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Review Article

# Compendious review on 3D-printed gels for effluent treatment

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# **1. Introduction**

One of the most trending topics in recent literature is effluent treatment [1–[3\]](#page-5-0), which involves the treatment of industrial wastewater by removal of pollutants like dyes, oils, hazardous chemical species, and heavy metal ions. If industrial wastewater is left untreated, it disrupts the aquatic ecosystem, while simultaneously rendering it unfit for human consumption [4–[6\]](#page-6-0). There are several methods for effluent treatment which can be classified into physicochemical, chemical, and electrochemical processes. Adsorption, a physicochemical process, is a phenomenon by which some molecules have an affinity towards the surface of a material and get adhered to it. Materials, including powders [[7](#page-6-0)], crystals  $[8]$  $[8]$  $[8]$ , membranes  $[9,10]$  $[9,10]$  $[9,10]$  $[9,10]$ , zeolites  $[11]$ , composites  $[12,13]$  $[12,13]$  $[12,13]$ , and gels [\[14](#page-6-0)] have been investigated for adsorption. Gels are preferred among these materials, due to their unique structure.

Gels form an interpenetrating three-dimensional (3D) network of solvent present in excess and a cross-linker, giving them a nonNewtonian nature and having more internal adsorption sites, Due to this intrinsic property, gels tend to have a higher adsorption capacity than materials in other forms. The current polymer gel market estimate is \$35.40 billion and is only expected to grow at a compound annual growth rate (CAGR) of 6.6 % through 2032. This has paved the way for major advancements, such as the extraction of adulterants present in food [[15\]](#page-6-0), removal of dyes [\[16\]](#page-6-0) and heavy metal ions from wastewater [[14\]](#page-6-0), separation of oil-water emulsions [\[17](#page-6-0)], and adsorption of greenhouse gases, including carbon dioxide and methane [18–[20](#page-6-0)] from the atmosphere, which incorporate gels as the adsorbent material. However, the synthesis of gels has its demerits, such as wastage of material as well as scalability issues [\[21](#page-6-0)] since the same methods cannot be reproduced on a large scale with identical results. Another challenge is the lack of control over the homogeneity of gels [[21\]](#page-6-0), consisting of additional components added to enhance their properties. Most conventional methodologies do not take into consideration the complex designs of the final product, rendering it useful only for limited applications. To

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overcome the shortcomings of gel synthesis by conventional methods, 3D printing has been explored as an alternative to the preparation of gels [[22,23](#page-6-0)]. The novel methods of gel synthesis using 3D printing consist exclusively of direct ink writing (DIW), which has been accepted for the precision and control it provides over other methods [[24,25\]](#page-6-0).

The existing gap in the literature regarding this topic highlights the necessity for a comprehensive review paper to examine the application of gels in effluent treatment through pollutant adsorption. Hence, this review provides valuable insights into the limitations of conventional treatment methods, paving the way for advancements in effluent treatment technologies. Additionally, DIW has emerged as a versatile and dependable technique capable of fabricating gels for use in effluent treatment. The comparative advantages of DIW in contrast to conventional methodologies have been thoroughly scrutinized, concomitant with an in-depth exploration of the properties inherent in gels produced through 3D printing, as reported in contemporary literature. This review delves into key parameters influencing the adsorption capacity of the gels, providing insight into adsorption isotherms [\[26,27](#page-6-0)] and adsorption kinetic models [\[28,29](#page-6-0)]. Importantly, it elucidates the pivotal role of 3D-printed gels in adsorbing a diverse range of pollutants in effluent treatment. This review also contemplates the potential evolution of this approach for future applications.

