Recent advances and challenges in management of urea wastewater: A mini review

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Abstract. Treating the wastewater with high level of urea and ammonia-nitrogen is one of the problems faced by different plants in the world. The basic methods of urea removal of wastewater streams are electrochemical oxidation, biological treatment, adsorption and hydrolysis using thermal treatment or enzymes and decomposition with the aid of catalyst, strong oxidant. This work reviewed recent of different nanosized and nanostructured particles in different techniques for urea removal from wastewater and the challenges for treatments to draw the attention of researchers and scientists toward novel research ideas in this area.

1. Introduction

Urea is abundant in the environment due to its presence as a major product in human and industrial plants effluents. In addition to enormous amount of urea in different industrial plants, huge amounts are leaching from agro-breeding farms and fields (figure 1). The major problem of urea as pollutants is its presence in toxic form and even if it hydrolyzes, it forms another toxic pollutant (ammonia gas). The later will decompose to yield additional pollutants such as NOx (x=1, 2 and 3), finally, these nitrogen oxides cause eutrophication. Most of the treatment methods are still under developing or being applied in small scale. These methods are mainly electrochemical oxidation (EO), decomposition (using catalysts, strong oxidants, biological film, adsorption and hydrolysis (with or without the aid of enzyme). Because urea is cheap, widely available, non-toxic, stable, it can be transported and stored easily, urea, was investigated as a source of hydrogen in fuel cell [1]. Ewelina Urban et al. reviewed techniques used for urea removal from wastewater [2]. Ljubica Matijašević et al. suggested some preferable modifications in the current urea industrial plants. They analyzed status of the current plant and developed a computer simulation based on the real process parameters. Finally, a scenario for minimizing the negative impact on the environment was proposed [3]. However, due to the rapid modernization, water shortage, the urea should be managed efficiently in the wastewater. Several researches investigated urea management via different systems from lab scale to full scale. Figure 1 concludes the main processes and products of urea management.
2. Methods of urea management in wastewater

2.1. Electrochemical oxidation

Electrochemical oxidation of urea involves destroying/decomposing of urea in oxidation reaction where it losses one or more electrons followed by reaction in solution and transformation to another compound according to the following reactions [4],[5]:

\[
\begin{align*}
\text{Anode:} & \quad \text{CO}(\text{NH}_2)_2+6\text{OH}^- & \rightarrow & \quad \text{N}_2+5\text{H}_2\text{O}+\text{CO}_2+6\text{e}^- \\
\text{Cathode:} & \quad 6\text{H}_2\text{O}+6\text{e}^- & \rightarrow & \quad 3\text{H}_2+6\text{OH}^- \\
\text{The overall reaction:} & \quad \text{CO} (\text{NH}_2)_2+\text{H}_2\text{O} & \rightarrow & \quad \text{N}_2+3\text{H}_2+\text{CO}_2
\end{align*}
\]

Bolzàn and Iwasita investigated electrochemical oxidation of urea on Pt electrode. They detected production of nitrogen oxides, CO\textsubscript{2} and H\textsubscript{2} [6]. Hernlem (2005) investigated decomposition of urea (up to 750 mg/l) in electrolysis unit. Formation of byproducts, effect of temperature and initial concentration on urea conversion were studied [7]. A lot of studies have suggested modifications and have investigated different techniques and catalysts. Nickel and nickel based materials have drawn the attention of numerous researchers (figure 2). In the next sections, some of these investigations.

2.1.1. Nickel based catalysts.

Nickel was preferred as electrode for urea removal due it its highly boosting of the interfacial electroactive sites, charging transfer rates for urea electro-oxidation [9], and high catalytic activity [10]. Wang, et al. synthesized electro-catalysts based on nickel hydroxide nano-sheets for urea EO. This electrode decreases the over potential and enhance the current density [11]. The nickel catalyst was also suggested by King and Botte for the oxidation of urea. They introduced Rh metal to the catalysts. The results showed that the later reduces both the surface blockage and the over potential for urea EO, increases catalyst stability and improves the current density [12]. Yan et al.
compared binary and tertiary composites based on Ni. They found that the tertiary one (ZnCo@Ni) lowered the urea onset potentials by 80 mV [13].

