the sewer. The content of nitrogen in the wastewater is reduced by 94 % [9].

Companies such as Stamicarbon and Snamprogetti also expanded the processes of urea wastewater purification based on hydrolysis. The Stamicarbon method consists of the hydrolysis of urea and the removal of the resulting ammonia and carbon dioxide from the purified solution under a pressure of 0.2–0.3 MPa using steam. After that, the solution is fed to a vertical hydrolyzer which operates in the temperature range of 170–230 °C and under the pressure of 1.7 MPa. The solution that leaves this system contains less than 1 ppm urea. The Snamprogetti method is based on the preliminary desorption of ammonium followed by hydrolysis in a horizontal hydrolyzer. Similarly, in this case, the purified solution also contains less than 1 ppm urea. However, this process is run at slightly higher temperature (230–236 °C) and under the pressure of 3.3–3.7 MPa [1, 2]. The kinetics of low-temperature urea hydrolysis processes in aqueous solutions were also investigated. The researchers, investigating the kinetics, started with a solution containing 5–20 g dm<sup>-3</sup> urea. The kinetics equation of the process, hydrolysis rate constant, and parameters of the Arrhenius equation were determined [1, 10]. Mahalik et al. investigated the kinetics of urea removal by hydrolysis and how it was affected by the urea concentration (20–40 wt%), stirring rate (100–700 rpm), and temperature (120–160 °C). It was found that the urea conversion and the reaction rate increased as the temperature and concentration of urea increased; meanwhile, the stirring speed had only a minimal influence [11].

### 2.2 Enzymatic decomposition of urea

Urea can also be removed from aqueous solutions by enzymatic decomposition. The first ureolytic enzyme was discovered in urine in 1874 by Musculus, but it was not until 1890 that the name urease was proposed. Ureases catalyze the hydrolytic decomposition of urea, and it can be used either in the free or immobilized form [12]. The activity of ureases is dictated by the structure of their binuclear nickel active center, where Ni(1) and Ni(2) atoms may have different coordination numbers (Fig. 1). This process is used for the determination of urea concentrations in blood, urine, and wastewater and for removing it from blood in the treatment of uremia. During the reaction, urea undergoes hydrolysis to ammonia and carbamic acid, which is then spontaneously decomposed to ammonia and carbonic acid. Carbonic acid and two molecules of ammonia in aqueous solution are at equilibrium with their respective ions, meaning that the reaction equilibrium is affected by the pH of the solution [13]. There are four main classes of urease inhibitors: hydroxamic acids [14], phosphoramidate compounds [15], boric and boronic acids [16], and heavy metal ions [17]. There is significant research



**Fig. 1** Schematic structure of the active center of native urease (Adapted with permission from [12]. Copyright (2009) Elsevier)

describing the influence of urease inhibitors on the enzymatic decomposition of urea.

Research conducted by Krajewska et al. [18] aimed to determine the effectiveness of the inhibition of the urea decomposition reaction catalyzed by urease, which was immobilized on a chitosan membrane using boric acid. A mixture of urea ( $6 \text{ g dm}^{-3}$ ) and boric acid ( $0.31 \text{ g dm}^{-3}$ ) was kept under constant pH 7 using a phosphate buffer. In their study, it was shown that, in the case of the immobilized urease, the decomposition of urea took place at a constant rate, even in the presence of an inhibitor. In other studies, the influence of heavy metal ions [19] and sodium fluoride [20] on the activity of free and immobilized urease was investigated. The effect of phosphate buffer on urease activity was also studied. The obtained results show that the most favorable conditions for urea ( $4.8\text{--}7.2 \text{ g dm}^{-3}$ ) hydrolysis under the influence of urease were at pH 6.5–7.6, because  $\text{H}_2\text{PO}_4^-$  ions inhibited the decomposition of urease [21]. The investigations proved that immobilized urease was less sensitive to pH changes; immobilized urease was slower to lose its activity. The initial activity of the urease (70 %) was retained past 15 cycles of reuse. In addition, immobilized urease was characterized by a higher stability, and its activation temperature was higher in comparison to free urease. This investigation proved that urea hydrolysis in the presence of a urease can be a very effective urea removal method [22]. In the work carried out by Magne et al. [23], a combination of the electro dialysis and catalytic hydrolysis of urea was used to purify aqueous solutions. This method required that the fabric with the immobilized urease being placed in the electro dialyzer between the cation and anion exchange membranes. Three current densities were studied (1, 5, and  $10 \text{ mA cm}^{-2}$ ). The proposed method was highly effective for removing the urea decomposition products under the influence of an

electric field. The concentration of ammonium ions decreased with the increasing current density. In addition to the studies involving the optimization of appropriate process parameters for the enzymatic hydrolysis of urea, many investigations concentrated on the mechanism and kinetics of this process. More attention has been paid to the structure of urease and the presence of nickel in the active center. In the study carried out by Musiani et al. [24], the mechanism of the enzymatic urea hydrolysis process in relation to the presence of two nickel atoms was presented. Studies showed that one of the nickel atoms bonded with the carbon atom of urea, while the other combined with the nitrogen. Similar results were presented by Andrich et al. [25], who investigated the kinetics of urea degradation in a model wine solution using an acid urease and immobilized urease. The researchers determined that the reaction is a pseudo-first-order reaction. The estimated kinetic equation did not change when changes in the reaction environment occurred [26]. Similar results were obtained by Andrich et al. [27]. Lin et al. [28] immobilized urease on polyacrylonitrile hollow fibers, which were used in the hydrolysis of urea. After 15 cycles of reuse, the initial activity of urease (86 %) remained unchanged. Yang et al. [29] also studied urease immobilized on the same material and its effectiveness in urea hydrolysis. The results shown in their paper suggest that the rate of urea removal was 2.7 times higher compared to free urease.

### 2.3 Removal of urea by biological methods

Biological methods of urea removal mainly involve the process scheme in which urea-rich water flows through a series of biofilters. Different strains of bacteria decomposing organic nitrogen to molecular nitrogen are present in these filters. In the first stage, the ammonification process, the nitrogen bacteria convert the organic nitrogen to ammonium ions. Then, the wastewater is fed to an aeration chamber where the nitrification process proceeds. In this stage, the *Nitrosomonas* bacteria convert the ammonium ions to nitrite ions and the *Nitrobacteria* bacteria convert nitrite ions to nitrate ions. In the last stage, denitrification takes place. In the oxygen-free environment, the denitrifying bacteria convert the nitrate ions to molecular nitrogen. In most cases, the denitrifying bacteria are heterotrophic bacteria such as *Pseudomonas*, *Micrococcus*, *Denitrobacillus*, and *Achromobacter* [2, 30].

The determination of the optimal conditions for the biological degradation of urea requires extensive research because of the complex behaviors of microorganisms in response to external stimuli. For example, the resulting course of the nitrification process in the biological filter follows acidification of the medium. To counteract acidification, this process should be operated at a pH of 8.0–8.2

[1]. Gupta et al. [31] investigated the biological oxidation of wastewater containing urea in an industrial installation. In this case, the products of urea decomposition depended on the pH of the solution. The conditions in the bioreactor influenced the vitality of the bacteria. In other studies, the rate of removal of urea, ammonia, and nitrate ions in a moving bed biofilter at different feed loadings was investigated. The wastewater containing these substances was purified, but the rate of urea removal was lower than that of ammonia and nitrates [32].

#### 2.4 Decomposition of urea by strong oxidants

The decomposition of urea can be realized via the oxidation of wastewater with strong chemical oxidants such as ozone or sodium chlorate. In the work conducted by Konyk et al. [33], an investigation of the oxidation by ozone of wastewater containing urea was presented. This process was conducted in a phosphate buffer solution (pH 6.1–6.2), and  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Fe}^{2+}$ , and  $\text{Fe}^{3+}$  ions were used as catalysts. It was found that this method was very effective; however, the cost of ozone production was high, and  $\text{NO}_3^-$  ions were present in the decomposition products. Meanwhile, Fuchs [34] reported the oxidation of urea from a swimming pool by sodium chlorate. It was found that the final products of the urea decomposition were nontoxic gases: nitrogen and carbon dioxide as well as sodium chloride [1].