## **2. Conventional methods for gel synthesis**

The effluent treatment contains a variety of pollutants, such as oil, dyes, and heavy metal ions, having different physical and chemical properties. Therefore, specific gels have been fabricated for specific applications [\[30,31](#page-6-0)]. Over the years, several methods of preparation have been designed specifically for the chemistry of each gel, such as ionic gelation and extrusion gelation for the preparation of Montmorillonite nanosheet-gelatin-sodium alginate hydrogel [[32,33](#page-6-0)], which adsorbs lead ions from wastewater. The maximum size of pores during morphological characterization is 130 μm in the case of the ionic gelation method. Hydrothermal synthesis and sol-cryo methods for the synthesis of graphene-coated carbon nanotube aerogels [[34,35](#page-6-0)] have been studied for the adsorption of dyes and the separation of oil and water [\[36](#page-6-0)]. The adsorption of heavy metal ions, including  $Co^{2+}$  and  $Cu^{2+}$ , has been correlated with TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl) cellulose nanofibrils based gels, which is prepared using D2O as a solvent [\[37](#page-6-0)]. Poly(3-acrylamidopropyl)-trimethylammoniumchloride-*co*-2-acrylamido-2-methylpropanesulphonic acid (ZI-SAH) copolymer gels were prepared using free-radical polymerization with BIS as a cross-linker and ammonium persulfate as an initiator. Synthesized at 60 ◦C for 30 min, ZI-SAH showed *>*75 % removal efficiency after multiple cycles and successfully removed crystal violet and congo red [ $38$ ]. Common materials for membrane fabrication include silica (SiO<sub>2</sub>), alumina ( $Al_2O_3$ ), zeolites, silicon carbide (SiC), titania (TiO<sub>2</sub>), and zirconia ( $ZrO<sub>2</sub>$ ).  $ZrO<sub>2</sub>$  membranes can be colloidal or polymeric gels with pore sizes from 65 nm to less than 1 nm, suitable for desalination, protein recovery, and complex separations. They offer higher water permeability, less fouling, better restoration of initial permeability after cleaning, corrosion resistance in acidic and alkaline media, and a lifespan exceeding 8 years [39–[49](#page-6-0)]. Rosangela A. Jacques et al. utilized silica gel with an aniline group, having a particle size of 0.02–0.05 mm. SiAn was found to be an efficient adsorbent for removing Cu(II), Cr(III), and Fe(III) from dilute aqueous solutions and wastewater. The maximum adsorption capacities were 16.02 mg/g for Cr(III), 11.18 mg/g for Cu(II), and 17.37 mg/g for Fe (III)  $[50]$  $[50]$ .

Conventional sol-gel methods utilize various materials, including ceramics, polymers, activated carbons, and other inorganic supports and adsorbents, for wastewater treatment. However, these methods elucidated previously carry inherent constraints that tend to confine the potential properties of gels within specific bounds. For instance, in the case of ionic gelation, the resultant pore size of gels is constrained, significantly impacting their adsorption capacity [\[51](#page-6-0)], a pivotal parameter. Similarly, techniques such as hydrothermal synthesis and the sol-cryo method are effective, but they suffer from prolonged processing durations and notably lack energy efficiency. Current conventional methodologies are regrettably grappled with deficiencies in precision and control, which are necessary for fine-tuning gel properties. These insufficiencies underscore the ongoing necessity for the development of alternative methodologies.

# **3. DIW for gels**

With the advent of technology, additive manufacturing has garnered attention for its ability to fabricate intricate and complex structures without any wastage of material. One of the most versatile techniques within layer-by-layer manufacturing is DIW [\[52](#page-6-0),[53\]](#page-6-0), which can utilize a wide range of raw materials including, but not limited to gels [\[24](#page-6-0)], polymers [[54\]](#page-7-0), ceramics [[55\]](#page-7-0), composites [\[56](#page-7-0)], metals [\[57](#page-7-0)] and metal oxides [[58\]](#page-7-0) in the form of inks. The setup consists of a nozzle, a 3-axis platform, and a computer [[59\]](#page-7-0). The 3-axis platform is attached to the nozzle and has multidirectional mobility to facilitate printing in variable directions. The nozzle diameter and length of the syringe control the pressure at which ink flows out, influencing the dimensions/thickness of the final product. The computer is used to pre-design the geometry of the final product with the help of modeling software, such as AutoCAD and SolidWorks. DIW nozzles vary in size ranging from 0.1 μm in diameter to several dm, hence being used for microfibrication to the concrete building because it is performed at room temperature and hence isothermal rheology has a major role to play [\[60](#page-7-0)]. 3D printing technology allows precise control over the material composition and structure of gels, minimizing waste. Traditional methods often result in significant material loss, whereas 3D printing uses only the necessary amount of gel material. The ability to tailor 3D printed gels to specific contaminants in effluents enhances the efficiency of treatment processes [[61\]](#page-7-0). This customization reduces the need for multiple treatment stages, lowering operational costs and time. Conventional effluent treatment often relies heavily on chemicals for coagulation and flocculation. 3D printed gels can be designed to have inherent adsorption and catalytic properties, reducing or eliminating the need for additional chemicals. This not only cuts down on chemical expenses but also minimizes the environmental impact of chemical residues [\[62](#page-7-0)]. The precision and efficiency of 3D printed gels in effluent treatment led to significant operational savings. Improved treatment performance reduces the need for energy-intensive processes and decreases the overall operational footprint [[63\]](#page-7-0).