Ding et al. compared mesoporous electrode (NiCo$_2$O$_4$) with cobalt oxide. They showed that the former is much stable and more active than the later. This electrode delivered 136 mA cm$^{-2}$ mg$^{-1}$ of current density and 0.7 V of oxidation potential when the initial concentration of urea was 0.33 M [9]. A screen printed electrode for urea EO was modified using multi-walled carbon nanotubes-nickel oxide nanoparticles composite [14]. Ewelina Urbanczyk et al. investigated three electrodes as EO cell anodes (Ni, Ni-Pt and Ti-Pt electrodes). Based on their results, the sintered Ni-Pt electrodes were more active than others [15]. Ye et al. synthesized low cost Ni@carbon sponge electrode (figure 3). The produced electrode was characterized and investigated for urea oxidation in alkaline solution. The electrode achieved an onset oxidation potential of 0.24 V, the peak current density in NaOH (5 M) and urea (0.1 M) solutions was 0.29 A/cm$^2$. They attributed these promising results to the highly porous network (0.40%) and the presence of enormous Ni active sites. The alkaline medium improved the electro-catalytic activity of the electrode due to the increase in current density of the anode > 0.35 V (vs. Ag/AgCl) [16]. Szypkowicz (2000) studied EO of urea wastewater from texture plant. The best EO results were obtained with Ti/Pt@Ir anode. They attributed the good results of the electrode catalytic activity to the Cl$^-$ electro-oxidation into Cl$_2$ [17].

Figure 3. Synthesis of Ni@carbon sponge electrode [16].

Nanotechnology have been used to modify the catalyst via increasing the specific surface area (internal and external) (figure 4). They used the doping technique to introduce active/new surface functional groups to the catalyst. Guo et al. prepared Ni nanowire electrode using electrodeposition technique. They tested the efficiency of this electrode for EO of ammonia using electrochemical impedance spectroscopy, cyclic voltammetry and chronocoulometry tests. The onset oxidation potential of this electrode vs. Ag/AgCl was 0.25 V and peak current density and urea in KOH (5M) were 0.16 A/cm$^2$ and 0.33 M, respectively [18]. Yang et al. (2019) investigated the effect of nanorods form of Ni/MO oxide on urea oxidation. They discovered that the ratio of Ni and MO oxides play a significant role in the overall process efficiency. A good urea catalytic stability was recorded at current density 0.096 A/cm$^2$ [19].
Figure 4. A schematic illustration of nickel hydroxide electrode for enhanced urea electrolysis [20].

Barakat et al. (2017) used doping technique to introduce N₂ to nanofibers of Ni-C. Then, they calcinated the nanofiber under temperature 750 °C in the presence of a noble gas (Ar). The proposed technique saved the energy required for electrolysis by saving significantly the urea onset EO potential [21]. Tammam et al. used nickel oxide nanoparticles to modify carbon electrode, the electrode was tested for EO of urea in alkaline medium. Also, it was found that the reticulated structure is much better than the planar and the maximum conversion is dependent on the loading extent [22]. Tungsten was suggested as a co-catalyst to increase the activity of Ni/C nanostructures in the urea EO, the nanofibers that containing 35 wt% tungsten showed the best performance (figure 5).

Figure 5. Influence of tungsten content on the electro oxidation activity of the NiW-C nanofibers for a 1.0 M urea EO in solution of KOH (1 M) [23].

Zeng et al. prepared NiCo@LDH as an efficient and highly durable catalyst for urea EO. They concluded that the spacing in the LDH interlayer structure played a control role for the EO of urea [24]. Li et al. developed Ni/N@graphene as a catalyst for urea EO. After modification with CeO₂, the oxidation current density of the catalyst was doubled. Introducing CeO₂ to the catalyst improved its activity, by improvement the pore volume and structure. This resulting in increase in NiO% and improve in catalyst mass transfer [25]. Alajami et al. prepared NiMn-incorporated carbon nanofibers
and studied the composition, morphology, and synthesis-temperature on EO of urea (2M). The results represented that the best values of current density and onset potential were achieved using nanofibers of NiMn@carbon, with manganese acetate (10 wt%) and calcination temperature 850 °C [26]. Rahimpour et al. proposed a membrane for decomposition of NH3 on Ni–Al2O3 catalyst. They suggested that more than 4500 tons of hydrogen can be produced yearly from the urea plant. They modeled the treatment loop of urea in wastewater. They concluded that any increase in temperature or pressure and membrane reactor diameter yielded high urea management. And the countercurrent flow was better than co-current one [27].

