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Review

Recent advances in nanoparticle–based potentiometric sensors

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ABSTRACT

Nanomaterials have become an important research topic in recent years due to the advantages they provide. Nanoparticles, which can be especially applied in many areas of industry, also come to the fore as sensor materials. Potentiometry-based devices offer significant advantages including wide concentration range, short response time, low cost, low detection limit, high selectivity and sensitivity. These important advantages allow potentiometric devices to be successfully applied in many fields such as food, environmental monitoring, medicine, pharmacy, industry and agriculture. In this mini review, we present a perspective on sensor and biosensor devices prepared with the unique properties of nanoparticles and potentiometry technique.

1. Nanotechnology

Nanotechnology, which was introduced to the scientific world in the 21st century, covers the synthesis, management, and application of materials with a size of less than 100 nm [1]. Nanotechnology has enabled the rapid development of bio- and nanosensors for the detection of agents such as various metal ions, proteins, pesticides and microorganisms [2]. Over the last 50 years, materials researchers have extensively investigated how to use nanostructured materials in different fields. Nanomaterials can be produced with magnetic, electrical, optical, mechanical and catalytic properties [3]. Nanomaterials offer extraordinary possibilities to a wide range of science and technology fields, including materials science, physics, chemistry, biology, engineering and medicine [4,5].

2. Nanoparticles

Nanoparticles (NPs), one of the components of nanotechnology, are small particulate matter with sizes between 1 and 100 nm. NPs can exist in different shape, size and structure such as hollow, conical, core, spiral, cylindrical, spherical and wire [6]. There are different types of nanoparticles such as gold (Au), platinum (Pt), silver (Ag) and palladium (Pd) in different colors (Fig. 1) [7]. Nanoparticles have important applications in different sectors such as biotechnology, environment, food, biomedical, pharmaceutical, medicine, and agriculture (Fig. 2) [8,9]. Nanoparticles can be synthesized using various techniques such as coprecipitation, hydrothermal, microemulsion, microwave, sol-gel, ultrasound, template and biological synthesis [10].

3. Nanoparticle-based potentiometric sensors

The size, structure and unique properties of nanoparticles have enabled them to be used as sensor materials in the production of various sensors [11–14]. Potentiometry-based sensors and biosensors have been extensively studied by researchers due to their many advantages. When compared to other analytical techniques, potentiometric methods offer multiple advantages including high selectivity and sensitivity, wide concentration range, low detection limit, long lifetime, short response time, low cost and ease of use [15–17]. Potentiometry-based devices are widely used in various areas such as environmental monitoring, process control, industrial, food, agricultural, and medicinal drug analysis (Fig. 3) [18–20].

Elmosallamyl et al. developed potentiometric sensors based on ZnS nanoparticles, for the determination of zinc(II) ions [21]. These sensors worked in the concentration range of 1.0×10^{-5}–1.0×10^{-1} M, and had detection limits of 2.86×10^{-6} and 4.60×10^{-6} M for solid-state membrane and coated wire sensors, respectively. They shown that the sensors had a short response time of 1s. In addition, solid state zinc(II)-selective sensor was reported to be used successfully in brass alloys and pharmaceutical preparations. Sharma and Kaur showed that impedimetric and potentiometric determination of silver(I) ions in various samples of water and packaged food products based on 3-hydroxy-N-(4-mercaptophenyl) benzamide (**1**) (Fig. 4) [22]. The linear concentration ranges and detection limits of the developed sensors were reported to be as following: 1.0×10^{-9}–1.0×10^{-4}, 3.6×10^{-9} M for impedimetric detection; 1.0×10^{-4}–1.0×10^{-1}, 4.46×10^{-5} M for potentiometric detection. They reported that the potentiometric method had a Nernstian response

