***Review:***

# Magnetic Solid Phase Extraction for Determination of Dyes in Food and Water Samples

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***Abstract:*** *Recently, magnetic solid-phase extraction (MSPE) is an important technology due to its use in analytical chemistry, biotechnology, and medicinal fields. MSPE shows rapid isolation of target analyte from large volume samples, the huge surface area of magnetic nanoparticles (MNPs), and simplicity in application due to using an external magnetic field instead of using packing column, centrifuge, and filter papers. The aim of this review is to evaluate the extraction and determination of dyes in food and water samples by using the MSPE technique.*

***Keywords:*** *adsorption; desorption; magnetic solid phase extraction; separation*

## ■ INTRODUCTION

There are more than a thousand different types of dye that can be commercially and frequently used in the textile, food, photography, cosmetics, plastics, and pharmaceutical industries. Dyes are at the forefront of the pollutant due to being hard to remove from clean water [1]. Dyes have a complex chemical structure that makes them more resistant to fading on exposure to water, light, and chemical materials. Because of that, many dyes are hard to remove or decolorize from wastewater; so, dyes are an effective risk to water, soil, fauna, plant, cattle, and human. For example, the highest toxicity was found in the diazo direct and basic dyes [2].

Due to mentioned reasons, dyes should be determined in different environmental samples by using suitable extraction methods, such as the liquid-liquid extraction (LLE) from aqueous solutions followed by UV–visible spectrophotometer for methylene blue dye [3], liquid-liquid microextraction (LLME) coupled with HPLC-DAD for Sudan dyes from tomato chili sauces [4], dispersive liquid-liquid microextraction (DLLME) based on the salting-out phenomenon followed by HPLC for Sudan dyes in turmeric powder, chili sauce, and water samples [5], solid-phase extraction (SPE) coupled with LC-ESI-MS/MS of disperse dyes in water samples [6], solid-phase microextraction (SPME) coupled with UPLC-MS for Sudan dyes in tomato sauce and hot-pot samples [7], microextraction by packed sorbent (MEPS) coupled with gas chromatography-mass spectrometry (GC–MS) of azo dyes in textiles [8], matrix solid-phase dispersion (MSPD) followed by HPLC–DAD of Sudan dyes in condiments and sauces [9], and stir-bar sorptive extraction (SBSE) coupled with HPLC of Sudan dyes in fruit juice and lake water samples [10]. Extraction methods require a long time, filter papers, centrifuge, slow packing of sorbent into the column, and a large volume of sample or solvent. To overcome these limitations, magnetic solid-phase extraction (MSPE) offers a quick extraction method that has ease of preparation with large-scale production, ease of operation by applying an external magnetic, and ease of surface modification due to many hydroxyl (–OH) groups on the surface of iron oxide. Moreover, it is considered a green chemistry method because of the ease of recoverability of magnetic particles that can be reused after rinsing a few times. It requires a small volume of sample and solvent without using filter papers and a centrifuge [11]. The aim of this review is to present the MSPE technique used for the extraction of dyes in food and water samples.

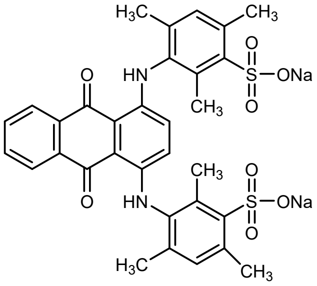
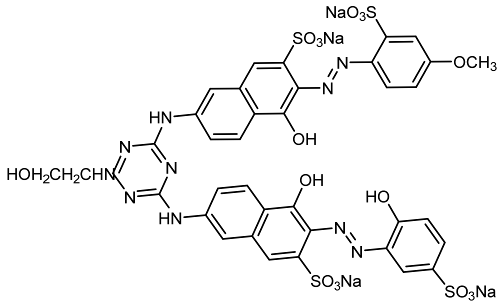
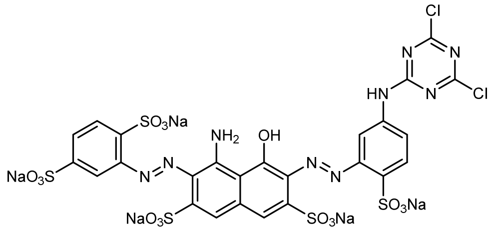
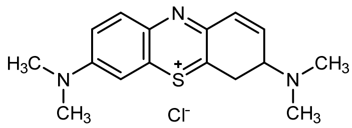
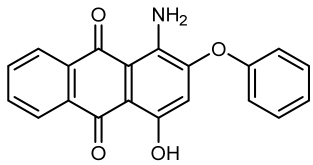
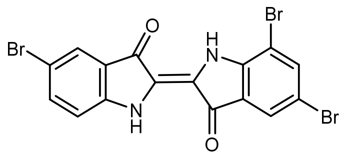
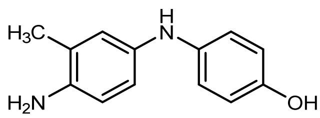
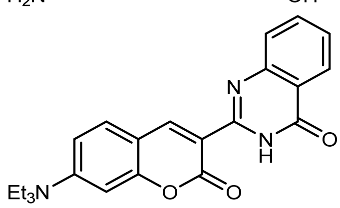
## ■ CLASSIFICATION OF DYES

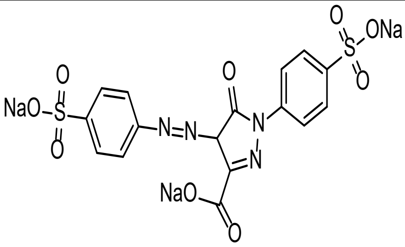
There are many structural classifications of dyes, such as disperse, base, acidic, anthraquinone-based, diazo, azo, and metal complex dyes. Dyes are classified in Table 1 according to their solubility in water, chemical constitution, and application in the industry [12-18] while the chemical structure of some dyes examples are listed in Table 2.