2.1.2. Other catalysts. Shuguang Shen et al. investigated different alumina catalysts loaded on ceramic particles in a fixed bed reactor to hydrolysis urea in wastewater. The order of activity was $\alpha$-Al2O3<$\gamma$-Al2O3<$\eta$-Al2O3. The results proved that the alumina catalysts depend mainly on temperature and it may depend also on the basic strength. The $\eta$-Al2O3 showed the best results concerned with hydrolysis temperature and the concentration of urea in the effluent (4.96 mg/l). They concluded that $\eta$-Al2O3 is a promising catalyst to replace current hydrolysis process [28]. Hernlem applied current (0.6- 2.5 A) using oxide-coated titanium electrodes in a bench scale electrolysis device for treating urea in stimulated solution. Increasing the temperature or even the urea initial concentrations increased the energy efficiency of urea decomposition [7]. Amstutz et al. (2012) compared EO of fresh and old urea synthetic solution using IrO2 anodes. It was found that urea could be managed efficiently in fresh solution in contrast to the old solution where the carbonate resulted from hydrolysis of urea by the bacteria hinder ammonia removal [29]. Mahmoud et al. studied graphite electrodes bench-scale electrochemical cell for decomposition of urea. They attributed the increasing in urea removal rates (0.78 g/h) to the increase in current density and the decrease in the current efficiency to 82%. In another study, graphite electrode was used for oxidation of urea (initial concentration 50-100 mg/l), they studied different parameters like energy consumptions, current efficiency and the rate of urea removal. They recorded a proportional relationship between the rate at which urea was removed and the current density rate, also the increasing in power consuming. They reached a maximum removal rate 0.33g/h for initial concentration of human urine 100 mg/l. The lowest energy consumption was 196x103 Wh/kg [30]. Jayishnu Singla et al. (2019) tested quaternary mixed metals oxides (Pt/Ru/Ir/Ti@titanium) anode for EO of urea. The optimum conditions for photo-EO to achieve >94.78% or urea oxidation was pH 4, initial concentration of NaCl 1.45g/l, and current density 0.018 A/cm² and reaction time 135 min. They attributed the high urea removal % to the development of reactive OH• and Cl2 species. They estimated the cost of operating for this process to be 0.78 $/m³. The durability tests showed that the developed electrode could work for 90 cycles without reduction in its efficiency. They recommended it for on-site urine treatment [31]. Simka et al. (2009) compared between Ti/(RuO2–TiO2) 40:60 and Ti/Pt electrodes for the decomposition of urea. They studied the process kinetics, and other parameters. It was found that in case of Ti/Pt electrode, the urea decomposed in the solution while in case of Ti/(RuO2–TiO2) electrode, urea decomposed on the electrode [32]. Mahmoud et al. tested porous graphite electrodes in electrochemical cell. The effect of salt strength, the rate and concentration at which urea flow along with the current density at the anode on urea management were deeply discussed. The results proved that when the current efficiency decreased and its density increased, the urea management increased. Finally, the energy power consumption increased, and the maximum urea removal rate was 0.78 g/h [33]. Rahimpour et al. introduced a membrane contain Pd that destruct urea in wastewater to $H2$. The effect of temperature, pressure, thickness of catalyst layer and configuration of flow were examined. The membrane reactor and urea treatment were modeled mathematically [27].

A lot of studies focused on Nickel in special way and also other catalysts like palladium, graphite, etc. The main challenge of urea management via EO process is the price of catalyst which increase the total cost of the process. The future studies should focus on finding low-cost electrodes, and searching for natural catalysts. Another trend is to improve the efficiency of the existing catalysts to compensate
the high cost. This will be done through introducing new functional groups to the catalyst or/and improving the specific surface area, structure and pore volume of the catalyst.