#### 2.5 Removal of urea by adsorbents

The process of the adsorption of urea is based on the flow of the solution containing urea through a bed of sorbent. There are many adsorbents available for this purpose: activated carbons, zeolites, ion-exchange resins (IERS), and silica.

Silica gels and porous polymers are very popular adsorbents in the modern literature. As an example, Nasuto et al. [35] investigated those materials modified with surface epoxy groups as possible adsorbents for urea removal. It was found that epoxy groups reacted with the ammonium group of urea, and the porous polymer network had a higher capacity of adsorption than that of silica. Another material suitable for adsorption of urea is chitosan and its derivatives. Xue et al. [36] researched the removal of urea using chitosan, chitosan cross-linked with glutaraldehyde and Cu(II) complex cross-linked chitosan. The kinetics for pseudo-first-order and pseudo-second-order models were analyzed. The rate of urea uptake was higher for cross-linked chitosan materials. The Cu(II) complex cross-linked chitosan was characterized by the highest values for the rate of urea uptake and for the uptake capacity. Liu et al. [37] also used a chitosan/Cu(II) membrane for urea adsorption. The

maximum urea adsorption capacity attained in this research was 78.8 mg urea/g membrane. Such a membrane could be successfully used in hemodialysis. In other investigation [38], cross-linked chitosan microspheres with immobilized Zn(II) were used. The kinetic of adsorption process was investigated. This process was exothermic and was characterized by pseudo-second-order kinetics. Additionally, it was found that the adsorption capacity depended on the pH, temperature, and concentration of urea in the treated solution. Zhu et al. [39], on the other hand, had proposed a membrane system for the adsorptive cleaning of hemodialysate to remove urea used in hemodialysis equipment. The authors used polydopamine surface-modified poly(lactic acid) membranes grafted with poly(carboxybetaine methacrylate) and determined that the smaller pores on the modified surface improved the separation capability of the membrane, while the negative surface charge of the membrane additionally helped to separate the solution from proteins such as those demonstrated with bovine serum albumin model molecules.

#### 2.6 Catalytic decomposition of urea

Urea removal by catalytic decomposition in an aqueous environment is another attractive alternative. In this category, various catalysts can be used. In the investigations of Ananiev et al. [40, 41], the catalytic decomposition of urea was reported using a Pt/SiO<sub>2</sub> catalyst in an aqueous solution containing nitric acid and formic acid at mild temperatures (58.5–76 °C). The authors found that the decomposition of urea proceeded with the formation of fulminic acid, which then reacted with nitric acid to eventually form nitrogen, ammonium ions, and carbon dioxide. However, urea itself did not react on the surface of the catalyst, but the reaction was initiated by the nitrite ions that were generated at the Pt active sites. Shen et al. [42] studied the catalytic decomposition of urea over different polymorphic forms of Al<sub>2</sub>O<sub>3</sub>. The  $\eta$  form of alumina was shown to exhibit the highest catalytic activity toward the hydrolysis of urea, because the catalyst has the higher alkalinity compared to other Al<sub>2</sub>O<sub>3</sub> forms. Lundström et al. [43] investigated the thermal decomposition of urea and the hydrolysis of HNCO with the use of titanium dioxide, Fe-Beta, and  $\gamma$ -alumina catalysts. The process was run at temperatures in the range of 25–500 °C. Fe-Beta was characterized by the selective adsorption of urea, and the best catalyst for this reaction was TiO<sub>2</sub>. Meanwhile, Bernhard et al. [44] described the thermolysis and subsequent hydrolysis reactions of urea by simulating reactions occurring in exhaust pipes utilizing SCR of NO<sub>x</sub> over anatase TiO<sub>2</sub>. They distinguished the reaction products and all of the intermediates formed during the process.

## 2.7 Comparison of nonelectrochemical methods of urea decomposition

Many of the nonelectrochemical methods of urea removal are well developed. A short comparison of these methods is shown in Table 1. However, it has to be taken into account that the effectiveness of removal of urea depends on the given variant a method. The best effectiveness was achieved by hydrolysis of urea (ca 94 %).

At present, hydrolysis of urea is a well-known and successful method for urea removal. Nevertheless, this process proceeds at high temperatures and under high pressure, which limits its application to the industrial scale. Although, attempts of reducing the cost of the process, mainly by decreasing both the temperature and pressure, have been undertaken, the problems associated with this issue are still unsolved. In turn, the enzymatic decomposition of urea seems to be a very effective method. In comparison to the uncatalyzed urea hydrolysis, the rate of the process can be even 1014 times faster [22]. However, a major problem concerning this approach is the stability of the enzyme. This issue is attempted to be solved by immobilization of the urease onto suitable carriers. Removal of urea by biological methods is often complicated due to the use of different strains of bacteria able to decompose urea in a series of biofilters. Moreover, the biological treatment of urea-containing wastes is not a selective method, since the strains of microbes are usually capable of metabolizing more than one substance at the time (not necessarily a drawback). Therefore, it is usually applied in the wastewater treatment. The use of strong

oxidizing agents to be significant it would be required to find an oxidant, capable of decomposing urea to nontoxic products (favorably—gases). Furthermore, the oxidant itself should be cheap, nontoxic, and reduce to a form which would not cause harm to the environment. It would seem that removal of urea by adsorbents is still an evolving and future-proof method. However, the issue optimization of both adsorbent chemistry and structure as well as process conditions for urea removal is still under investigation. Finally, the catalytic decomposition of urea is an expensive method, due to the high cost of sufficiently active catalysts and needs more work in terms of determination of optimum process conditions for maximum efficiency.

The most advanced and promising method of decomposition of urea that can be used in industrial scale seems to be hydrolysis of urea combined with the use of enzymes to increase its efficiency. However, each method has its advantages and disadvantages and to select the appropriate one, it has to be taken into account both the concentration and the amount of the waste water to be purified, the required purity of the effluent as well the cost of the process.

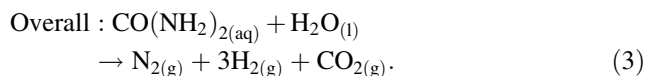
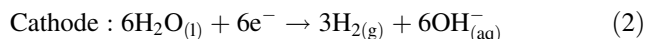
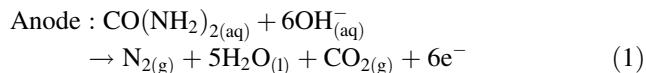
## 3 Electrochemical oxidation of urea

The most straight-forward method of electrochemical waste removal is to subject the waste to anodic treatment, whereby the molecule to be decomposed is destroyed during the oxidation reaction due to the subtraction of one or more electrons from its structure, followed by reactions

**Table 1** Comparison between different nonelectrochemical methods of urea removal from aqueous solutions

Method of decomposition of urea	General principle	Process parameters	Decomposition products	References
Hydrolysis	Application of high temperature and pressure	Temperature (120–236 °C), pressure (1.7–3.7 MPa) and residence time	Ammonia and carbon dioxide	[1, 2]
Enzymatic decomposition	Addition of an enzyme (urease)	Immobilization or modification of the enzyme and pH (6.5–7.5)	Ammonia and carbon dioxide	[12–29]
Biological treatment	Flow through biofilters	Bacterial strain, pH (7.0–9.0), flowrate (e.g., 100 L h <sup>-1</sup> )	Nitrogen or nitrite ions and carbon dioxide (depends on the strain)	[1, 2, 30–32]
Decomposition by strong oxidants	Addition of a strong oxidizing agent	Oxidant (ozone, sodium chlorate, metal ions), pH	Nitrate ions and carbon dioxide or nitrogen and carbon dioxide (depends on the oxidant)	[1, 33, 34]
Adsorption	Flow through a bed or addition of a sorbent	Sorbent (activated carbon, zeolites, ion-exchange resins or silica), flow rate	n/a	[35–39]
Catalytic decomposition	Addition of a catalyst	Catalyst (Pt, Al <sub>2</sub> O <sub>3</sub> , TiO <sub>2</sub> ), temperature (RT–90 °C)	Nitrate ions, nitrogen, carbon dioxide, ammonia, and possibly NO <sub>x</sub> (depends on the catalyst and conditions)	[40–44]

in the bulk of solution (direct electrochemical oxidation, or electro-oxidation). Similarly, the pollutant can be removed from the solution by a chemical attack on the reactive species generated at the electrodes (indirect electrochemical oxidation). The electro-oxidation of urea in its simplest form should occur according to the following electrode half-reactions [1, 45, 46]:

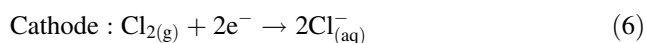
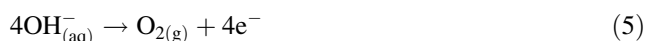


The first obvious advantage of the electrochemical approach to urea decomposition is the fact that the overall electrochemical process produces only gaseous products that are not harmful to the environment (perhaps with the exception to  $\text{CO}_2$ ). However, the exact mechanism of urea decomposition on various electrode materials may differ, and the effluent from the treatment may contain some intermediate products. In recent years, considerable investigative scientific effort has been put forth to test different compositions of solutions and electrode materials as well as their influences on the effectiveness of urea electro-oxidation.