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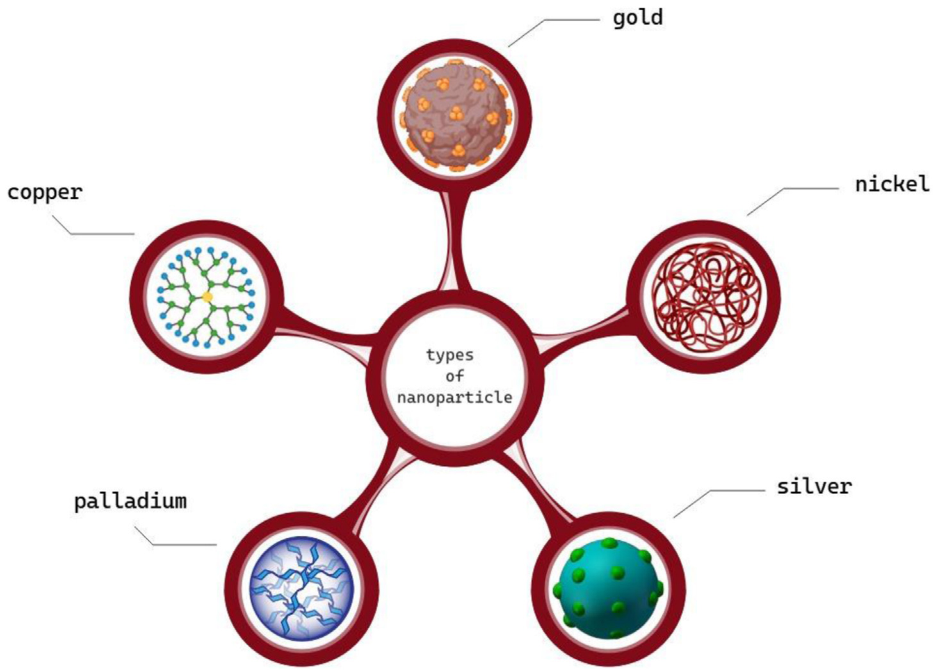

Fig. 1. Types of nanoparticles.

(61.70 ± 0.02) and the response time of 15 s. The ultrasensitive potentiometric sensor was designed and characterized by Li et al. for lead(II) ions in different real samples [23]. This sensor worked in the concentration range of 1.0×10^{-3}–1.0×10^{-10} M and had a wide pH working range from 3.5 to 7.0. The developed sensor with a detection limit of 2.2×10^{-11} M was shown to have a response time between 22 s. Ali et al. reported the development of new potentiometric sensors using copper oxide nanoparticles (CuO NPs) as ionophore, for the determination of copper(II) ions in pure solutions and different real spiked water samples [24]. These sensors worked in the concentration range of 5.3×10^{-7}–1.0×10^{-2} and 6.1×10^{-8}–1.0×10^{-2} M, and had detection limits of 5.3×10^{-7} and 6.1×10^{-8} M for modified carbon paste (MCPEs; electrodes I and II) and screen–printed electrodes (MSPEs; electrodes III and IV), respectively. In addition, they observed that the fast response time of the novel sensors were 8, 10, 5 and 7 s for electrodes I, II, III and IV, respectively. Authors reported that using the developed sensors, they had consistent results with