2.1.3. Fuel cell. Urine can be utilized as fertilizer, in struvite form, but this technology consumes intense energy. Microbial Fuel Cell (MFC) consider a promising technology with added value where urea wastewater will be managed effectively and electricity will be produced. Because urea is safer and less toxic than hydrazine and ammonia, it was investigated as a hydrogen-storage material for low-temperature fuel cells. The low-power density resulting from the sluggish anode reaction is still the main challenge for applying urea in fuel cells. Another drawback is that microorganisms are only able to metabolize the organic substrates rather than urea in urine. Wei Xu et al. reviewed urea electrocatalysis in numerous fuel cells [34]. Jiseon You maximized urine utilization in production of energy and struvite. At the beginning, MFC increases the urea hydrolysis rate in the same time of producing electricity which improved struvite formation. Later, the initial effluent was mixed with Mg, and additional reduction in COD was achieved. The system produced 14.32 W/m² of power [35]. Barakat et al. introduced nanoparticles of NiMn@activated carbon as new effective onset potential electrocatalyst for urea oxidation in fuel cell. This system delivered 130 mA/cm² of current density and -85 mV of onset potential combined with manganese up to 10 % [36]. Doping technique was suggested by Abdelkareem et al. to increase the overall efficiency of urea fuel cell. They found that introduction of cadmium to nickel@carbon (nano-fibers) worked as a co-catalyst. Cadmium binds the carbon nano-fibers, and improved the active site for urea oxidation [37]. Wang et al. studied urea EO in fuel cell to generate power. This fuel cell delivered 78% of coulombic efficiency when urea initial concentration was high as 3940 mg/L. In addition to remove more than 80% of nitrogen of initial concentration 2630 mg/L [38]. Wei Xu et al. prepared NiCo/C bimetallic nanoparticles with various weight % of Co (0-40 %) in direct urea fuel cell (DUFC). The maximum power density (1.6 mW/cm²) delivered at Co 10 %. The oxidant was O2 at temperature 60°C and urea (0.33 M) was the fuel. The effects of temperature and urea initial concentration on DUFC electrocatalytic activity were also studied [10]. Rong Lan and Shanwen Tao (2011) developed Ni nano-catalyst to be used in fuel cell for oxidation of urea/urine. The optimum condition to achieve a power of density 14 mW/cm² was urea (1M), as fuel, at room temperature. When the temperature increased to 60 °C, the power density reached 4 mW/cm² [39]. C. Santoro et al. (2013) investigated fresh urine as a fuel in single chamber microbial fuel cell. The power generation was doubled when Pt was introduced to the cathode (figure 6). After 4 d, 75% of COD was reduced [40]. Carpenter and Stuve (2019) suggested urea oxidation to be paired with co-current reduction of water to produce H2 for energy storage, or reduction of O2 to directly produce energy in a DUFC. The challenge is that urea concentration in their study was 0.33 M to simulate human urine concentration in contrast to diluted urea concentrations in wastewater, this resulting in reduction in the overall urea oxidation rate. However, the urea oxidation occurred at potentials that favor generation of Ni3+ which encourage Ni2+/Ni3+ reversible redox equation [41]. The human urine was directly fed to MFCs (batch and continuous modes) as a fuel [42, 43]. Barakat et al. applied NiSn@carbon nanofibers as anode for urea EO in DUFC. Measurements of electrochemical process shown that applying a co-catalyst (Tin 15%) that was calcinated at temperature 850 °C enhanced significantly the electro-catalytic activity [44].
However, the challenges facing feasibility of EO using DUFC technique is the catalyst material, morphology, cost and efficiency. The researchers should search for lowering the cost and increasing the efficiency of the catalyst via increasing the specific surface area or modification using different techniques like doping, mixing in composites, etc. It can be seen also, that the researchers focused on investigating the current density, onset potential to track the urea management and generate energy. They concluded that increasing temperature would increase the catalyst activity. The targeted modification of catalyst surface improves its efficiency. Another challenge in this research area is the fuel cell itself. This recent technique is still under development, production of energy in the fuel cell is very low, there is still much research for maximizing the power production and also increase the treatment efficiency. However, fabrication of fuel cell on the large scale will promote management of urea in the wastewater. Subsequently, research of urea management in wastewater will be developed parallel with research in fuel cell development.

However, the future research should focus on urea management in DUFC, optimization of electrochemical oxidation process in the cell and lowering the cost of operation. As this technique is clean, the waste will be water or energy (H2) and both of them are clean and safe for the environment.