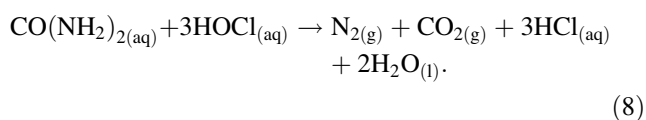
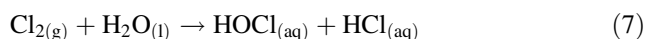
### 3.1 Solutions used in electrochemical oxidation of urea

In many older works concerning urea electro-oxidation, the solution used in this process contained chloride ions. Due to their presence, additional reactions along with reactions (1) and (2) may take place at the electrodes and in bulk of the solution [1, 47 and references therein]:

Anode:

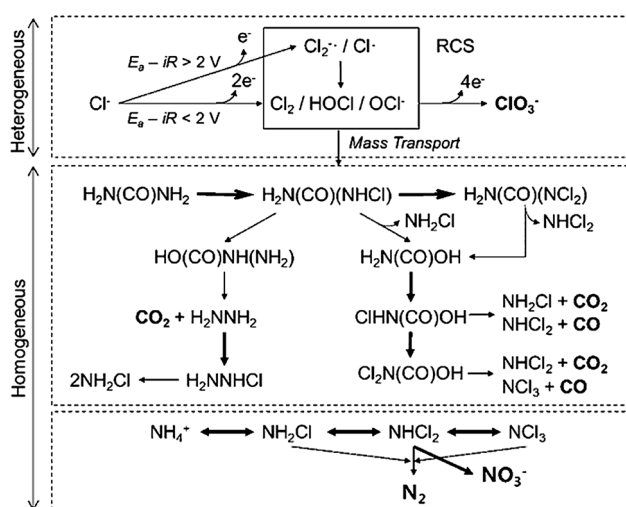


Bulk of the solution:



Apparently, from the Eqs. (4), (6), (7), and (8), it can be deduced that it is best to separate the anode and cathode compartments to ensure that the reduction of  $\text{Cl}_2$  does not occur at the cathode, which would be a waste of energy.

Both the direct and indirect routes of urea electro-oxidation lead to the generation of nitrogen and carbon dioxide as major oxidation products. Chlorine generated at the anode is termed “active chlorine” or reactive chlorine species (RCS), because it can undergo further reactions leading to the destruction of organic species, most notably, when sodium hypochlorite is formed [48–50]. The chlorine-mediated destruction of urea was studied as early as the 1970s [47 and references therein]. Early attempts were based on electrolytic systems with Pt electrodes under potentiostatic polarization. A number of products were found in the reaction mixtures depending on the process conditions, i.e.,  $\text{CO}_2$ ,  $\text{N}_2$ ,  $\text{H}_2$ ,  $\text{CNO}^-$ ,  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ ,  $[\text{N}_2\text{O}_2]^-$ ,  $\text{N}_2\text{O}$ ,  $\text{NO}_2$  and urea cation radical— $\text{NH}_2\text{CONH}_2^{*+}$ . Urea was observed to undergo decomposition mainly to  $\text{CO}_2$  and  $\text{N}_2$  when the anodic potential was above 1.7 V versus NHE in an acidic environment [51, 52]; meanwhile, at potentials below 1.6 versus NHE, urea was majorly oxidized by hydroxyl radicals  $\text{OH}^*$ , and the products of this reaction remain in the solution [53]. It was shown that at high potentials in a phosphate buffer solution, the rate-limiting step for urea decomposition was the direct route according to Eq. (1), and the rate did not depend on the pH of the solution [54]. In neutral solutions (also at high anodic potentials), urea was decomposed mainly to nitrite and nitrate ions and resulted in  $\text{CO}_2$  generation [55]. When the process was run at relatively low potentials, a urea cation radical formed, which can react further to form oligomers and polymers [55]. The rate and effectiveness of urea decomposition increased with the acidity of the solution and with the process temperature [53, 56]. When the process was realized on a surface of  $\text{RuO}_2\text{--TiO}_2$ -coated titanium electrode, urea decomposed into  $\text{CO}_2$  and  $\text{N}_2$  with the formation of chlorourea and subsequently dichlorourea [57]. Hernlem studied an electrolytic system in which a urea-contaminated solution was treated with the addition of a chloride species [47]. The rate of urea removal was higher at higher temperatures (RT to 34.5 °C), and the removal efficiency was very high, leaving only residual nitrogen in the form of nitrate ions. A more contemporary study of the mechanism of chloride-mediated destruction of urea was reported by Cho et al. [58]. The proposed reaction scheme is shown in Fig. 2. In the first step, chloride ions are undergoing electrode reactions to form either gaseous chlorine or chlorine radicals at potentials higher or lower than 2 V versus NHE, respectively. It is possible to produce perchlorate ions through another oxidation reaction of  $\text{OCl}^-$  ions on the electrode. Then, urea reacts with chlorate and can decompose to  $\text{CO}_2$  and to mono-, di-, or trichloroamine, by chlorinated carbamic acid or chlorinated hydrazine routes. In the last step, chloroamines undergo redox reactions producing nitrogen and nitrate ions. Simka et al. [1, 59] investigated different electrode materials and determined



**Fig. 2** Reaction pathways of urea degradation by electrochemically generated reactive chlorine species (RCS) proposed Cho et al. (Adapted with permission from [58]. Copyright (2014) American Chemical Society)

the optimum conditions for treating urea in a chloride-containing medium; meanwhile, Carlesi Jara et al. [60] studied the effect of a combined direct and indirect electro-oxidation of urea and determined the optimum chloride concentrations to minimize nitrate generation at different current densities.

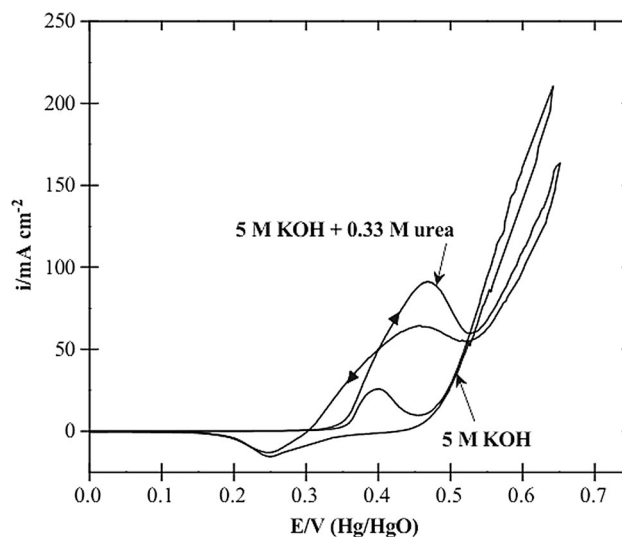
Since Botte et al. [45] proposed their approach to urea electrolysis using an inexpensive nickel catalyst, there have been many reports using variations of nickel-based anode materials for urea electro-oxidation in alkaline media, most often in potassium hydroxide. By using nickel electrodes, one can not only eliminate problematic urea waste but can also produce hydrogen at a cell voltage lower than that required for splitting water. The first reaction which can take place at the surface of Ni electrode during urea electro-oxidation is the following [45]:



The next step is anodic oxidation of urea at the modified Ni surface (1), with the simultaneous generation of hydrogen at the cathode (2). Urea electrolysis is catalyzed by the trivalent nickel ions in NiOOH, which is the reason why the total cell voltage in a electrolytic cell operating according to reactions (1–2) and (9) is equal to 0.37 V which is notably less than 1.23 V, which is a requirement for commencing the water splitting reaction. So far, there have been only a few reviews and theoretical deliberations published concerning urea as a potential hydrogen and energy carrier [61, 62]. In these papers, it is argued that urea is much more convenient to store and transport than hydrogen; however, there is a

need for the on-site conversion of urea to hydrogen, and the use of an electro-catalytic process at nickel-based anodes seems to be a very promising alternative for this purpose.