#### *3.1. Advantages of DIW*

DIW proposes significant advantages over other traditional approaches, including versatility, efficient waste minimization, superior morphological characteristics, cost-effectiveness, and fabrication of intricate and complex structures. The expansive versatility in utilizing a diverse spectrum of raw materials [[64,65\]](#page-7-0) for structure printing confers a notable advantage. This flexibility enables amalgamation with various additives, such as fillers [[66\]](#page-7-0), stabilizers [[67,68\]](#page-7-0), and plasticizers [\[69](#page-7-0)]. When the additives are integrated with the gel, they enhance the intrinsic properties of the resultant printed product. DIW epitomizes an additive manufacturing paradigm, wherein the construction of the final product is carried out well, meticulously, and layer upon layer [\[70](#page-7-0)]. Within this framework, even if remnants of raw materials persist in post-product fabrication, they do not align with the conventional notion of waste. Rather, they remain valuable reservoirs poised for future utilization, embodying a prudent approach to resource management. This discerning practice not only mitigates cost implications through the reduction of material wastage but also aligns harmoniously with the tenets of sustainable development [\[71](#page-7-0)].

Porosity plays an important role in the determination of the adsorption capacity of a gel, as a larger pore size indicates more internal sites available for adsorption. During the preparation of montmorillonite nano (MMTN) sheet-based gel via ionic gelation method [\[33](#page-6-0)], reported the maximum pore size to be within the range of 80–130 μm. On preparing the same gel using DIW, the pore size was reported to be several hundred microns long and the microstructural analysis depicted the presence of lamellae formed by scaling of MMTN from the surface and intercalation [[72\]](#page-7-0). Another noteworthy consideration is the genesis of an ordered structure, conferring a sense of uniformity to the inherent properties of the bulk material. This can be attributed to the components that constitute the DIW equipment. The 3-axis platform, a fundamental component, facilitates the intricate process of object printing by offering the capacity to maneuver and construct in a multitude of spatial orientations and directions. Moving forward, improvisation of the mechanism of extruding ink from the nozzle by using piezoelectric materials, pressurized air, and motor-driven pistons has enabled the fabrication of intricacies and complexities involved in certain structures, as shown in Fig. 1. As DIW is an additive manufacturing process, the usage of precursors is extremely precise and limited to the quantity required to create the final product, which is a useful aspect in avoiding material wastage. This is especially advantageous when precursors used are expensive and are scarce in availability. In addition, it is much more feasible to scale up the production of gels to achieve the quantity-based requirements of industries for effluent treatment when compared with the conventional chemical methods of gel preparation [[73](#page-7-0)].