**Table 1.** Classification of dyes

| Type of dye | Solubility | Functional group or constituent | Application |
|---|---|---|---|
| Acid dyes (anionic dyes) | Soluble in water | Sulphonic, carboxylic acid, azo, anthraquinones, triarylmethane, iminoacetone, nitro, nitrous, and/or quinoline | Nylon, silk, modified acrylic, wool, paper, food, and cosmetics |
| Direct dyes (anionic dyes) | Soluble in water when in the presence of salts and electrolytes | Azo compounds with thiazoles, phthalocyanines, and oxazines | Cotton and regenerated cellulose, paper, leather, and nylon |
| Reactive dyes (anionic dyes) | Soluble in water with the sodium salt of sulphonic acid groups | Azo, anthraquinone, and phthalocyanine | Fiber (cotton, wool, or nylon) |
| Basic dyes (cationic dyes) | Soluble in water as chloride, sulfate, or nitrate salts | Azo, anthraquinone, triarylmethane, methane, thiazine, oxazine, acridine, and quinoline | Modified acrylic, modified nylon, modified polyesters, and papers, and some of them have biological activity and are used in medicine as antiseptics |
| Dispersive dyes (non-ionic dye) | Insoluble in water | Azo dyes | Dyeing of nylon, polyamide, and polyester |
| Vat dyes (non-ionic dye) | Insoluble in water | Anthraquinone and indigo | Dyeing cellulosic fibers, such as leuco-soluble salts, after reduction in an alkaline bath (sodium hydrosulfite) |
| Sulfurous dyes | Insoluble in water but can be made soluble in water by treating them with reducing agents | Contain sulfur linkage within their molecules | Applied to cotton, linen, cotton, and jute after alkaline reduction bath, with sodium sulfite as reducing agent |
| Fluorescent dyes (group of the xanthenes) | Soluble in water | Fluorescent carbonyl dyes (coumarins, naphthalimides, perylenes, benzanthrone derivatives, benzoxanthones, and benzothioxanthones), rhodamines, and methine fluorescent dyes | Fluorescent dyes for textiles, daylight fluorescent pigments, dyes for lasers, solar collectors, electroluminescence, analytical, biological, and medical applications |
| Dye precursors | Insoluble in water | Acid Yellow 23 (pyrazole), Acid Orange 7 (monoazo), Acid Red 92 (xanthene), Acid Violet 43 (anthraquinone), 4-hydroxypropylamino-3-nitrophenol (nitro aniline), HC Yellow No. 2 (nitro aniline), *p*-phenylenediamine, *p*-aminophenol, 4-amino-2-hydroxytoluene (aromatic substituted) | Commercial hair dying systems can be divided into two main categories, oxidative or non-oxidative |

**Table 2.** Examples of dyes

| Type of dye | Functional group or constituent | Molecular formula | Structure | Ref. |
|---|---|---|---|---|
| Acid dyes | Anthraquinone | $C_{32}H_{28}N_2Na_2O_8S_2$ |  | [19] |
| Direct dyes | Direct red 243 | $C_{38}H_{28}N_{10}Na_4O_{17}S_4$ |  | [20] |
| Reactive dyes | Reactive blue 109 | $C_{25}H_{12}Cl_2N_9Na_5O_{16}S_5$ |  | [21] |
| Basic dyes | Methylene blue (Basic Blue 9) | $C_{16}H_{18}ClN_3S$ |  | [22] |
| Dispersive dyes | Dispersive red 60 | $C_{20}H_{13}NO_4$ |  | [23] |
| Vat dyes | Vat blue 5 | $C_{16}H_6Br_4N_2O_2$ |  | [24] |
| Sulfurous dyes | Sulphur blue 7 | $C_{13}H_{14}N_2O$ |  | [25] |
| Fluorescent dyes | Disperse yellow 186 | $C_{21}H_{19}N_3O$ |  | [26] |

| Type of dye | Functional group or constituent | Molecular formula | Structure | Ref. |
|---|---|---|---|---|
| Dye precursors | Acid yellow 23 | $C_{16}H_9N_4Na_3O_9S_2$ |  | [27] |

## CLASSIFICATION OF MAGNETIC MATERIALS

There are four types of classification of magnetic materials depending on how they react with the magnetic field as described in Fig. 1 [28-30].

Ferromagnetic or superparamagnetic materials have been used widely in the MSPE technique as sorbent magnetic nanoparticle forms due to their high magnetic moments, ease of preparation, biocompatibility, and small size particles. Chemical, biological, and physical methods have been used for synthesizing iron oxides like magnetite ($Fe_2O_3$), spinel ferrites ($MFe_2O_4$), and maghemite ($\gamma$-$Fe_3O_4$).

## HISTORY AND PRINCIPLES OF MSPE

The first authors to publish on MSPE were Safarik et al. [31]. It depends on adding a magnetic sorbent into an aqueous sample to adsorb the target analyte. Then, the sorbent target analyte is separated by using an external magnetic field. After that, the addition of solvent to the analyte with used external magnetic again to collect the liquid analyte, which is determined by different analytical techniques [32]. The mechanism separation of MSPE is based on the interaction between the surface functional groups of the sorbent with the analyte. The types of interactions are dispersion, ionic, hydrogen