The mechanism for the electro-oxidation of urea on nickel catalysts in an alkaline environment was investigated by Vedharathinam et al. [63–66]. The oxidation process is usually studied with the use of cyclic voltammograms (CV), such as the one shown in Fig. 3. It can be seen that during a forward scan in a urea-free alkaline solution, nickel surface undergoes anodic reaction, at the onset potential of ca. 0.35 V versus Hg/HgO, which is ascribed to  $\text{Ni}^{2+}/\text{Ni}^{3+}$  redox couple. Then, after reaching an oxidation peak at 0.39 V versus Hg/HgO, the oxygen evolution commences with the sharp increase in current density up to 0.65 V versus Hg/HgO. During the reverse scan, a reduction peak can be observed at 0.26 V versus Hg/HgO, corresponding to the reduction of  $\text{Ni}^{3+}$ . When 0.33 M of urea is added to the solution, the voltammogram exhibits additional features. The onset potential of oxidation is shifted to ca. 0.3 V versus Hg/HgO and the oxidation peak is both slightly shifted in terms of potential (0.46 V vs. Hg/HgO) and in current density (3.6 times higher than in a urea-free solution). The onset potential for oxygen evolution is also shifted to more positive potential due electrode surface blockage by the adsorbed urea. The anodic peak is also visible during reverse scan, which is explained by the regeneration of the  $\text{Ni}^{3+}$  active sites. It



**Fig. 3** Cyclic voltammogram (CV) of Ni electrode in 5 M solution with and without the addition of 0.33 M urea (scan rate  $10 \text{ mV s}^{-1}$ ).  $\text{Ni}^{2+}/\text{Ni}^{3+}$  redox pair is visible in the CV in the absence of urea. The addition of urea results in the increase of current density with the onset at 0.35 V versus Hg/HgO, which is associated with the electro-oxidation of urea (Adapted with permission from [63]. Copyright (2012) Elsevier)



was established that, as with most of reactions of organic molecules on nickel electrodes, urea electro-oxidation can progress based on two mechanisms: direct (with electron transfer to the urea molecule catalyzed over NiOOH) and indirect [63]. The indirect mechanism involves the chemical oxidation of urea via NiOOH and catalyst electroregeneration according to reaction (9). A schematic representation of the mechanism is shown in Fig. 4. Further studies on urea electro-catalytic oxidation on Ni(OH)<sub>2</sub> were then reported [64], in which the authors deposited the Ni(OH)<sub>2</sub> catalyst layer on a roughened gold electrode. Raman spectroscopy in tandem with electrochemical techniques was used to investigate urea electrolysis on NiOOH. It was confirmed that the urea electrolysis reaction proceeds through an indirect route with the chemical oxidation of urea via NiOOH resulting in the formation of N<sub>2</sub>, H<sub>2</sub> and CO<sub>2</sub>. An EC (electrochemical-chemical) indirect oxidation mechanism of urea over Ni in alkaline medium was confirmed further from potential oscillations experiments [65] and X-ray diffraction studies [66]. EIS and chronoamperometric study of electro-oxidation in a solution that contained 1 M KOH and 0.1 M urea was performed by Guo et al. [67]. The authors confirmed direct/indirect mechanism of the process and pointed that the low stability of the catalyst can be attributed to the electrocatalyst poisoning by CO<sub>2</sub>.

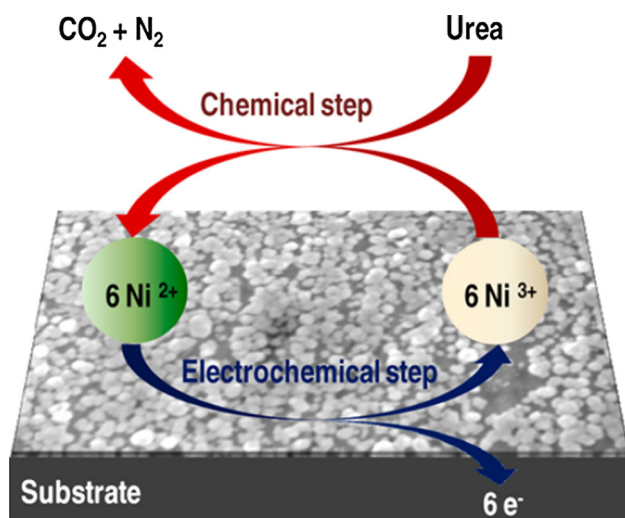
Zhang et al. [68] studied the effect of alkali metal cations on the catalytic activity of NiOOH electro-catalyst of the urea electro-catalyst. It was demonstrated that the activity was increasing in the sequence Li<sup>+</sup>–Na<sup>+</sup>–K<sup>+</sup>. The authors explained this by surface blockage ability of the

cations to form OH–M<sup>+</sup>(H<sub>2</sub>O)<sub>x</sub> on the surface of Ni electrodes.

An alternative approach was investigated by King and Botte [69], in which a poly(acrylic acid)/KOH gel electrolyte was used as a replacement for the universally applied aqueous KOH solution. This approach could be applied as the electrolytic system in portable devices. The authors showed that the most promising material was a gel composed of 8 M KOH and 15 wt% poly(acrylic acid), which was only marginally worse than a typical aqueous KOH system.

### 3.2 Anode material

In the modern literature, the most attention has been devoted to nickel-based electro-catalysts; however, the first attempts to decompose urea from urine were realized with the use of noble metals, such as platinum [70, 71] and ruthenium in the form of ruthenium-titanium oxide system. Wright et al. [57] investigated the decomposition of urea from artificial kidney dialysate in solutions with different amounts of urea and sodium chloride using RuO<sub>2</sub>–SnO<sub>2</sub>–TiO<sub>2</sub> electrodes. The urea was decomposed by anodically generated active chlorine and the major products of the electrolysis were N<sub>2</sub>, CO<sub>2</sub>, H<sub>2</sub>, and O<sub>2</sub>. However, at high urea concentrations (30 g dm<sup>–3</sup>) and low sodium chloride concentrations (0.58–5.84 g dm<sup>–3</sup>), the decomposition proceeded through a direct electrochemical route. Amstutz et al. [72] studied the effectiveness of the electrodes prepared from Ti/IrO<sub>2</sub> (1 mg IrO<sub>2</sub> cm<sup>–2</sup> Ti) system, prepared by thermal decomposition, in the process of NH<sub>3</sub> and urea removal from fresh or store urine. The removal of nitrogen species from the fresh solution was found to be more effective and the process was realized through the chlorine-mediated oxidation. Meanwhile, in the case of the stored urine solution, carbonates derived from the hydrolysis of urea inhibited the ammonia oxidation reaction. Cataldo Hernández et al. [73] conducted research on the removal of urea from aqueous solutions using different anodes, such as Pt, TiO<sub>2</sub>–RuO<sub>2</sub>, boron-doped diamond (BDD), and antimony-doped tin oxide. The results show that the complete removal of urea may be obtained only with the use of BDDs. In the case of Pt, TiO<sub>2</sub>–RuO<sub>2</sub>, and antimony-doped tin oxide, the urea decomposition was only partial and urea removal efficiency for these electrodes was 75, 60, and 85 %, respectively. The BDDs and Ti/IrO<sub>2</sub> electrodes were also investigated by Li et al. [74]. It was found that the oxidation of urea over BDD electrodes was complete and the products were inorganic ions, such as ClO<sub>4</sub><sup>–</sup> and NO<sub>3</sub><sup>–</sup> ions, while on Ti/IrO<sub>2</sub> electrodes, urea was oxidized to NO<sub>2</sub><sup>–</sup> ions and toxic N<sub>2</sub>H<sub>4</sub>. The incomplete oxidation of urea was probably caused by relatively low oxidizing activity of IrO<sub>2</sub> on the surface of the electrode. The effect