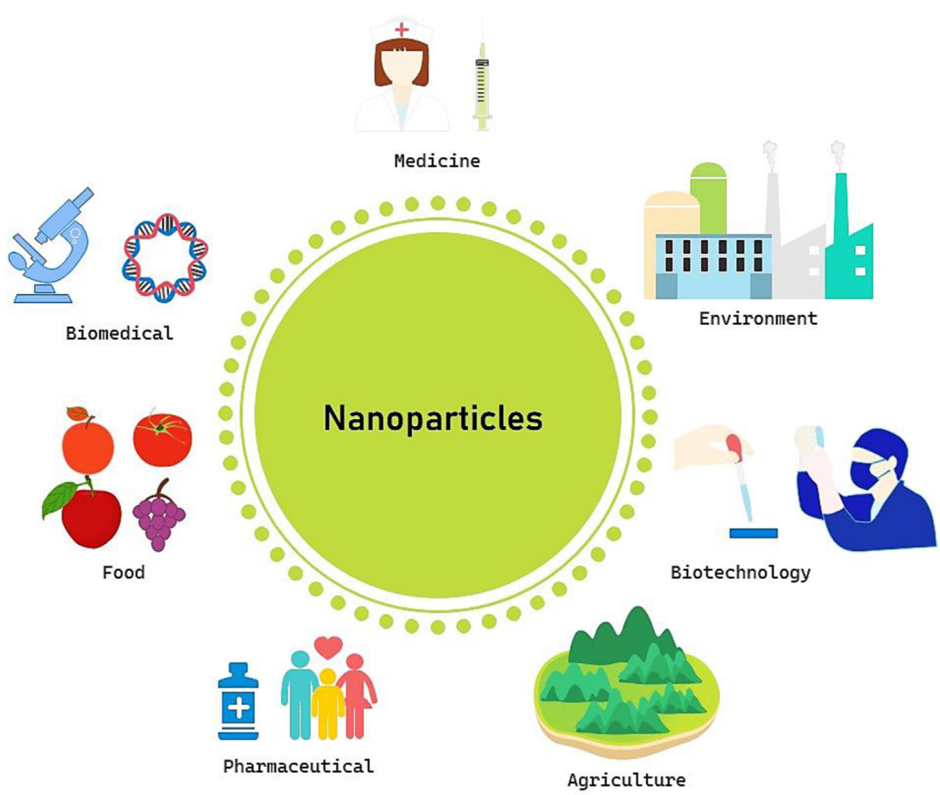

Fig. 2. Application areas of nanoparticles.

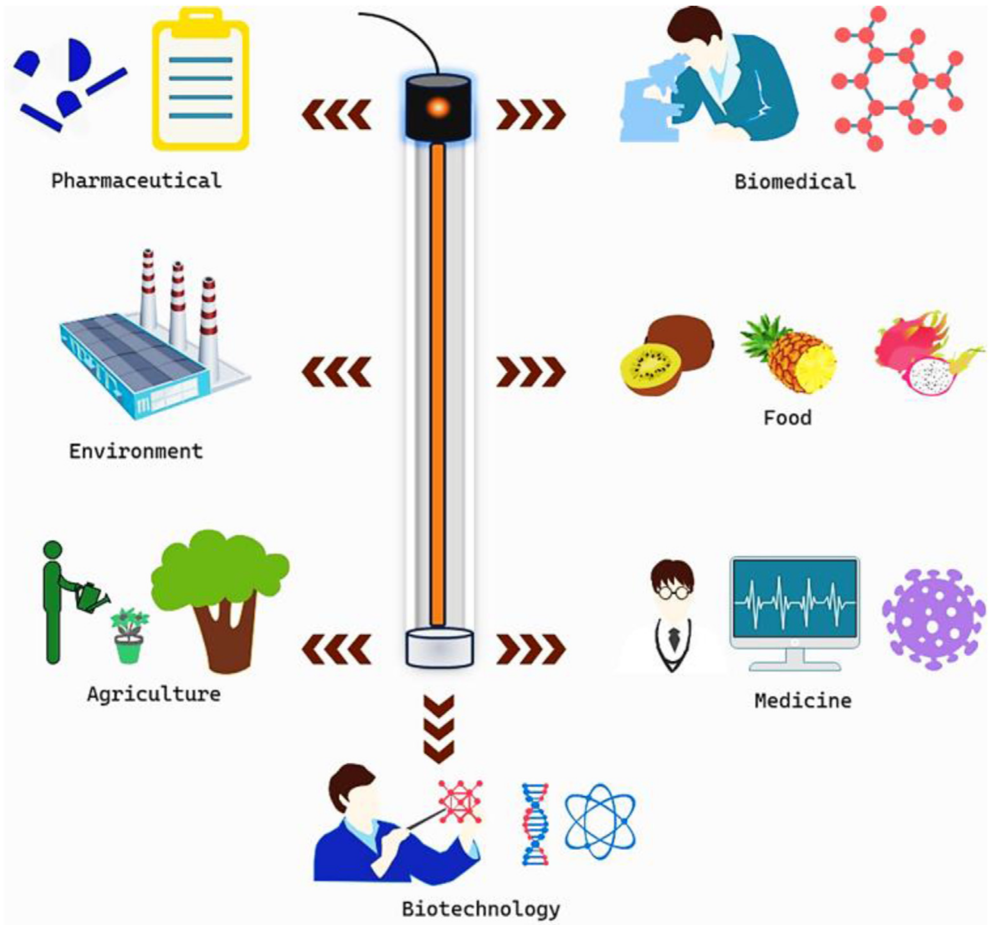

Fig. 3. Application areas of potentiometric sensors.

that of the inductively coupled plasma atomic emission spectrometry (ICP-AES).