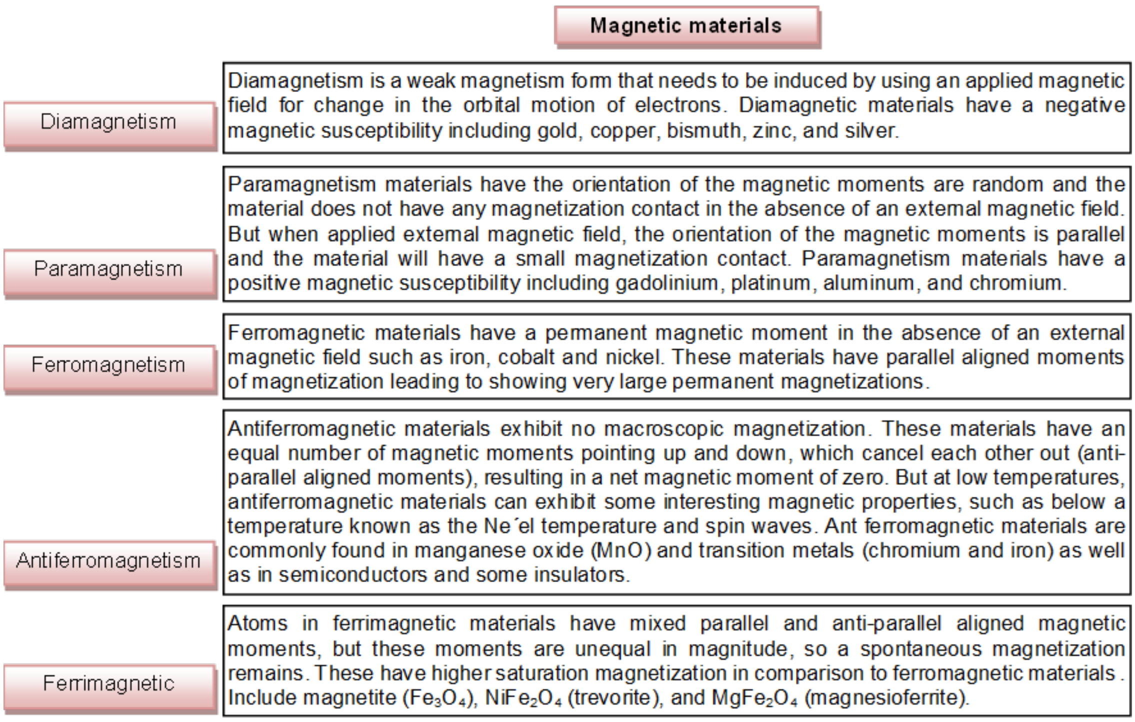



**Fig 1.** Classification of magnetic materials

bonding, dipole-induced dipole, and dipole-dipole forces. The dipole-dipole interactions, hydrogen bonding, and π-π interactions are the base of the analyte retention mechanism, but chemical bonding interactions are not used in the separation and retention of analyte because of their irreversibility. Other properties affect the interaction of the sorbent with the analyte, such as solubility, concentration, and polarity of the analyte with the choice of the right sorbent and solvent [33].

MSPE principles include three steps: first, the analyte was captured or adsorbed by the addition of MNPs into the sample solution (MNPs are dispersing in the sample solution). Then, the separation step uses the external magnet to separate the target analyte from the solution. The last is the desorption step, which is analyte desorption from the surface of MNPs using an appropriate solvent. Acidic solutions are used as a good solvent for the inorganic analyte and an organic solvent is used for the organic analyte. Then, HPLC coupled to MS or UV-Vis is often preferred for the separation and determination of the analyte (Fig. 2) [34-35].

## ■ PREPARATION OF MAGNETIC NANOPARTICLES

The magnetite of $Fe_3O_4$ and γ-$Fe_2O_3$ are widely used in the preparation of the magnetic core for the MSPE method [36]. Many methods have been used for the preparation of $Fe_3O_4$, such as thermal decomposition, microemulsion, high-energy ball mill, hydrothermal synthesis, sonochemical synthesis, and co-precipitation. The advantage of a thermal decomposition method to obtaining a narrow particle size distribution of MNPs, size control, and a high degree of crystalline. This method is based on the decomposition of $Fe(acac)_3$ with oleylamine, an 1,2-alkanediol and oleic acid in a high boiling point ether [37]. Microemulsion method based on microemulsion route above room temperature (65 °C). The microemulsion solution consists of forming the ternary system cyclohexane (organic phase)/Brij-97 (a non-ionic surfactant)/aqueous solution of $FeSO_4{\cdot}7H_2O/FeCl_3{\cdot}6H_2O$ in the different mole ratio. MNPs obtain from this method are higher in saturation magnetization and smaller in size [38]. A high-energy ball mill is a simple and low-cost technique. Ball milling in a hardened steel vial was used for prepared the sample ($Fe^{2+}/Fe^{3+}$), the molar ratio of $Fe^{2+}/Fe^{3+}$ was 20:1, and the sample was milled to 96 h with a rotation speed of 200 rpm to obtain a 12 nm size of the magnetite particles [39]. In the hydrothermal synthesis method, the average diameters were 25 or 14 nm for α-$Fe_2O_3$ or $Fe_3O_4$, respectively. Hydrothermal reaction $FeSO_4$ solution was heated at 473 K and using *n*-decanoic acid ($CH_3(CH_2)_9COOH$) or *n*-decylamine ($CH_3(CH_2)_9NH_2$) as a surface modifier. At a higher temperature over room