**Fig. 4** Graphical representation of the two-step mechanism of urea decomposition in alkaline medium over Ni electro-catalyst surface (Adapted with permission from [65]. Copyright (2014) American Chemical Society)

of the composition of Ti-based systems (Ti/Pt, Ti/(Pt–Ir), Ti/RuO<sub>2</sub>, Ti/(RuO<sub>2</sub>–TiO<sub>2</sub>), Ti/(RuO<sub>2</sub>–TiO<sub>2</sub>–IrO<sub>2</sub>), Ti/(Ta<sub>2</sub>O<sub>5</sub>–IrO<sub>2</sub>)) used as anode materials on the process of electrochemical decomposition of urea was reported by Simka et al. [59]. It was found that only the Ti/(Pt–Ir) and Ti/(Ta<sub>2</sub>O<sub>5</sub>–IrO<sub>2</sub>) electrodes were sufficiently active to decompose urea to nontoxic products (N<sub>2</sub> and CO<sub>2</sub>). There have also been reports of BiO<sub>x</sub>/TiO<sub>2</sub> electrodes used in urea electro-oxidation [58], which yielded N<sub>2</sub> and CO<sub>2</sub> gases and a small amount of NO<sub>3</sub><sup>−</sup> ions as the products. Hernlem et al. [47] studied industrially oriented, dimensionally stable electrodes (DSA<sup>®</sup>) coated with RuO<sub>2</sub>. The concentration of urea in the solution used in this study was up to 750 ppm, the concentration of chloride ranged from 100 to 400 ppm with addition of 2000 ppm NaHCO<sub>3</sub>. The efficiency of urea decomposition was found to be increasing with temperature and initial urea and chloride concentrations.

Faradaic current efficiency of the process gives an estimate of the economics of the process as well as informs of any side reactions taking place at the electrode surface and it is defined as a percentile value of a ratio of the practical yield of the process to the theoretical one. Some of the anode materials for the urea oxidation were compared in terms of current efficiency in a number of different electrolyte solutions, and the results are summarized in Table 2. Generally, it seems that the current efficiency increases with the increasing anodic current density and with the amount of urea present in the electrolyte. Pt is characterized by a rather low current density (up to 25 %). Among the studied electrodes for indirect oxidation of urea by chlorate ions (or OH<sup>−</sup> radicals), the most effective are BDD and Ti/RuO<sub>2</sub> electrodes, for which the efficiency approached 100 %.

Since 2008, a wide variety of approaches, many using nanotechnology, have been undertaken to improve the electro-catalytic properties (such as high surface blockage and low current density) of nickel-based electrodes for hydrogen generation from urea. A nanostructured nickel–cobalt hydroxide Ni<sub>80</sub>Co<sub>20</sub>(OH)<sub>2</sub> electrode was investigated by Vidotti et al. [76]. It was found that the cobalt atoms increase the Ni electrode activity in comparison to cobalt-free system in 0.1 M KOH. King and Botte [77] investigated multi-metal catalysts (Pt–Ni, Pt–Ir–Ni, Rh–Ni and Ru–Ni) and their effectiveness in urea electrolysis. The paper reports that the formation of NiOOH in 1 M KOH commenced at 0.45 V and 0.50 V versus Hg/HgO for Rh–Ni and Pt–Ni (or Pt–Ir–Ni), respectively. In addition, of the three systems studied, the catalytic effect was the most pronounced for the Rh–Ni system. They determined that there is a synergistic effect from Rh–Ni electrodes favorable for the electro-catalytic oxidation of urea, with Ni contributing to a high current density (200

times in comparison with pure Ni) and Rh providing the reduction of overpotential at which the reaction commences and enhancing the stability. The urea oxidation current density obtained on this electrode was ca. 80 mA cm<sup>−2</sup>. Wang et al. on the other hand, turned again to nano-sized structures in their paper. They described Ni(OH)<sub>2</sub> exfoliated nanosheets and their performance in urea electrolysis [78]. Compared with bulk Ni(OH)<sub>2</sub>, a 170-fold increase in the current density (154 mA cm<sup>−2</sup> mg<sup>−1</sup>) during the urea electrolysis reaction was reported in the case of Ni(OH)<sub>2</sub> nanosheets. At the same time, the addition of nanosheets decreased the reaction overpotential by 100 mV. Another paper published by the same group [79] reported Ni<sub>57</sub>Co<sub>43</sub>(OH)<sub>2</sub> electrodes employed for hydrogen production from urea. These materials were prepared using a one-step electrodeposition process, and it was shown that the reaction onset potential decreased by 150 mV (at max. Co content 43 at %) with respect to pure Ni(OH)<sub>2</sub> anodes. The addition of Co to the electrodes also inhibited water electrolysis, which ensured a constant voltage over the cell and improved the efficiency of urea decomposition. In their next paper [80], the authors reported Ni(OH)<sub>2</sub> nanoribbons obtained through a hydrothermal process as electro-catalysts for urea electrolysis. Rather than 2-D nanosheets, the nanoribbons were one-dimensional. The urea oxidation current density measured for the nanoribbons was 10 times higher compared with bulk Ni(OH)<sub>2</sub> powders, which was due to their enhanced electroactive surface area (nanoribbons—2.114 cm<sup>2</sup> mg<sup>−1</sup>; powders—0.097 cm<sup>2</sup> mg<sup>−1</sup>). Next, the effect of adding Zn and Zn along with Co to the Ni(OH)<sub>2</sub> electrodes was reported [81]. Electrodes with different compositions were obtained by electrodeposition and alkaline leaching. The addition of Zn and Zn–Co decreased the onset of urea electrolysis by 40 and 80 mV, respectively and improved the faradaic efficiency of the process at a cell voltage of 1.5 V from 71 to 83 and 87 %, respectively. Miller et al. [46] investigated different Rh-loading amounts on Ni electrodes for the preparation of Rh–Ni anodes for urea electrolysis in an alkaline environment. The electro-catalytic activity of the Rh–Ni electrodes in the urea oxidation process was found to be dependent on the electrodeposition potential (which determined the Rh content in the electrodes). It was reported that the highest current density during urea oxidation was exhibited by the electrodes obtained at a potential of −0.60 V versus Ag/AgCl at an Rh loading of 0.5 mg cm<sup>−2</sup>. In the work conducted by Wang et al. [82], nanocomposites composed of electrochemically reduced graphene oxide and Ni were investigated for the urea electro-oxidation process. A synergistic behavior for graphene and nickel sheets was demonstrated with the increase in the oxidation current density (ca.

**Table 2** Effect of anode material and electrolyte composition on the current efficiency of urea decomposition

Anode materials	Compositions of electrolyte solution	Current density of oxidation ( $A\ dm^{-2}$ )	Current efficiency for urea decomposition (%)	Reference
Pt	0.019 M NaClO <sub>4</sub> + 0.033 M urea	0.5	4 <sup>a</sup>	[73]
		1	13 <sup>a</sup>	
		2	25 <sup>a</sup>	
SnO <sub>2</sub> -Sb	0.019 M NaClO <sub>4</sub> + 0.033 M urea	0.5	13 <sup>a</sup>	[73]
		1	17 <sup>a</sup>	
		2	29 <sup>a</sup>	
BDD	0.019 M NaClO <sub>4</sub> + 0.033 M urea	0.5	63 <sup>a</sup>	[73]
		1	65 <sup>a</sup>	
		2	68 <sup>a</sup>	
Ti/IrO <sub>2</sub>	Artificial human urine <sup>b</sup>	4	98.4 <sup>a</sup>	[74]
	Fresh urine <sup>c</sup>	1.5	37.9 <sup>d</sup>	[72]
Ti/(Pt-Ir) <sub>70:30</sub>	0.086 M NaCl + 0.017 M urea 0.086 M NaCl + 0.050 M urea 0.086 M NaCl + 0.166 M urea	8	31.9 <sup>e</sup>	[74] [59]
			92.4 <sup>a</sup>	
			28	
			35	
Ti/(Ta <sub>2</sub> O <sub>5</sub> -IrO <sub>2</sub> ) <sub>70:30</sub>	0.086 M NaCl + 0.017 M urea 0.086 M NaCl + 0.050 M urea 0.086 M NaCl + 0.166 M urea	8	56	[59]
			16	
			20	
BiO <sub>x</sub> /TiO <sub>2</sub>	0.05 M NaCl	0.9	49	[58]
			6 <sup>f</sup>	
			8.5 <sup>f</sup>	
			20 <sup>f</sup>	
DSA <sup>®</sup> -RuO <sub>2</sub>	0.024 M NaHCO <sub>3</sub> , 200 ppm Cl <sup>-</sup> +375 ppm urea +750 ppm urea	1.4	31.5 <sup>f</sup>	[47]
			21.4	
			24.7	