2.2. Biological treatment

Biological treatment of urea referred to contact the urea wastewater with microorganisms in biofilter where the microbes will catalobalize the urea to final products/byproducts. Campos et al. (2003) utilized urea wastewater in both a biofilm airlift nitrifier reactor and an anoxic sludge blanket up-flow reactor for both urea hydrolysis and nitrification. The maximum nitrogen removal percentages were obtained at 1.0 (formaldehyde/N-NH4+). The efficiency of N removal decreased when this percentage reached 1.5 due to increase in the formaldehyde quantity which decreased the nitrification [45]. Converti (2006) used cultivations of Spirulina platensis in batch system. The maximum nitrogen concentration of 1.7 mM sustained the growth of these microalgae without inhibition. Transferring NH3 into the cell was controlled by hydrolysis of urea by urease enzyme. The pulse-feeding of urea nitrogen sources can sustain the long term-cultivation of S. platensis [46]. Yan Lilong et al. (2013) studied biological aerated filter to manage urea of highly concentrations in sewage from a chemical plant. They stated that the heterotrophic bacteria were the main bacteria among different communities responsible for the urea hydrolysis. Nitrobacteria and nitrosobacteria also contributed to some extent in the hydrolysis process [47]. Dahlan et al. applied Fenton oxidation process on urea from fertilizer plant using P. Fluorescens bacteria. The study estimated the inhibition concentration (723,219 mg/l). No observed effect of concentration (2533,658 ppm) and lowest observed effect of concentration (393,992 mg/l) versus the P. Fluorescens cell accumulation for 96 h. The highest average percentage of ammonium reduction was 94.50% at 2500 ppm of ammonium-nitrogen [48]. Yavari et al. treated urea wastewater from industrial wood (timber) plant using teak phyto remediation. A constructed bench-scale was

Figure 6. Ammonium concentration profile in SCMFCs at 2d cycles [40].
studied in term of plant biomass, nitrogen recovery and influent flow rate for 56 d. The teak showed a considerable nitrogen uptake [49].

Here, the challenge is the sensitivity of the microorganisms, complexation of reaction and difficulty in the control. The process is costly due to intensive control of the process parameters (temperature, pH, inhibitors, initial concentration and flowrate of urea). The researchers should investigate resistance of microorganisms in sever conditions of pH, temperature and high initial urea concentrations. Another challenge in this technique is the production of undesirable products which act as additional burden to the environment. The configuration of the treatment system plays important role, any fault in the design could cause leakage of the urea with the downstream, overloads on the system, and failure in the process.