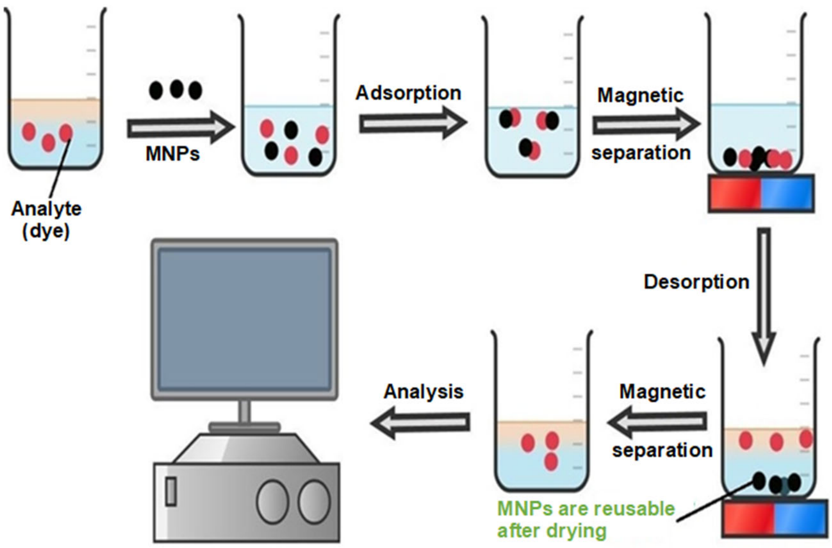



**Fig 2.** Steps of dye determination with MSPE

temperature, the solubility of surface modifier increased in water, but the dielectric constant of water decreased and reacted with the surface of the nanoparticles. This method is environmentally economical and without the use of organic solvents [40]. Sonochemical synthesis of $Fe(acac)_3$ in water under an argon atmosphere with tetraglyme as a solvent. Water amount had allowed control of the surface area and size of MNPs to obtain surface-modified ultra-small (1–2 nm) [41]. Co-precipitation is the simplest method used to prepare magnetite MNPs from aqueous $FeCl_2·4H_2O/FeCl_3·6H_2O$ solutions with a concentration ratio of 2:1 by the addition of ammonia in a vacuum or nitrogen at 80 °C or less. This method was used to obtain magnetite MNPs with diameters of 2–4 nm [42]. The morphology and microstructure of the MNPs were characterized by IR, XRD, TEM, and SEM.

## ■ MODIFICATION OF MAGNETIC NANOPARTICLES

Surface modification of MNP was used to ensure sensitivity and selectivity for the target analyte and to avoid weakened magnetism due to agglomerate and oxidation. Surface modification with $Fe_3O_4$ MNPs is commonly used to functionalize the surface of the particles and improve their selectivity for specific analytes. $Fe_3O_4$ MNPs have similar properties to $Fe_2O_3$ MNPs or FeO MNPs, but they are typically more stable, high magnetization, high surface area, and large surface-to-volume ratio. $Fe_3O_4$ MNPs is that they have a higher surface area than FeO MNPs, which can improve their binding capacity for target analytes [43-44].

$Fe_3O_4$ has been intensively investigated for the modification of MNPs because of its superparamagnetic, non-toxic, low Curie temperature, high coactivity, and biocompatible. Physical modification methods include plasma radiation, ultraviolet, adsorption, and deposition of the surfaces. In the chemical modification, the surface of MNPs was changed by chemical reactions. The external layer of MNPs was modified by three main materials: inorganic substances, organic substances, and metal-organic frameworks (MOFs) (Fig. 3).

## ■ MODIFICATION OF INORGANIC SUBSTANCES

One of the well-coated is $SiO_2$, which is prepared by the sol-gel method. This method's advantage is to obtain a spherical particle's shape, a size-controlled and it is considered a simple method for synthesizing MNPs [45]. Metallic oxides such as $ZrO_2$, $CoFe_2O_4$, CoO, NiO, $TiO_2$, and $Al_2O_3$ are usually used to modify MNPs. Coating using metallic oxide provides several advantages, such as the prevention of agglomeration and increased stability biocompatibility, and hydrophilicity of MNPs. For example, $Fe_3O_4@Al_2O_3$ core-shell NPs were more air-stable than the naked $Fe_3O_4$ NPs, $Fe_3O_4$@ZnO core-shell NPs were antioxidation and $Fe_3O_4@CoFe_2O_4$ have more magnetic properties than $Fe_3O_4$ NPs [46]. Composite materials were used in MSPE methods, such as $Fe_3O_4@ZrO_2$@*N*-cetylpyridinium and

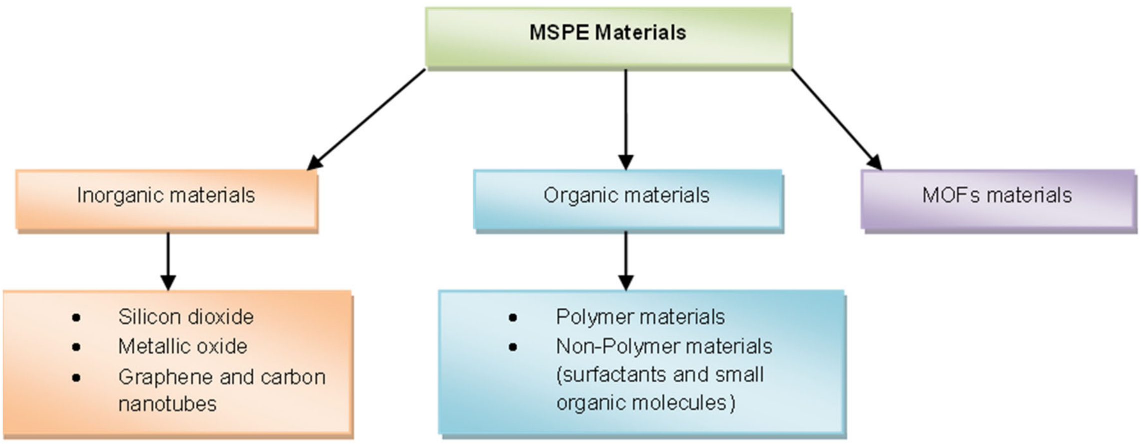



**Fig 3.** Materials used for modification of the MSPE method

alumina-coated $Fe_3O_4$ MNP modified by dithizone and sodium dodecyl sulfate (SDS) in acidic media [47-48]. Ring-structured compounds and carbon-based have been adsorbed by graphene and carbon nanotubes from different samples. For example, $Fe_3O_4@SiO_2@G@PIL$ was magnetite graphene modified with ionic liquids and through electrostatic interactions; graphene oxide was modified with the amino-functional silica-coated $Fe_3O_4$spheres [49].