<sup>a</sup> Calculated from the amount of total organic carbon removed from the solution according to the formula proposed by Elaoud et al. [75]

<sup>b</sup> 0.200 M urea; 0.001 M uric acid; 0.004 M creatine; 0.005 M trisodium citrate; 0.054 M NaCl; 0.030 M KCl; 0.015 M NH<sub>4</sub>Cl; 0.003 M CaCl<sub>2</sub>; 0.002 M MgSO<sub>4</sub>; 0.002 M NaHCO<sub>3</sub>; 0.0001 M Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub>; 0.009 M Na<sub>2</sub>SO<sub>4</sub>; 0.0036 M NaH<sub>2</sub>PO<sub>4</sub>; 0.0004 M Na<sub>2</sub>HPO<sub>4</sub>; pH = 6.4

<sup>c</sup> 0.266 M urea; 0.0337 M NH<sub>3</sub>/NH<sub>4</sub><sup>+</sup>; 0.107 M Cl<sup>-</sup>; 0.125 M acetate; 0.184 M Na<sup>+</sup>; 0.0563 M K<sup>+</sup>; 0.00389 M Mg<sup>2+</sup>; 0.0046 M Ca<sup>2+</sup>; 0.0162 M SO<sub>4</sub><sup>2-</sup>; 0.0242 M PO<sub>4</sub><sup>3-</sup>; pH 6.1

<sup>d</sup> Oxidation to N<sub>2</sub>

<sup>e</sup> Oxidation to NO<sub>3</sub><sup>2-</sup>

<sup>f</sup> Efficiency calculated for the generation of RCS

20 mA cm<sup>-2</sup>) with respect to the pure composite components. Additionally, the surface blockage of the composite was negligible. Ding et al. described the synthesis of spinel NiCo<sub>2</sub>O<sub>4</sub> nanostructures and their performance in urea electro-oxidation [83]. The obtained materials were mesoporous and exhibited very large electroactive surface areas (ca. 1900 cm<sup>2</sup> mg<sup>-1</sup>), which was evidenced in the paper. These electrodes showed higher catalytic activity, better stability as well as lower overpotential compared to cobalt oxide electrode. The current density in

a 1 M KOH and 0.33 M urea solution was determined to 136 mA cm<sup>-2</sup> mg<sup>-1</sup> at 0.7 V versus Hg/HgO. Meanwhile, Yan et al. [84] synthesized nickel nanowires via electrodeposition on nanoporous anodic aluminum oxide (AAO) templates; the resulting materials were effective electro-catalysts for urea electrolysis. The nanowires had much larger electroactive surface area (79.1 cm<sup>2</sup> mg<sup>-1</sup>) in comparison to bulk nickel films (18.6 cm<sup>2</sup> mg<sup>-1</sup>). The current density measured during urea oxidation in a KOH solution was ca. 100 mA cm<sup>-2</sup> at 0.65 V versus Hg/HgO.

Another nano-sized material was prepared by Wang et al. [85]. Ni–WC/C nanoclusters were synthesized by sequential impregnation. The materials were composed of Ni nanoparticles that were clustered and uniformly distributed on a WC/C network. The authors hypothesized that the enhanced activity of their electro-catalyst toward urea electrolysis resulted from the synergistic effect between Ni and WC as well as the nanostructure of the composite. The addition of WC into Ni/C matrix increased the electroactive surface area (ESA) of the electrode to ( $507.3 \text{ cm}^2 \text{ mg}^{-1}$ ). The highest value of current density measured during the urea oxidation reaction was close to  $700 \text{ mA cm}^{-2} \text{ mg}^{-1}$  versus Hg/HgO (20 % Ni and 20 % WC). Another paper [86] published by the same group described a Ni catalyst supported on WC/MWCNT (multi-walled carbon nanotubes). The MWCNTs were uniformly distributed on the material, thus increasing the amount of active sites. It was observed that the addition of nanotubes to the WC/C system decreased the electron-transfer resistance of the urea electro-oxidation reaction from 12.6 to  $8.6 \Omega$ . The ESA of the material was relatively large ( $1138.7 \text{ cm}^2 \text{ mg}^{-1}$ ), while the current density measured during anodic oxidation in a 1 M KOH and 0.33 M urea solution was as high as  $46.6 \text{ mA cm}^{-2}$  versus Hg/HgO. Wu et al. [87] investigated the preparation of a Ni(OH)<sub>2</sub> monolayer of nanopillar arrays and their effectiveness in hydrogen production from urea. The material was obtained through controlled electrodeposition on a polystyrene colloidal monolayer. The authors described the high electro-catalytic activity of their material as resulting from the existence of an extensive network of interconnected walls that provided more conductive paths for electrons. Additionally, a large surface area was available for the reaction to take place and facilitated the evacuation of the generated gaseous products. The efficiency of the oxidation reaction determined for this electrode was ca. 96.7 % at the current density in a 1 M KOH and 0.33 M urea solution above  $400 \text{ mA cm}^{-2} \text{ mg}^{-1}$  at 0.7 V versus SCE. In their subsequent publication [88] the authors proposed a hydrothermal method for the preparation of mesoporous nickel oxide nanosheets, which were aligned vertically to one another. The material was deposited on a nickel framework and was tested for its electro-catalytic activity during urea electrolysis in 1 M KOH and 0.33 M urea solution (max. current density =  $700 \text{ mA cm}^{-2} \text{ mg}^{-1}$  vs. at 0.7 V SCE). Guo et al. [89] described a method for the preparation of nickel nanowire arrays (NWAs) by electrodeposition on a polycarbonate template. The electrodes exhibited lower onset potentials for urea electrolysis in an alkaline medium compared to flat Ni electrodes. The ESA of this electrode was ca. five times larger than that of the flat Ni electro-catalyst. While the current density