2.3. Adsorption

Adsorption technique for wastewater management is widely used [50]–[54]. It involves contact the wastewater (synthetic or real) with a definite amount of adsorbent. The maximum capacity of adsorption attributed to the adsorbent surface area or/and the surface functional groups. Adsorption of urea from wastewater onto nanoporous and nonporous adsorbent was investigated. In 1975, Roger Parsons investigated adsorption of urea (initial concentration 0.1–4 M) onto mercury. They suggested that the urea molecule oriented parallel to mercury. The data was modelled using Langmuir equation [55]. Climent et al. investigated urea management using adsorption onto Pt electrode. They stated that only nitrogen atom is responsible for the adsorption mechanism [56]. Abd El-Lateef et al. investigated the adsorption of urea onto nano-iron phosphate as a function of temperature, agitation speed, reaction time, catalyst mass and solution pH. The highest capacity of adsorption recorded was 102 mg/g at pH (7-9). The kinetic data showed that film diffusion model controls the process at the beginning and then the matrix diffusion model was the predominant. The thermodynamic parameters have been also determined and analyzed. The nanoparticles were stable and the adsorbent recyclability reached 10 cycles [57]. Kameda et al. studied management of urea using ordinary activated carbon. The urea attraction mechanism was the linkage via dipole–dipole reaction between amino and carbonyl/hydroxyl groups of urea and activated carbon, respectively. Then the adsorbed molecule interacted with another one via –C=O group of the former and –NH₂ group of the later which form a multilayer physical adsorption [58]. Simha et al. investigated fly ash as adsorbent for urea from urine. They stated the optimum condition of pH 6, temperature 30 °C, mass of ash 1.9 and urea initial concentration 13.5 g/L maximize the adsorption capacity to 410 mg/g. The reaction mechanism was described to be spontaneous physical adsorption, they attributed the physical nature of adsorption to Van der Waal’s force and electrostatic interactions. The film diffusion played important role in controlling that adsorption process. Further, they derived a model to minimize the fly ash amount required for the maximum adsorption capacity to design a multistage batch adsorber [59]. Ooi et al. transformed oil palm to activated carbon fibers (ACF). They explained that the ionized electronegative -OH groups on the adsorbent surface in the alkaline urea solution caused ionic repulsion towards partially anionic urea. The strength of this ionic repulsion increases in case of increasing OH functional groups onto ACF [60]. Wang et al. successfully deposited MgAl@LDH on η-Al₂O₃ to improve urea hydrolysis. They concluded that the highest urea degradation rate, resulted from the high basicity attributed to the active sites of Mg–OH. The urea concentration reached 8.162 mg/L at 165 °C after 120 min which is below the effluent standard. The most important finding of that study is that the prepared adsorbent could efficiently recycled. The slight reduction in activity was referred to the decreasing in basicity [61]. Ooi et al. investigated urea removal by adsorption onto empty fruit bunch based ACF, mesoporous silica, palm kernel shell based granular activated carbon. The porous and nano-sized adsorbents present high affinity for urea. They attributed this to the presence of carboxyl and amine functional groups on the adsorbents surfaces that facilitated the urea adsorption via hydrogen bonding [62]. Liu et al. prepared chitosan/cupper membrane for urea removal. The maximum capacity of urea adsorption was 78.8 mg/g. This value was highly depending on Cu % in the membrane matrix. This was owned to that the presence of four coordinated sites of Cu(II), two of
them attached Cu to the chitosan membrane through –NH$_2$ groups and the other two sites are available for binding urea [63]. Abidin et al. suggested oxidized starch nanoparticles as adsorbent for urea. The developed adsorbent showed a promising adsorption capacity (185.2 mg/g). High removal percentage (95 %) was achieved in a relatively short time (4 h). Finally, 91.6 % of the adsorbent was recovered or reused [64]. Ganesapillai and Simha evaluated activated carbon from bamboo for urea adsorption in terms of reaction time, temperature and urea initial concentration. The maximum capacity of urea adsorption reached 146.1 mg/g. The process was described as spontaneous physical reversible exothermic process. And both of intraparticle diffusion and surface adsorption control the kinetics of urea adsorption onto the surface of the adsorbent [65]. Ganesapillai et al. evaluated walnut shells, microwave activated carbonized based on bamboo shoots, and coconut shells for the adsorption of urea in terms of agitation speed, temperature, adsorbent dose, and urea initial concentration. The kinetic studies proved that pseudo 2$^{nd}$ order kinetic model is the best to describe adsorption process of urea onto microwave activated carbon and walnut shells while pseudo 1$^{st}$ order model is fitted coconut shells [66]. Safwat et al. compared activated alumina with activated carbon for the removal of urea from wastewater. The management efficiency was recorded as function of pH strength. The optimum pH to achieve maximum efficiencies of activated alumina (24 %) and activated carbon (31%) was 9. Pseudo 2$^{nd}$ order model expresses the kinetic results for urea adsorption onto activated alumina. Equilibrium studies stated that Redlich-Peterson isotherm was the preferable to describe ureas/alumina adsorption system while Temkin isotherm was the best to describe the other [67]. The major materials used for the adsorption of urea from different systems were activated carbon, zeolite [68,69] (figure 7) and silica and its based materials [70].

![SEM images of powdered zeolites](image)

Figure 7. SEM images of powdered zeolites [69].

However, there are many research gaps in urea adsorption studies such as: the adsorption technique is more effective in dealing with low urea concentration, the reaction is also sensitive to pH or/and temperature. Additionally, the adsorption technique is implemented on small volumes of wastewater, scaling up the process is under development. Regeneration of the adsorbents is another challenge where the adsorbents losses percentage of their mass and activity during regeneration process and even the regeneration process is costly. Also, the reaction resulted sludge (wasted adsorbents) which is consider as additional burden on the environment. The upcoming studies should search for recycling this sludge in the process or reusing it in another application like road pavement, fillers, etc. Using biodegradable adsorbents is preferable. And finally, the impact of this sludge on the environment should be accessed.
2.4. Hydrolysis
Zhigang et al. investigated both urea hydrolysis and nutrients (phosphorus and nitrogen) recovery. They studied the effect of temperature, pH and stored/fresh urea ratio on hydrolysis process. It was found that high temperature (> 20 °C), low pH (< 8) and stored urea enhanced the hydrolysis process. Under optimum conditions, the recovery of PO$_4^{3−}$-P and NH$_4^+$-N reached > 85% and 95%, respectively [71]. Rahimpour et al. investigated urea management in wastewater using a cascade of hydrolyser/desorber. They targeted to approach 0 ppm of urea in the effluent. They stated that the removal efficiency of urea and ammonia could be improved by increasing the inlet wastewater temperature, steam flow rate and decreasing the reflux ratio [72]. Rahimpour et al. developed and validated a model for different ranges of urea concentrations in thermal hydrolyser/desorber loops. They solved the model and suggested desorbers/reactors height, flow rate and temperature [73]. Rahimpour and Mottaghi compared countercurrent and cocurrent modes in thermal hydrolyzer for urea decomposition, they applied equilibrium-stage model to the two modes. The simulation data showed that countercurrent mode was superior than concurrent in achieving high removal efficiency and new environmental standards [74].