Gutiérrez-Climente et al. developed a novel enantioselective potentiometric sensor based on chiral imprinted nanoparticles for the determination of antidepressant citalopram (**2**) (Fig. 4) in spiked urine samples [25]. The developed sensor worked in the concentration range of 2.5×10^{-7}–1.0×10^{-3} M with a limit of detection of 1.25×10^{-7} M. The response time of the sensor was shown to be 30 s. Potentiometric detection of cocaine (**3**) (Fig. 4) in blood serum samples was performed based on molecularly imprinted polymer nanoparticles (nanoMIPs) by Smolinska-Kempisty et al. [26]. The authors developed the first potentiometric sensor in which molecularly imprinted nanoparticles with high affinity for cocaine were prepared. According to their results, the authors reported that the developed sensor could accurate measurement of drug content in blood serum and within a wide range of concentrations (linear range between 1 nM and 1 mM).

The zeolite-carbon paste potentiometric sensor was designed and characterized by Elshahed et al. for prucalopride succinate (**4**) (Fig. 4) in tablet dosage form [27]. The highly sensitive sensor displayed a linear response over the concentration range from 2.0×10^{-6} to 1.0×10^{-2} M with a limit of detection of 1.0×10^{-6} M. The authors reported the sensor response time as 16 s. Liang et al. reported the development of a potentiometric sensor based on molecularly imprinted nanoparticles for the determination of triclosan (**5**) (Fig. 4) in toothpaste samples [28]. The developed sensor has a detection limit at the nanomolar level (1.9×10^{-9} M). The authors reported that the method they developed is promising for developing molecularly imprinted polymers–based potentiometric sensors.

Al-Haidari et al. developed a solid contact potentiometric sensor based on nanoparticles for the determination of theophylline (**6**) (Fig. 4) in different types of tea extract [29]. The sensor showed Nernstian behavior (58.36 mV dec^{-1}) over the concentration range of 1.0×10^{-2}–1.0×10^{-7} M with a detection limit of 2.5×10^{-8} M. The developed sensor displayed a short response time of less than 10 s and lifetime of more than 46 days. The proposed sensor was shown to be useable in the pH range of 5.5–7.0. In a study by Prkić, development of a novel potentiometric sensor based on home-made iodide ion selective electrode enriched with ZnO nanoparticles for the determination of penicillamine (**7**) (Fig. 4) [30]. The sensor was shown to work in the concentration range of 2.45×10^{-6}–1.0×10^{-2} M and to have a detection limit of 2.24×10^{-6} M.

For the determination of clidinium (**8**) (Fig. 4) in pure solutions, pharmaceutical preparation, biological fluids and surface water samples based on β-cyclodextrin and dibenzo 18-crown-6 ionophores/mesoporous silica nanoparticles was reported [31]. Authors prepared two novel potentiometric sensors based on β-cyclodextrin/mesoporous silica nanoparticles (β-CD/MSNs-CPS, sensor I) and dibenzo 18-crown-6/mesoporous silica nanoparticles (DB18C6/MSNs-CPS, sensor II). The sensors were shown to have detection limits of 6.0×10^{-8} M (R^2: 0.999) and 9.0×10^{-8} M (R^2: 0.999) and linear concentration ranges of 9.9×10^{-8}–1.0×10^{-2} and 2.9×10^{-7}–1.0×10^{-2} M, respectively. Response times were 4 and 8 s for the developed sensors I, and II, respectively. Potentiometric multisensory arrays for the determination of dicarboxylic amino acids (aspartic and glutamic acid) (**9** and **10**) (Fig. 4) and potassium cations were performed by Safronova et al. using perfluorinated membranes and silica nanoparticles with surface modified by proton-acceptor groups [32]. The proposed sensors simultaneously detect potassium cations and amino acid anions to concentrations ranging from 1.0×10^{-4} to 1.0×10^{-2} M.