While DIW offers numerous advantages when compared with its disadvantages, it is essential to contemplate specific limitations. Notably, the relatively slow printing speeds, typically in the range of 5–10 mm/s [[69\]](#page-7-0), give rise to concerns regarding the overall time invested in the complete product printing process. The UDMA-TEGDMA-fumed silica inks utilized in these experiments exhibit shear thinning behavior. The viscosity-frequency curves conform to the Carreau-Yasuda Cross model, with near-zero shear viscosities ranging from 20 to 120 Pa s. Considering that shear strain rates are calculated as the stage speed (1.5–9.5 mm/s) divided by the stand-off distance (100–250 μm), the shear strain rates in this experiment are approximately 10–100 Hz within the nozzle-substrate gap, where viscosities are approximately 0.5–5 Pa s. As anticipated, increasing the TEGDMA content reduces the viscosity of the ink. [\[75](#page-7-0)], a parameter influenced primarily by the chosen material and nozzle diameter. However, this concern is amenable to resolution through a methodical trial-and-error



**Fig. 1.** Formation of intricate patterns through DIW. Reprinted with permission from Ref. [\[74](#page-7-0)], Copyright 2021, Elsevier.

approach.

# *3.2. General method of preparing ink for gels*

The primary step comprises the preparation of a suspension of additives for incorporation into gels. For the enhancement of the adsorption capacity and efficiency of gels, additives such as montmorillonite nanosheets or activated carbon are added [\[72](#page-7-0),[76\]](#page-7-0). These additives exist in a solid state and are powdered, followed by the formation of suspension in solvents with the help of surfactants. Subsequently, gelating agents are added to the suspension as gelators are responsible for initializing the cross-linkage of polymer networks, resulting in a gel formation [\[36](#page-6-0),[72,77\]](#page-7-0). The use of gelatin, sodium alginate, and TOCNF as the gelating species depends on the type of gel to be fabricated. Mechanical stirring and ultrasonic stripping [\[72](#page-7-0)], manual stirring [\[76](#page-7-0)], or ultrasonication [[74\]](#page-7-0) are some of the methods utilized to disperse and distribute the suspended species uniformly within the solvent medium. Depending on the gel, a high temperature may be required for homogenization, as used by Ref. [[72\]](#page-7-0). Some gels form when exposed to cold temperatures, such as the formation of GEL-CNT wet gel [[74\]](#page-7-0), where the temperature was as low as 10 ◦C. Conversely, the final mixture was heated to 65 ◦C for 2 h to form MMTN-based gel [\[72](#page-7-0)]. This stage of the preparation methods influences the rheological behavior of the ink, such as rigidity, viscosity, and modulus of storage and loss. [Fig.](#page-3-0) 2 depicts the overview of the general method of preparing inks for 3D printing. While the former is a generalized idea of the preparation of inks using gels, some methods may require extra steps. According to Ref. [[74\]](#page-7-0), GEL-CNT wet gels were rigidized through a coacervation reaction between ethanol solvent and gelatin, followed by critical point drying to assist removal of surfactants and carbonization at high temperatures to obtain Gr-CNT aerogels [\[74](#page-7-0)]. [Fig.](#page-3-0) 3 shows the image of the final product of an activated carbon-based gel printed by DIW.

The process for preparing gels and setting up the DIW system can vary, contingent on the specific gel used. Factors, including the inner diameter of the nozzle, are influenced by the viscosity of the ink. Additionally, temperature control and certain post-printing procedures are necessary to ensure the stability of the final product. Ink viscosity determines the printability of the composition, so the colloidal volume fraction ratio at the gelation point must be high to ensure large elastic properties in the target ink gel. Thus, highly concentrated pure nanomaterials or DIW ink with additives (crosslinkers, binders, etc.) are preferred for freestanding monolith fabrication. The elastic modulus must be slightly larger than the viscosity during the gelation stage to preserve ink and monolith shape integrity but lower during the extrusion stage. Ink viscosity determines the printability of the composition, so the colloidal volume fraction ratio at the gelation point must be high to ensure large elastic properties in the target ink gel. Thus, highly concentrated pure nanomaterials or DIW ink with additives (crosslinkers, binders, etc.) are preferred for freestanding monolith fabrication. The elastic modulus must be slightly larger than the viscosity during the gelation stage to preserve ink and monolith shape integrity but lower during the extrusion stage. Cooling or heating/UV light exposure, phase changes, and mixing with reactive components can enhance viscosity in the deposited layers on the printing platform [78–[80\]](#page-7-0). These diverse parameters are presented *in* [Table](#page-3-0) 1.