2.5. Other techniques
Rychen Philippe et al. (2016) suggested ion exchanging column for removing urea from water by adding nitrite to the influent before passing through a strong cation exchange resin. The NO$_2^-$ could be added in different forms (nitrous acid, nitrogen dioxide gas or sodium nitrite salt). Regeneration of the column is conducted using an acidic solution [75].

Machdar et al. (2018) studied adding MgCl$_2$, KH$_2$PO$_4$, and KOH to a fertilizer plant wastewater. This resulting an added-value, where the urea in the wastewater is treated and slow-release fertilizer is produced. The effects of molar ratios and solution pH were discussed. It was found that, the highest ammonium removal efficiency was 94.7% at the ratios 1.2/1/1 of Mg$^{2+}$/NH$_4^+$/PO$_4^{3-}$ at pH 9 [76].

Eiroa et al. analyzed thermal decomposition of urea. They stated that the production of ammelide, ammeline and cyanuric acid begin at temperature > 190 °C and completed at 250 °C. Urea was hydrolyzed under anoxic environment. The efficiency of conversion reached 100 % even in the presence of formaldehyde in continuous reactor [77]. Lundström et al. (2011) investigated the impact of TiO$_2$, Fe-Beta, and γ-Alumina on the thermal destruction of urea. The best results dedicated to TiO$_2$, also the humid condition was preferable [78].

Although there are numerous techniques for urea management in wastewater, but still most of them are achieved in small scale. This is attributed to the high cost of reactants. Much efforts are still required to minimizing the cost of the materials, systems and the overall process.

Barmaki et al. modeled the thermal hydrolysis of urea from industrial wastewater. They used three models to provides the hydrolyser height, concentrations distribution and temperature for numerous components. They examined the wastewater flowrate, steam and temperatures. They concluded that any increase in temperature would increase the urea removal efficiency [79].

3. Recommendations for future research on urea wastewater management
It can be seen that discharging urea to water bodies cause negative impact on human and the environment. Subsequently, urea should be managed efficiently in wastewater. Different techniques were discussed in this review. Every technique has its advantages and challenges. One of the main challenges in all these techniques is the possibility to produce further wastes. So, it is highly recommended that the future studies in this area should investigate green materials. The researchers could study biodegradable materials to reduce their negative impacts on water bodies and also, they can work on industrial wastes to add values to these wastes and protect the environment from additional wastes.

Implementation of nanotechnology in urea management is highly recommended to improve the efficiency of the treatment process. The nanotechnology increase the materials performance through improving the mechanical, physical and chemical characteristics of the materials and also minimize
the amounts of the used materials which conserve these materials and lowering the total cost of operation.

Due to the world trend of replacing the fossil fuels with renewable energy, electrooxidation process in microbial fuel cell has drawn the attention recently due to the fact that this technique is efficient and clean (no waste) for wastewater management in parallel with energy production. The researchers should focus on modification of the current electrodes and searching for others to rise the anodic current densities and improve the electrodes stability, which will simultaneously reduce the onset potential for urea oxidation reaction resulting in efficient urea management and improvement the power density in the urea-based fuel cells. Electrochemical oxidation of urea wastewater in industrial scale should be economically feasible in the future.

4. Conclusions
Along the past decades, urea management in wastewater was investigated through different techniques. Some techniques are costly due to the cost of materials and maintenance. Some techniques like adsorption release additional wastes to the environment. Other techniques are complex in operation and control. But still the electrochemical oxidation method until now is the superior technique compared to others. It releases less waste, especially in the case of fuel cell where nanoparticles have been applied as anode for management of urea beside energy (hydrogen) production. Additionally, it yields low harmful environmental impacts, although the overall efficiency of the electro-oxidation processes and fuel production were improved in the last years but further research is required for industrial and transportation applications. The sustainability and success in urea management in wastewater could be achieved if the researchers work on developing all these techniques and materials.

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