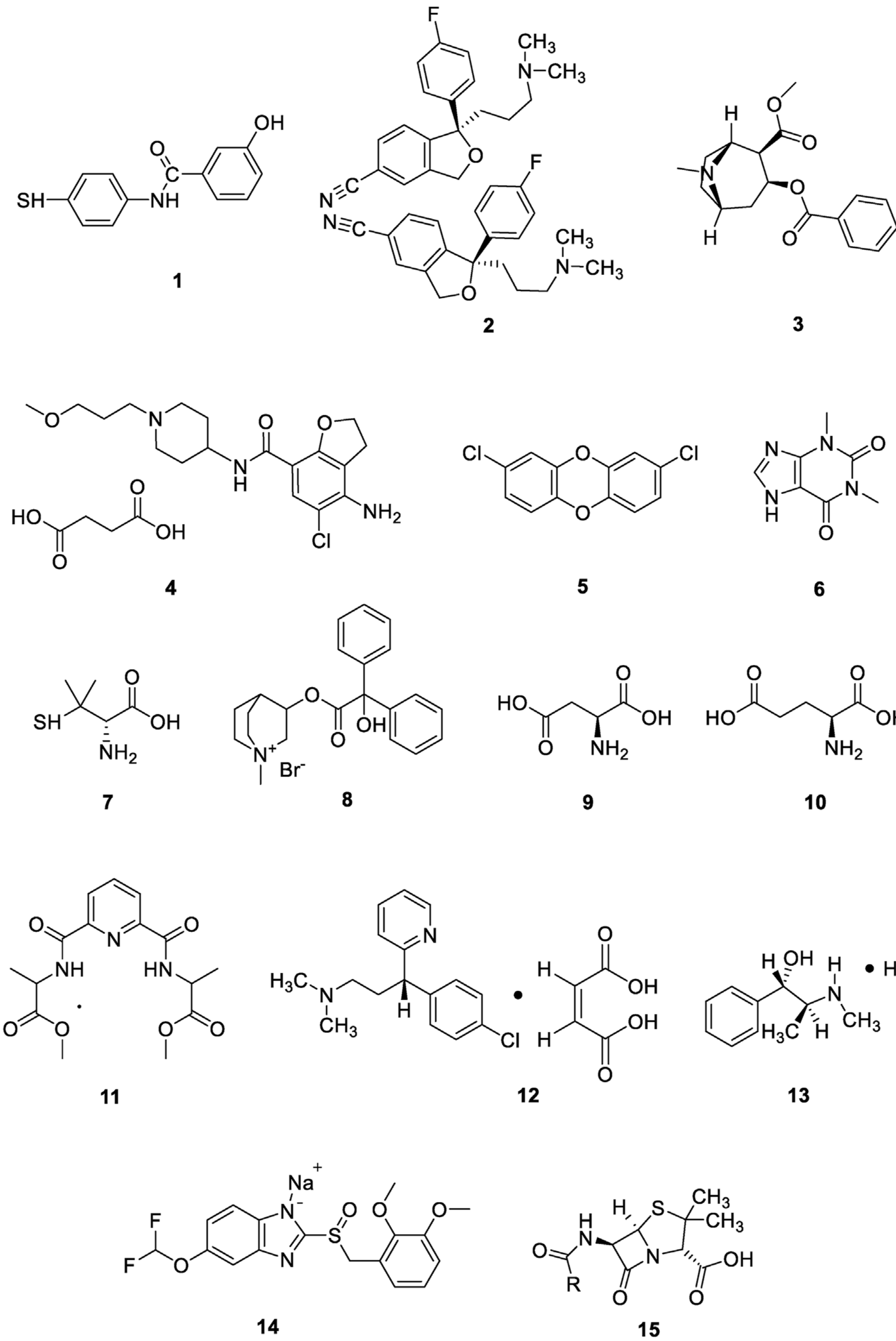

Fig. 4. The chemical structures of the molecules.