## MODIFICATION OF ORGANIC SUBSTANCES

There are many advantages of polymer modification. It can effectively prevent MNPs oxidation, reduce agglomeration, and dipole-dipole interaction to become weakened between MNPs. 3D network polymer types with stability and adsorption capabilities are molecularly imprinted polymers (MIPs). Covalent organic frameworks (COFs) modification allows through van der Waals forces, hydrogen bonding, and the size-exclusion effect to adsorb target analyte [50]. Non-polymer materials include two types; the first type is surfactants, which include octadecyl trimethyl ammonium chloride (OTAB), cetyltrimethylammonium bromide (CTAB), and SDS, which have a good extraction ability, high chemical stability, and large specific surface area. The second type of non-polymer material is small organic molecules, including oleic acid and fatty acid, which improve the stability and dispersion of MNPs [51].

## MODIFICATION OF METAL-ORGANIC FRAMEWORKS (MOFs) SUBSTANCES

Metal-organic frameworks (MOFs) are crystalline inorganic-organic hybrid materials that give rise to new materials which have an internal surface area, porous, tunable pore size, and hollow structure. Magnetic MOFs materials were used in MSPE, such as MOF-5 ($Zn_4O(BDC)_3$) (BDC=1,4-benzenedicarboxylate) with a cubic 3D porous structure, ZIF-8($[Zn(MeIM)_2]$) and ZIF-67 ($[Co(MeIM)_2]$) (MeIM=2-methylimidazole). The advantages of MOFs are large pore volume, mechanical and chemical stability, superparamagnetism, and working at a high temperature, making MOFs more useful for the MSPE [52-54]. Overall, the choice of inorganic, organic, or MOF modification will depend on the specific application and the properties required for the MNPs. Organic modifications are often preferred for biological applications, where biocompatibility and dispersibility in solution are critical, while inorganic modifications are often preferred for chemical and environmental applications, where chemical stability and magnetic properties are more important. MOF-coating MNPs can provide higher stability and selectivity, and they can be used in a variety of applications, including water treatment, drug delivery, catalysis, lithium-ion batteries, and luminescence [55].

## MAGNETIC TEXTILE SOLID-PHASE EXTRACTION (MTSPE)

MTSPE is using magnetically modified textile materials as a new type of pre-concentration method. It Includes a piece of fabric textile 1 × 1 $cm^2$ with an office stapler, which is rapidly and easily separated magnetically by using an external magnetic field [56]. MTSPE is considered a green chemistry method due to its advantage of simplicity, readily, and low cost. Furthermore, this method is easy separation and recovery of the analytes, reducing the need for additional purification steps. Many materials were used for modified the textile fibers to provide a high surface area and a porous structure as a 1% chitosan solution was applied to determine azorubine, indigo carmine, tartrazine, and blue fountain ink dyes [57-58]. Polysaccharide κ-carrageenan combination with agarose was applied to determine Nile blue A, safranin O, and methylene blue [59].

## APPLICATIONS AND OPTIMIZATION OF THE MSPE

MNPs are widely used in analytical chemistry, medicine, bioanalytical, environmental pollutants, and food samples. MSPE has been used to determine estrogens in milk [60], phthalic acid esters in carbonated soft drink [61], tetracyclines in milk [62], organophosphorus pesticides in water [63], phthalate monoesters in urine [64], Co(II) and Hg(II) in water and food [65], polycyclic aromatic hydrocarbons in grilled meat [66], lignans in sesame oil [67], a free fatty acid in edible oils [68], and non-steroidal anti-inflammatory drugs (naproxen, ketoprofen, and diclofenac) in biological and water and samples [69]. However, the large surface area and high magnetic responsiveness of magnetic nanoparticles make them excellent sorbents for a variety of applications. To achieve the best extraction efficiency, various conditions, such as the sorbent categories, the pH, sorbent amount, extraction time, desorption solvent, the volume of desorption solvent, desorption temperature, and desorption time, were optimized (Table 3).