measured in a 5 M KOH and 0.33 M was below  $250 \text{ mA cm}^{-2}$  at 0.5 V versus Ag/AgCl. Liang et al. [90] showed that the deposition of NiMoO<sub>4</sub>·xH<sub>2</sub>O nanosheet arrays on Ni foam was beneficial in the electrolysis of urea in an alkaline medium. The obtained electrode was characterized by high catalytic activity and stability. Current density measured during electro-oxidation in a 1 M KOH and 0.33 M urea solution was  $830 \text{ mA cm}^{-2} \text{ mg}^{-1}$  at 0.5 V versus SCE, which was approximately 4.2 times higher compared to Mo-free system. The increase was due to enhancement of the ESA of the electrode. Ye et al. [91] used a carbon sponge as a template to produce a 3-D Ni electro-catalyst via an easy-to-conduct and inexpensive synthesis route. The nickel@carbon electrodes exhibited high stability during electrochemical oxidation in a 5 M NaOH and 0.1 M urea solution and the max. current density was  $290 \text{ mA cm}^{-2}$  at 0.6 V versus Ag/AgCl. Barakat et al. [92] used nickel acetate and graphene oxide in different proportions under reflux at 120 °C for 10 h, which were then calcinated to produce nickel-graphene composites. The formed composite electrodes were investigated in 1 M KOH solutions with different concentrations of urea. The highest current density of urea on the composite electrodes was obtained for the nickel acetate to graphene oxide molar ratio 1:1. The current density in a 2 M urea solution was about  $125 \text{ mA cm}^{-2}$  at 0.8 V versus Ag/AgCl. In the work conducted by Vilana et al. [93], nickel–cobalt nanowire electro-catalysts for urea electro-oxidation obtained on AAO templates were compared with pure nickel and nickel–cobalt bulk films. The nanowires exhibited good stability and activity. The experiments carried out in a 0.33 M urea solution revealed that the current density for this electro-catalyst was ca.  $55 \text{ mA cm}^{-2}$  at 0.6 V versus Hg/HgO. The authors also attempted an alternative method of preparation of Ni-based urea electro-catalysts [94]. They have synthesized Ni and Mn nanoparticles-decorated carbon nanofibers and from the obtained results it was deduced that both carbon nanofibers as well as manganese nanoparticles increased the electro-activity of nickel-based electrodes for the urea oxidation reaction. The maximum current density of urea electro-oxidation was  $300 \text{ mA cm}^{-2} \text{ g}^{-1}$  with an onset potential of 290 mV (vs. Ag/AgCl). Ni–Co with different compositions electro-catalysts were also obtained by Vilana et al. [95] through electrodeposition. In addition, it was possible to control the surface morphology of the electrodes by changing the electrodeposition parameters such as: temperature, potential or stirring speed. Surprisingly, it was found that the presence of cobalt in the electrode material obtained in this way decreased the current density during urea electro-oxidation. Chen et al. [96] investigated the ionic liquid Ni(II)-graphite composites as electrodes for electro-

oxidation of urea. They prepared composites by introducing divalent nickel into different room temperature ionic liquids and subsequent mixing with fine graphite powder. The obtained pastes were spread on screen-printed carbon electrodes. The composites were tested in a 1 M NaOH with the addition of urea. The best activity and stability in this process was exhibited by the electrode prepared from 1-butyl-1-methylpyrrolidinium bis((trifluoromethyl)sulfonyl) imide with Ni ions introduced by anodic dissolution of Ni metal. This approach shows much promise; however, the fabrication of the electrode is required to be more reliable to improve the reproducibility.

In most of the current works concentrated on preparation of Ni-based electrodes the researchers are focused on two factors: enhancing the ESA of the electrode, thus increasing the anodic current density and decreasing the oxidation potential, which would improve economics of the process. Results reported from the selected studies, showing how the anodic current density is affected by the preparation of the electrode are summarized in Table 3. There is a tendency to incorporate nano-sized structures (most notably—carbon nanomaterials) into the electrodes to increase ESA and to add Co, Zn, Mn and noble metals to affect the onset potential of urea oxidation. Unfortunately, it was demonstrated that the decrease in the onset potential is usually associated with the decrease in the measured current density.

### 3.3 Electrochemical regeneration of spent dialysate

Dialysis, as a treatment for uremia, requires a process for cleaning the spent solution (dialysate); electrochemical methods have been investigated as alternatives for this purpose in the last century [70, 97–99]. The first attempts to accomplish urea removal along with the removal of other metabolites used chloride-mediated electro-oxidation [99]. Ginval'd et al. described specific concepts for the design of artificial kidneys coupled with an electrochemical dialysate regenerator system [8, 100–102]. According to a review of electrochemical methods for urea removal in portable dialysis devices written by Wester et al. [103], chloride-based electrolytes were still taken into consideration. In this work, different electrode materials (Pt, Ru, and graphite) were studied. Graphite was identified as the most promising material for the removal of urea from blood in a wearable dialysis device.

In light of recent progress being made in the development of Ni-based electro-catalysts, it would be interesting to see how the aforementioned electrodes compare with the noble metal- or graphite-based systems. However, the dialysate would have to be alkalinized prior to the process.

### 3.4 Urea-based fuel cells

Urea can be utilized with direct urine fuel cells (DUFs) where it acts as a power source. The theoretical open-circuit voltage (OCV) of DUFs is calculated to be 1.146 V [104].

The diagram showing feed and output streams in the fuel is depicted in Fig. 5. This voltage is only slightly lower than that from  $H_2/O_2$  fuel cells making DUFs an attractive option because of the combined waste utilization and power generation. Lan et al. [104] in their work experimented with proton exchange membrane fuel cells (PEMFCs) with different electrode materials (both electrodes from Pt/C as well as Ni/C anodes combined with either Ag/C or  $MnO_2/C$  cathodes) and different concentrations of urea (1–7 M), including a commercially available urea solution—AdBlue<sup>®</sup> (32.5 wt% urea aqueous solution). Conventional alkaline fuel cells with 6 M KOH are not suitable for this type of system due to the absorption of  $CO_2$  in KOH, which poses a problem that PEMFCs aim to solve using wet air as an oxidant. The maximum power density and OCV for these fuel cells decrease with increasing dilution of both urea and AdBlue<sup>®</sup> solutions. The best results were obtained for the Ni/C– $MnO_2/C$  configuration fueled by either 1 M urea solution of 100 % AdBlue<sup>®</sup> (maximum power density =  $1.7 \text{ mW cm}^{-2}$ ). The same authors also tried to employ commercial and nano-sized nickel electro-catalyst in the construction of DUFs with the use of urea and urine solutions, Nano-sized nickel was found to be more effective than flat nickel electrodes. Among the tested configuration, the best results were obtained for the nano-sized nickel electrode with a 1 M urea solution (maximum power density =  $14.2 \text{ mW cm}^{-2}$ ). At the same time, it was found that urine-based fuel cell operated at 60 °C achieved a maximum power density of  $4.23 \text{ mW cm}^{-2}$ . According to authors, this would be enough to justify a real-life application [105]. AdBlue<sup>®</sup> was also investigated by Cinti and Desideri [106] as a potential fuel for solid oxide fuel cells. Energy efficiencies up to 40 % were achieved, and the system was characterized by a high power density, which shows good promise when combined with the broad availability of AdBlue<sup>®</sup>. In the investigations of Xu et al. [107], a power density of  $0.19 \text{ mW cm}^{-2}$  with an OCV of 0.38 V at 60 °C was obtained for NiCo/C bimetallic nanoparticle DUFs; meanwhile, Serban et al. [108] described a urea/hydrogen peroxide fuel cell. The latter cell having twin Pt/C electrodes or Ni/MWCNTs–Pt/C electrodes exhibited maximum power densities of  $0.03 \text{ mW cm}^{-2}$  (at OCV = 0.4 V) and  $0.05 \text{ mW cm}^{-2}$  (at OCV = 0.25 V), respectively. Nagao et al. [109] investigated a wide variety of materials (Pt/C, Ru/C, Ni/C, Pd/C, and Rh/C) in DUFs at 300 °C. The ruthenium catalyst was identified as the most active