A miniaturized potentiometric sensors based on PbS nanoparticles and a newly synthesized ionophore (**11**) (Fig. 4) was developed for the determination of lead(II) ions in water samples and biological fluids [33]. This novel potentiometric sensors displayed near–Nernstian responses (28.2–33.5 mV dec^{-1}) over the concentration range of 1.0×10^{-7}–1.0×10^{-3} M. The sensors had a pH working range from 3.0 to 6.5. and a response times ranging from 10 to 20 s. The authors reported that the applications of the sensor in real samples are in agreement with the data obtained using the atomic absorption spectroscopy (AAS) method.

Akl and Ali developed a highly sensitive potentiometric sensors based on silver nanoparticles for the determination of thorium ions in water samples using morpholine derivative (L1) self-assembled on silver nanoparticles (L2) [34]. The developed sensors displayed a linear response in the concentration range from 4.0×10^{-7} to 1.0×10^{-1} and 6.3×10^{-9} to 1.0×10^{-1} M, worked in the pH range of 2.5–9.0 and 2.0–9.5 with a limit of detection 4.0×10^{-7} and 6.3×10^{-9} M, respectively. Their response time were reported to be 11 and 5 s, and their lifetime were more than 6 and 7 months, respectively.

Table 1
Potentiometric performance characteristics of nanoparticle–based sensors.

Analyte	Linear concentration range (M)	Detection limit (M)	Response time (s)	Slope (mV dec^{-1})	Reference
Zn^{2+} (solid state)	1.0×10^{-5}–1.0×10^{-1}	2.86×10^{-6}	1	28.9 ± 0.2	[21]
Zn^{2+} (coated wire)		4.60×10^{-6}	1	25.9 ± 0.2	
Ag^{+}	1.0×10^{-4}–1.0×10^{-1}	4.46×10^{-5}	15	61.70 ± 0.02	[22]
Pb^{2+}	1.0×10^{-10}–1.0×10^{-3}	2.2×10^{-11}	22	29.3	[23]
Cu^{2+} Electrode(I)	5.3×10^{-7}–1.0×10^{-2}	5.3×10^{-7}	8	29.65	[24]
Cu^{2+} Electrode (II)	5.3×10^{-7}–1.0×10^{-2}	5.3×10^{-7}	10	28.99	
Cu^{2+} Electrode (III)	6.1×10^{-8}–1.0×10^{-2}	6.1×10^{-8}	5	30.01	
Cu^{2+} Electrode (IV)	6.1×10^{-8}–1.0×10^{-2}	6.1×10^{-8}	7	29.35	
Citalopram	2.5×10^{-7}–1.0×10^{-3}	1.25×10^{-7}	30	50.77 ± 1.32	[25]
Prucalopride succinate	2.0×10^{-6}–1.0×10^{-2}	1.0×10^{-6}	16	58.6589 ± 0.47	[27]
Triclosan	1.0×10^{-8}–1.0×10^{-6}	1.9×10^{-9}	~3 min	Not reported	[28]
Theophylline	1.0×10^{-7}–1.0×10^{-2}	2.5×10^{-8}	<10	58.36	[29]
Iodide	2.45×10^{-6}–1.0×10^{-2}	2.24×10^{-6}	45	29	[30]
Clidinium (β-cyclodextrin)	9.9×10^{-8}–1.0×10^{-2}	6.8×10^{-8}	4	59.9 ± 0.5	[31]
Clidinium (Dibenzo 18-crown-6)	2.9×10^{-7}–1.0×10^{-2}	9.0×10^{-8}	8	56.6 ± 0.3	
Pb^{2+} Electrode(I)	1.0×10^{-7}–1.0×10^{-3}	0.01 μg mL^{-1}	<10	28.2	[33]
Pb^{2+} Electrode(II)	1.0×10^{-7}–1.0×10^{-3}	0.007 μg mL^{-1}	<20	33.5	
Thorium Electrode (I)	4.0×10^{-7}–1.0×10^{-1}	4.0×10^{-7}	11	14.30 ± 0.71	[34]
Thorium Electrode (II)	6.3×10^{-9}–1.0×10^{-1}	6.3×10^{-9}	5	15.11 ± 0.47	
Chlorpheniramine maleate	1.0×10^{-7}–1.0×10^{-2}	5.0×10^{-8}	5–10	58.17	[35]
Pseudoephedrine HCl	1.0×10^{-8}–1.0×10^{-2}	4.0×10^{-9}	5–10	57.79	
Iodide	8.0×10^{-9}–1.0×10^{-3}	7.0×10^{-9}	60	−55.3	[37]
Penicilin	1.0×10^{-2}–1.0×10^{-5}	ND	<60	24.8	[38]