**Table 3.** Optimization factors of the MSPE procedure

| Analyte | Magnetic material | Sample pH | Sorbent amount | Extraction time | Desorption solvent | Vol. of desorption solvent | Desorption temperature | Desorption time | Ref. |
|---|---|---|---|---|---|---|---|---|---|
| Basic violet 7, Basic red 13 and Basic orange 21 | M-S-RGO | 10 | 5.0 mg/mL | 20 min | Acetone with 5% acetic acid | - | - | - | [73] |
| CV, MV, MB, and MG | MNPs-POLP | 10 | 20.0 mg | 15 min | Methanol | 2 mL | Room temperature | 10.0 min | [82] |
| MR and MO | MHNTs | 7.5 | 60.0 mg | 10 min | Methanol containing 1% acetic acid | 2 mL | 25 °C | - | [83] |
| MG(Cationic) | MWCNT@$Fe_3O_4$ | 6–8 | 60.0 mg | - | Acetonitrile | 1 mL | Room temperature | 2.0 min | [84] |
| Sudan I, II, III and IV(azo dye) | $Fe_3O_4$@PANI | 7 | 8.0 mg | 15 min | Ethanol | 2 mL | Room temperature | 4.0 min | [85] |
| MG | $Fe_3O_4$-$NH_2$@HKUST-1@PDES | 4 | 5.0 mg | 108 min | - | 1 mL | 31.65 °C | - | [74] |
| Sudan I, II, III and IV | MPCDPs(C) | 7 | 4.0 mg | 20 min | Methanol | 3 mL | - | - | [75] |
| Sudan I-IV, Para Red and Sudan Red 7B | $Fe_3O_4$-$NH_2$@MIL-101 | - | 3.0 mg | 2 min | Ethyl acetate | 2 mL | - | 10.0 min | [76] |
| Sudan Black B, Sudan Red 7B, Para Red and Sudan I, II, III, IV | cMWCNT-γ-$Fe_2O_3$ | 8 | 40.0 mg | 15 min | Acetonitrile | 0.3 mL | - | 4.0 min | [77] |
| Sunset yellow, allure red and tartrazine | $Fe_3O_4$-fullerene-activated carbon | 4.0 | 0.01 mg | 15 min | Methanol solution containing NaOH $10^{-3}$ M | 500 µL | - | 5.0 min | [87] |
| Triphenylmethane dyes (MG and CV) | γ-$Fe_2O_3$@CNM | 7 | 1.0 mg | 5 min | Methanol containing 0.2% formic acid | 1 mL | Room temperature | 30.0 s | [87] |
| Sudan I, II, III and IV | magnetic $Fe_3O_4$ NPs | 7 | 0.5 g | 20 min | Methanol | 5 mL | Room temperature | 1.0 min | [78] |
| MG and CV | $Fe_3O_4$@$SiO_2$-Flu | 5 | 30.0 mg | 20 min | Methanol | 0.5 mL | Room temperature | 2.0 min | [88] |
| Rhodamine B | $Fe_3O_4$@SiO2@IL | 3 | 0.1 g | 10 min | Ethanol | 4.0 mL | 30 °C | 5.0 min | [79] |
| Sudan red | Fe@NiAl-LDHs | 7 | 80.0 mg | 60 min | Acetone | 7.5 mL | - | 9.0 min | [89] |
| Sudan dyes (I, II, III, and IV) | $Fe_3O_4$ MNPs/PSt | 4 | 70.0 mg | 15 min | Acetonitrile | 4.0 mL | Room temperature | 1.5 min | [80] |

| Analyte | Magnetic material | Sample pH | Sorbent amount | Extraction time | Desorption solvent | Vol. of desorption solvent | Desorption temperature | Desorption time | Ref. |
|---|---|---|---|---|---|---|---|---|---|
| Sudan dyes (I, II, III, and IV) | Magnetic argan press cake nanocellulose (MNC) | 3 | 50.0 mg | 10 min | Methanol | 2.0 mL | Room temperature | 5.0 min | [81] |
| Congo Red and Basic Red 2 | ZIF-8@$CoFe_2O_4$ | 7 | 10.0 mg | 15 min | Methanol and water | | Room temperature | 1.0 min | [90] |
| Rose Bengal | C-MIONPs | 6 | 0.5 g | - | Methanol | 5.0 mL | 25 °C | - | [91] |
| Acridine orange, Amido black 10B, Bismarck brown, Congo red, Crystal violet, Malachite green, Safranin O | Magnetically modified Spent coffee grounds | - | 30.0 mg | 90 min | Methanol | 2.0 mL | Room temperature | 20.0 min | [92] |
| Acridine orange, CV, MG, Safranin O, Methylene blue | Magnetically modified *S. horneri* biomass | - | - | - | - | - | - | - | [93] |
| MG and CV | $Fe_3O_4$/GO magnetic nanoparticles | 6 | 0.13 mg | 15 min | Acetonitrile/acetic acid | 0.2 mL | Room temperature | 15.0 min | [94] |

## FOOD ANALYSIS

Azo dyes are used for coloring food products due to their low cost and high stability to the oxygen, pH, and light compared to the dyes obtained from natural sources [70]. Many countries have forbidden synthetic azo dyes using in food products because they are shown to be genotoxic, potentially neurotoxic, and carcinogenic additives [71]. For example, Tartazin dye causes genotoxicity in rodents, and allura red and brilliant blue cause allergic reactions. Tartrazine, sunset yellow, erythrosine, and allura red can be carcinogenic [72]. MSPE was successfully used for the removal, analysis, and determination of cationic dyes from different samples (food and water) (Table 4). Cui et al. [73] developed a novel adsorbent magnetic sulfonated reduced graphene oxide (M-S-RGO) based on (M-S-RGO) with HPLC–MS/MS for analysis and determination of Basic violet7, Basic red 13 and Basic orange 21 in food samples. This method was applied for a wide range of basic dyes with lower LOD 0.01–0.2 µg/L [73]. A new $Fe_3O_4$-$NH_2$@HKUST-1@PDES-MSPE (Polymeric deep eutectic solvents (PDES)) based on 3-acrylamidopropyl trimethylammonium chloride/D-sorbitol functionalized amino-magnetic ($Fe_3O_4$-$NH_2$) metal-organic framework (HKUST-1-MOF) composites) was used for the extraction and determination of MG and CV cationic dyes from fish samples, with the successful recovery of 89.43–100.65% for MG and 95.29–98.03% for CV indicating that this method was a successful application in extracting cationic dyes in fish samples [74]. Sudan dyes are class 3 carcinogens, so using these dyes in food is considered illegal. Determination Sudan dyes were developed by using magnetically modified porous β-cyclodextrin polymers (MPCDPs) coupled with HPLC. MPCDPS was a good analytical adsorbent for the separation and concentration of Sudan dyes in food and water samples [75]. Magnetic trimeric chromium octahedral metal-organic framework ($Fe_3O_4$-$NH_2$@MIL-101) combined with HPLC was used to determine Sudan I-IV, Para Red, and Sudan Red 7B in tomato sauce with a good RSD of ≤ 9.2% [76]. Sudan Black B, Sudan Red 7B, Para Red, and Sudan I, II, III, IV were extracted by using $\gamma Fe_2O_3$ magnetic nanoparticle functionalized with carboxylated multiwalled carbon nanotube (cMWCNT-$\gamma$-$Fe_2O_3$) coupled with HPLC in chili products and ketchup [77]. $Fe_3O_4$ MNPs were used for the extraction of Sudan dyes from chili oil, chili powder, tomato paste, and different water samples coupled with HPLC for separation and determination of