**Table 3** Comparison of properties of Ni-based electro-catalysts extracted from cyclic voltammograms in alkaline media

Anode materials	Compositions of electrolyte solution	Current density of oxidation (A dm <sup>-2</sup> )	Oxidation potential (V vs. Hg/HgO)	Electroactive surface area (m <sup>2</sup> g <sup>-1</sup> )	Reference
Ni	5 M KOH + 0.33 M urea	8.5	0.55	–	[45]
		9	0.46	–	[63]
		2.9	0.52	–	[65]
	5 M KOH + 1 M urea	0.5	0.60	–	[66]
Pt–Ni	1 M KOH + 0.33 M urea	0.4	0.70	–	[77]
Pt–Ir–Ni		0.52	0.70	–	
Ru–Ni		0.72	0.70	–	
Rh–Ni	1 M KOH + 0.33 M urea	0.82	0.70	–	[77]
	5 M KOH + 0.33 M urea	10	0.55	–	[46]
Ni–Zn	5 M KOH + 0.33 M urea	0.67	0.52	–	[81]
Ni–Zn–Co		0.24	0.50	–	
Ni <sub>x</sub> Co <sub>y</sub> (OH) <sub>2</sub>	5 M KOH + 0.33 M urea	(70:30) 9.5 (57:43) 4.7 (27:73) 3.4 (11:89) 0.9 (1:0-fcc) 0.09 (7:3-fcc) 0.15 (7:3-hcp) 0.20 (5:5-fcc) 0.32 (0:1-fcc) 0.85	0.60	–	[79]
Co <sub>x</sub> Ni <sub>y</sub>	0.5 M NaOH + 0.1 M urea				[95]
NiCo <sub>2</sub> O <sub>4</sub>	1 M KOH + 0.33 M urea	13.5	0.70	–	[83]
Ni(OH) <sub>2</sub> /Au	5 M KOH + 1 M urea	20	0.58	–	[64]
Ni(OH) <sub>2</sub> nanosheets	5 M KOH + 0.33 M urea	15 (mg <sup>-1</sup> )	0.45	–	[78]
Ni(OH) <sub>2</sub> nanoribbons	5 M KOH + 0.33 M urea	0.2 (mg <sup>-1</sup> )	0.65	54.9	[81]
Ni(OH) <sub>2</sub> cup-like pore arrays	1 M KOH + 0.33 M urea	41 (mg <sup>-1</sup> )	0.80	–	[87]
Ni–Co nanowires	1 M KOH + 0.33 M urea	5.5	0.60	–	[93]
Ni/C sponge	1 M NaOH + 0.1 M urea	24	0.65	–	[92]
Ionic liquid Ni(II)-graphite	1 M NaOH + 0.01 M urea	0.45	0.60	–	[96]
Ni/graphene	1 M KOH + 0.5 M urea	13.7	0.80	–	[92]
ERGO–Ni	1 M KOH + 0.33 M urea	3.5	0.70	–	[82]
Ni–WC/C	1 M KOH + 0.33 M urea	50 (mg <sup>-1</sup> )	0.52	50.7	[85]
Ni–WC/MWCNT	1 M KOH + 0.33 M urea	4.75	0.55	113.9	[86]
Ni and Mn nanoparticles-decorated carbon nanofibers	1 M KOH + 0.5 M urea	27.5 (mg <sup>-1</sup> )	0.60	–	[94]
Nickel nanowires/AAO	1 M KOH + 0.33 M urea	10	0.65	7.9	[84]

Table 3 continued

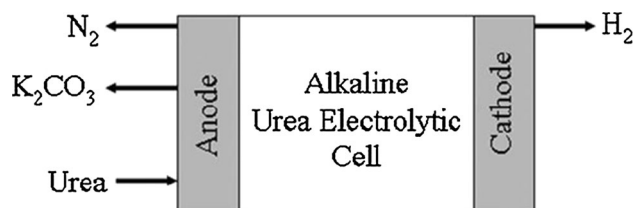
Anode materials	Compositions of electrolyte solution	Current density of oxidation (A dm <sup>-2</sup> )	Oxidation potential (V vs. Hg/HgO)	Electroactive surface area (m <sup>2</sup> g <sup>-1</sup> )	Reference
OM-NiO nanosheets/ Ni foam	1 M KOH + 0.33 M urea	70 (mg <sup>-1</sup> )	0.80	–	[88]
Ni nanowire arrays	5 M KOH + 0.33 M urea	24.5	0.65	–	[89]
NiMoO <sub>4</sub> ·H <sub>2</sub> O nanosheet arrays/Ni foam	1 M KOH + 0.33 M urea	85 (mg <sup>-1</sup> )	0.60	102	[90]

among the tested materials, with a maximum power density of 26.5 mW cm<sup>-2</sup>. An interesting approach was reported by Xu et al. [110]. The authors investigated a fuel cell in which urea acted as fuel and Cr(VI) served as an oxidant with a nano-sized nickel electrode. When the neat urine was used as an anolyte and catholyte composed of 50 mg dm<sup>-3</sup> Cr(VI) in 0.25 M H<sub>2</sub>SO<sub>4</sub>, the maximum power density at OCV of 1.3 V was 0.34 mW cm<sup>-2</sup>. In course of the process, 90 % of Cr(VI) was removed from the solution and 78 % of urea was oxidized. In two works by Guo et al. [111, 112], different forms of nickel–cobalt electro-catalysts (3D foams and NWAs) were investigated. The authors investigated the effectiveness of the electrodes in urine-hydrogen peroxide fuel cells. A maximum power density of 31.5 mW cm<sup>-2</sup> was measured at an OCV of 0.83 V for the 3D Ni-Co foam fuel cell operated at 70 °C on 7 M KOH + 0.5 M urea solution. The Ni-Co NWAs-based fuel cell reached maximum power density of 7.4 mW cm<sup>-2</sup> at an OCV of 0.92 V at RT operated on 9 M KOH + 0.33 M urea anolyte and H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O<sub>2</sub> catholyte.

As it can be seen, the efforts of the researchers are focused on improving the maximum power density of the fuel cells, with the possibly low OCV. A breakthrough in this field was possible due to contributions of Ni-based electrodes and the application of nano-structural electrodes which improve the power density of the cell and reduce the cost of the apparatus by eliminating the necessity of the use of precious metals. It seems that a steady progress is being made in this area and we may expect a commercial application of DUFCs in near future.

### 3.5 Bio-electro-oxidation of urea

The combination of urease and electrochemical oxidation can be termed bio-electro-oxidation. Watanabe et al. [113] investigated the mechanism of the electrochemical oxidation of urea with urease on a glassy carbon electrode. The electrode surface was aminated during cyclic voltammetry runs. Urease decomposed urea to NH<sub>3</sub> and carbamic acid, which then either decomposed to ammonia and carbon dioxide or underwent further electrochemical transformations to eventually form nitrogen. Laurinavicius et al.



**Fig. 5** Scheme of direct urine fuel cell (DUFC) proposed by Botte in 2008 (Reproduced from Ref. [45] with permission from the Royal Society of Chemistry)

published research in which the products of the enzymatic decomposition of urea with urease were treated by electrochemical oxidation using a carbon black electrode [114]. The proposed system was developed to serve as a urea biosensor. Urea bio-electro-oxidation was also considered as a possible method for the treatment of urine at space stations [115]. In the first step, urea is converted to ammonia in a bioreactor based on urease. Then, the electrochemical cell utilizes ammonia as fuel and converts it to power. The proposed system removes >80 % of the TOC and converts ca. 86 % of urea to ammonia.

Microbial fuel cells (MFCs) are another approach to bio-electrochemical urea decomposition. In their basic form, MFCs utilize microbial digestion to degrade organic waste, driving electrons into external circuits and generating power. An extensive study of single-chamber MFCs was reported by Santaro et al. [116, 117], where raw human urine was treated over a 45-day period. It was shown that the electrode material (noble metal or not) is significant only during the initial stages of the process and becomes less important when the process is prolonged. The chemical oxygen demand in urine was effectively degraded in single-chamber MFCs, with longer cycles leading to better removal efficiencies. Then they proved that a nonnoble cathode has a similar performance to Pt-based cathode. Haddadi et al. [118] have shown that the addition of urea to MFCs can help maintain a neutral pH, because urea hydrolysis liberates ammonia, which counteracts the acidification process. The experiments were conducted in microbial electrochemical cells with cation and anion exchange membranes in batch mode and were intended for ammonium recovery (61 %). You et al. [119] have shown that urine can be treated in MFCs to produce energy and recover struvite, which can then be used as a fertilizer.

#### 4 Summary

A review of methods of urea removal from aqueous solution was described in the present work. It can be noticed that electrochemical methods are not outdated. On the contrary, novel approaches are being developed, especially those connected with concurrent urea waste treatment and energy generation. This is owed to the trend of transition from conventional fossil fuels such as carbon and oil to alternatives with comparable energy density. Urea is one of the most abundant wastes on earth; therefore, effective and green technologies are still investigated to turn it from a problematic pollutant to an attractive economical commodity.

Unless there will be a breakthrough in the area of anode materials, it is probable that researchers will concentrate on modification of Ni-based electrodes to increase their

stability and improve the obtained anodic current densities, with lowered onset potential for urea oxidation reaction at the same time. This approach will improve the potential of this material for electrochemical method of urea removal and improve the power density of urea-based fuel cells. In light of using urine or urea-containing wastewater for power generation, industrial scale electrochemical decomposition of urea-contaminated waters might be economically feasible in the future and take the place of high temperature/pressure hydrolysis.

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