Moustafa et al. reported the development of a potentiometric sensors based on functionalized Fe_3O_4 magnetic nanoparticle for the determination of chlorpheniramine maleate (**12**) and pseudoephedrine HCl **(13)** (Fig. 4) in pharmaceutical formulation [35]. The linear working range of the prepared six different sensors varies between 1.0×10^{-2}–1.0×10^{-8} M. The pH working ranges of the prepared sensors vary between 4.0 and 8.0 and the response times vary between 15 and 40 s. Potentiometric determination of pantoprazole sodium (**14**) (Fig. 4) in an authentic sample was performed by Alshehri et al. using modified coated membrane sensors [36]. The authors synthesized two metal oxide nanoparticles, nickel oxide and iron oxide nanoparticles, from green sources *Matricaria recutita* flower and *Salvia officinalis* leaf extracts, respectively. Their linear concentration ranges were reported to be 1.0×10^{-9}–1.0×10^{-2} and 1.0×10^{-10}–1.0×10^{-2} M. Detection limits of sensors were shown to be 2.3×10^{-10} and 2.8×10^{-11} M. These sensors worked in the pH range 4.0–8.0 without being effected by the changes in pH.

Wang et al. reported the development of a potentiometric solid carbon paste electrode based on nanoparticles of silver iodide and silver sulfide for the determination of urinary iodide in human urine samples [37]. Authors showed that this electrode had a linear concentration range of 8.0×10^{-9}–1.0×10^{-3} M, a detection limit of 7.0×10^{-9} M and response time of <60 s. Karakus and Turan reported a novel nanoparticle–based biosensor for the determination of penicillin in pharmaceuticals [38]. This biosensor had a linear concentration range of 1.0×10^{-1}–1.0×10^{-3} M and a fast response time of 1 min. The authors reported that the optimum pH for the biosensor they developed was 7.4 and the optimum temperature was 25 °C.

The linear concentration range, limit of detection, response time and Nernstian response (slope, mV dec^{-1}) of nanoparticle-based sensors are summarized in Table 1. The structures of the molecules used in these studies are given in Fig. 4.

Studies using nanoparticles as sensor materials are summarized in different review articles in the literature. Silver nanoparticle-based electrochemical sensors developed for the determination of organic pollutants in water were investigated by Zahran et al. [39]. Ghosh et al. have written a comprehensive review article on nanoparticle-based sensors for monitoring the quality and shelf life of food products [40]. Rahimpour et al. presented nanoparticle–based sensors developed for the detection of coronaviruses as a mini–review [41]. Willner and Vikesland investigated nanomaterials used in the determination of organic pollutants in the literature [42]. Nanomaterial-based sensors for the detection of pathogens and microbial toxins in the food industry in the literature are summarized by Abedi-Firoozjah et al. [43]. In addition, studies on the applications of nanoparticle-based sensors in biomedical, food and agricultural fields have been comprehensively summarized in different review articles [44–47]. In this review article, sensors developed using the potentiometry technique, unlike those in the literature, are summarized.

4. Conclusion

The unique properties of nanomaterials have a wide place in the field of sensors as well as in many application areas. Nanosensors are sensors widely used to collect nanosized data that cannot be obtained by normal sensors. Nanosensors are prepared using nanoparticles such as silver, platinum and palladium. Nanosensors are much smaller, easily adjustable, lightweight and portable. The most important feature that distinguishes nanosensors from normal sensors is their ability to detect smaller particles. Potentiometric sensors have an important place in many areas due to the unique features they offer [48–51]. Potentiometric sensors prepared with nanoparticles have become the focus of attention in recent years, and studies on this subject will continue rapidly in the future.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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