**Table 4.** Application of MSPE

| Analyte | Type of dye | Magnetic material | Sample | Technique | Limit of detection | Recovery | Ref. |
|---|---|---|---|---|---|---|---|
| Illegal basic dyes (Basic violet 7, Basic red 13 and Basic orange 21) | Cationic | M-S-RGO | Frozen grass carp, frozen yellow croaker, and tomato sauce | HPLC-MS/MS | 0.01–0.2 μg/L | 70–110% | [73] |
| MV, MB, MG, CV, and NR from MR | Cationic | MNPs-POLP | Aqueous solution | UV-Vis HPLC | - | - | [82] |
| and MO | Anionic azo dye | MHNTs | Water samples | | MR: 0.042 μg/L MO: 0.050 μg/L | MR:85–87% MO: 89–93% | [83] |
| MG and GV | Cationic | MSPE method based on MWCNT@$Fe_3O_4$NPs | Water samples | HPLC-FLD | MG: 0.22 ng/mL GV: 0.09 ng/mL | 87.0–92.8% | [84] |
| Sudan I, II, III and IV | Azo dye | $Fe_3O_4$@PANI | Water samples | UFLC-UV | 0.041–0.151 ng/mL | 92.4–106.9% | [85] |
| MG and CV | Cationic | $Fe_3O_4$-$NH_2$@HKUST-1@PDES-MSPE | Fish samples | UV-Vis | MG: 98.19 ng/mL CV: 23.97 ng/mL | MG: 89.43–100.65% CV: 95.29–98.03% | [74] |
| Sudan I, II, III and IV | Azo dye | MPCDPs(C) and MPCDPs(M) | Food samples and water samples | HPLC | MPCDPs(C): 0.013–0.054 ng/mL MPCDPs(M): 0.028–0.039 ng/mL | Food samples: 85.8–102.8% Water samples: 88.3–103.2% | [75] |
| Sudan I-IV, Para Red and Sudan Red 7B | Azo dye | $Fe_3O_4$-$NH_2$@MIL-101 | Tomato sauce | HPLC-DAD | 0.5-2.5 mg/kg | 72.6–92.9% | [76] |
| Sudan Black B, Sudan Red 7B, Para Red and Sudan I, II, III, IV | Azo dye | cMWCNT-γ-$Fe_2O_3$ | Chilli products and ketchup | HPLC | 0.13-0.84 ng/mL | - | [77] |
| Sunset yellow, allure red and tartrazine | Anionic azo dye | $Fe_3O_4$-fullerene-activated carbon | Water samples | Capillary electrophoresis | 1.0-2.0 mg/L | 95–106% | [86] |
| Triphenylmethane dyes (MG and CV) | Cationic | γ-$Fe_2O_3$@CNM-based MSPE | Spring water, lake water, fishpond water, seawater, and mineral wastewater | LC-MS/MS | 0.004 ng/mL | MG: 73.4–101.5% CV: 83.1–102.7% | [87] |
| Sudan I, II, III and IV | Azo dye | Magnetic $Fe_3O_4$ NPs | Food samples (chili oil, chili powder and tomato paste) and water samples (tap and river water) | HPLC | 0.02 μg/L | Water samples: 91.9–98.1% Food samples: 92.9–109.9 % | [78] |
| MG and CV | Cationic | $Fe_3O_4$@$SiO_2$-Flu | Water samples | UV-Vis | 2.82–3.27 ng/L | 88–96% | [88] |
| Rhodamine B | Cationic | $Fe_3O_4$@$SiO_2$@IL | Chili powder | HPLC | 0.08 μg/L | 99.0–100.9% | [79] |
| Sudan red | Cationic | Fe@NiAl-LDHs | Water samples | HPLC | 0.002–0.005 μg/L | 97.6–105.7% | [89] |
| Sudan dyes (I, II, III, and IV) | Azo dye | $Fe_3O_4$ MNPs/PSt | Red wines, juices, and mature vinegar | UFLC-UV | 0.0039, 0.0063, 0.0057, and 0.017 ng/mL | 76.3–96.6% | [80] |
| Sudan dyes (I, II, III, and IV) | Azo dye | Magnetic argan press cake nanocellulose (MNC) | Barbeque and ketchup sauces | Capillary liquid chromatography | 0.05–0.07 μg/L | 93.4–109.6% | [81] |
| Congo Red and Basic Red 2 | Congo red is azo dye and Basic Red 2 is cationic | ZIF-8@$CoFe_2O_4$ | Aqueous solution | UV-Vis | - | - | [90] |
| Rose Bengal | Xanthenes dye | C-MIONPs | Brucella Antigen solution and water samples from the Karoon River | UV-Vis | $5.91 \times 10^{-3}$ μg/mL | 95.7–98.9% | [91] |

| Analyte | Type of dye | Magnetic material | Sample | Technique | Limit of detection | Recovery | Ref. |
|---|---|---|---|---|---|---|---|
| Acridine orange, Amido black 10B, Bismarck brown, Congo red, Crystal violet, Malachite green, Safranin O | Acridine orange is a fluorescent dye. Black 10B, Congo red, CV, and MG are azo dyes. Safranin O is azonium compound | Magnetically modified Spent coffee grounds | Aqueous Solution | UV-Vis | - | - | [92] |
| Acridine orange, CV, MG, Safranin O, Methylene blue | Acridine orange isa fluorescent dye | Magnetically modified *S. horneri* biomass | Aqueous solution | UV-Vis | - | - | [93] |
| MG and CV | Cationic | $Fe_3O_4$/GO magnetic nanoparticles | Water samples | HPLC | MG: 0.091 μg/L<br>CV: 0.120 μg/L | 91.5–116.7% | [94] |

dyes, with LOD values down to 0.02 μg/L for all samples [78]. $Fe_3O_4$@$SiO_2$NPs were coated with three ionic liquids [HMIM]$PF_6$, [BMIM]$PF_6$, and [OMIM]$PF_6$ to prepare fluconazole-functionalized $Fe_3O_4$@$SiO_2$ nanoparticles ($Fe_3O_4$@$SiO_2$@IL) coupled with HPLC for the determination of Rhodamine B in Chili powder, RSD value was 0.51%, and this MNPs could be reused up to 10 times [79]. Nanocomposite of polystyrene-coated magnetic nanoparticles (MNPs/PSt) coupled with UFLC-UV was used for the determination of Sudan dyes in different types of drinks and RSDs were lower than 9.6% [80]. Sudan dyes in the barbeque and ketchup sauces were extracted using magnetic/non-magnetic argan press cake nanocellulose coupled with capillary liquid chromatography and SD achieved was lower than 3.46% [81].

## ■ WATER ANALYSIS

Synthetic dyes are used to produce plastics, rubber and textiles which cause environmental pollution (water and soil). Most dyes are toxic and cause skin irritation, dermatitis, and allergy. They are harmful to humans and aquatic biota. MSPE is a new technique that has been used in the extraction of dyes from wastewater, tap water, and river water samples. MSPE was used for the extraction of dyes from water samples due to their selectivity, low volume of solvents, and high throughput (Table 4). Adsorption of cationic dyes (methyl violet (MV), methylene blue (MB), malachite green (MG), crystal violet (CV), and neutral red (NR)) from aqueous solution by using *Platanus orientalis* leaf powder (MNPs-POLP) coupled with UV-Vis spectrophotometer [82]. Mixed hemi micelle based on magnetic halloysite nanotubes and ionic liquids (MHMSPE) was prepared from ionic liquid [C16mimBr] and MHNTs to determination of anionic dyes (methyl red (MR) and methyl orange (MO)) in different water samples, lower RSD was achieved in this method, 2.5–5.4% for lake water, and 1.6–3.1% for tap water [83]. Multiwalled carbon nanotubes modified-$Fe_3O_4$ nanoparticles (MWCNT@$Fe_3O_4$ NPs) was used for extraction of MG and gentian violet (GV) dyes in water samples and followed by HPLC-FLD to give RSD values of 4.6–5.9% [84]. Sudan dyes were extracted by using $Fe_3O_4$@polyaniline particles ($Fe_3O_4$@PANI) coupled with UFLC-UV in water samples (lake water, rainwater, surface water, reservoir water and tap water) and RSD were found in the range of 1.6–6.8% [85]. $Fe_3O_4$-fullerene-activated carbon followed by capillary electrophoresis was used for extraction and analysis of anionic dyes (allure red, sunset yellow, and tartrazine) in water samples and RSD was found to be less than 10% [86]. Caramelized carbonaceous shell-coated γ-$Fe_2O_3$ (γ-$Fe_2O_3$@CNM-based MSPE) coupled with LC-MS/MS was used for the extraction and analysis of MG and CV dyes in spring water, fishpond, lake, sea, and industrial wastewater, RSD below 5.2% for MG and RSD below 5.5% for CV dyes [87]. Cationic dyes (MG and CV) were extracted and determined using $Fe_3O_4$@$SiO_2$-Flu followed by UV-Vis spectrophotometer in Caspian seawater and wastewater, and RSD was computed to be 4.77–4.17% [88]. Fe@NiAl-LDHs (layered double hydroxide) coupled with HPLC was used for the extraction and determination of Sudan red dyes in Ming Tombs Reservoir water, Changping Park water, and Binhe Park water, with low LOD from 0.002 to 0.005 μg/L [89]. Adsorption of Congo Red and Basic Red 2 was achieved using core–shell heterostructure of 24 $CoFe_2O_4$-Zeolitic

Imidazolate Framework-8 (ZIF-8@$CoFe_2O_4$) followed by a UV-Visible spectrometer with a high removal efficiency of 97% [90]. CTAB-coated magnetic iron oxide nanoparticles (C-MIONPs) coupled with a UV-Visible spectrometer were used for the separation and determination of RB dyes in Karoon river water and Brucella Antigen solution. RSD values were found to be 4.1 and 1.1% [91]. Adsorption of seven different types of dyes (Acridine orange, Amido black 10B, Bismarck brown, CR, CV, MG, Safranin O) was achieved by using a magnetically modified spent coffee grounds coupled with UV-Vis spectrometer in potable water [92]. Adsorption of acridine orange, CV, MG, Safranin O, and MB by using low-cost adsorbent magnetically modified *S. horneri* biomass followed by UV-Vis spectrometer [93]. Finally, $Fe_3O_4$/graphene oxide nanoparticles ($Fe_3O_4$/GO) coupled with HPLC were successfully applied to the extraction and determination of MG and CV dyes in the pond, lake, and river samples [94].

## ■ CONCLUSION

MSPE technique has the advantages of a simple synthesis of MNPs, selectivity to the target analyte, low cost due to using an external magnet which avoids the need for filtration or centrifugation steps, and avoiding using columns packed by sorbents that need to consume a long time to prepare these columns. Moreover, its ability to extract and pre-concentrate target analytes from complex matrices such as food and water samples. Dyes are often used in the food industry to enhance the appearance of food products. MSPE can be used to extract and quantify these compounds in food and water samples due to its high selectivity, sensitivity, and simplicity of operation. MSPE technique has been coupled with different analytical instruments such as UV-visible spectrometer, HPLC, LC-MS/MS, and capillary electrophoresis for the determination of dyes amount in food and water samples. Most past studies focus on the determination of dyes in the food or water samples, so efforts should be made to expand studies to soils, sediments, and other environmental samples. Future methods should seek to automate the MSPE method and couple it with the online system.

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