#### **4. Adsorption isotherm**

Adsorption isotherm is the change in the amount of adsorbate adsorbed, plotted as a function of pressure at a constant temperature [[86\]](#page-7-0). It is a key feature in determining the nature of bond formation between adsorbent and adsorbate, whether it is physisorption or chemisorption, as depicted in [Fig.](#page-4-0) 4. Furthermore, it possesses the capability to ascertain whether the adsorption is confined to a monolayer or if it extends into multiple layers, offering a deeper understanding of the adsorption process [[87\]](#page-7-0). This can help to determine

<span id="page-3-0"></span>

**Fig. 2.** Schematic of the preparation of DIW ink for gels.



**Fig. 3.** Images of the product after 3D printing. Reprinted with permission from Ref. [[76\]](#page-7-0) Copyright 2022, Multidisciplinary Digital Publishing Institute (MDPI).

whether the gel is suitable for a specific application or not. There are multiple models for adsorption, out of which the most important models are the Freundlich model, Langmuir isotherm, and Brunauer Emmett Teller (BET) isotherm, which are empirical models. They are classified based on layers of adsorption and the nature of interaction between adsorbent and adsorbate species.

Freundlich isotherm describes the adsorption of gas molecules by solid adsorbent as a function of pressure at constant temperature and reports chemical adsorption.

The linear form of an equation for the Freundlich isotherm model is

described as Eq. (1) [\[88](#page-7-0)]:

$$
q_e = K_F C_e^{1/n}
$$
 (1)

where  $q_e$  is the concentration of adsorbate and  $C_e$  is the equilibrium adsorbate concentration.  $K_F$  and n are adsorption coefficients.

Langmuir isotherm describes monolayer adsorption, which is purely physical in nature. Any adsorption process that fits into this model occurs at low adsorption densities. Eq. (2) is an expression that fits the Langmuir adsorption isotherm model [[88\]](#page-7-0).

$$
q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{2}
$$

where  $K<sub>L</sub>$  is the ratio of adsorption rate to the desorption rate and the maximum adsorption capacity in the Langmuir model is represented by qm.

Another model is the BET adsorption isotherm (Eq. (3)), which is for a multilayer adsorption process that is purely physical in nature. Each adsorption site is considered to be isolated from other adsorption sites, meaning there is no interaction between neighboring sites [\[88](#page-7-0)].

$$
q_e = \frac{q_m K_1 C_e}{(1 - K C_e)[1 - K C_e + K_1 C_e]}
$$
\n(3)

where  $K_1$  and  $K_2$  are adsorption equilibrium parameters in the first and upper layers, respectively.

#### **Table 1**

Parameters for different gels used for DIW.

Parameters/Gels	Max pore size	Needle diameter	Flow rate	Printing speed	Temperature of printing $(^{\circ}C)$	Post-printing process	References
CelloZIF gel	$20 - 900$ nm $(ZnO)$ and $100 - 600$ nm (Hmim)	$410 \mu m$	$70 - 120$ $\frac{0}{0}$	$10 - 80$ mm/ s	$23 \pm 2$	Soaked in $Hm/m^2$ sat. Solution for 24 h	Abdelhamid et al. [77]
MMTN based hydrogel	Several $100 \mu m$	$0.6$ mm	25-30 psi	$20 \text{ mm/s}$	25	Sprayed with 3 wt% CaCl <sub>2</sub> Soln. for 30 min, $+$ freeze-drying at $-70$ °C for $24$ h.	Miao et al. [72]
Gr-CNT-Aerogel	Mostly between 1 and $10 \text{ nm}$	$500 \mu m$			10		Jeong et al. [74]
Activated carbon-based gel	$2.5 - 6.0$ nm	$0.838$ mm	$0.6$ mL/ min	$\overline{a}$		Carbonization at 900 °C	Comroe et al. [76]
Na-based geopolymer	9.58 nm	$840 \mu m$	$0.5$ and 1L/min	$10$ mm/s	25	Heated in the oven at 75 °C for 2 days and washed in deionized water for 8 h at flow rate 1L/h	Franchin et al. [81]
Dehydrofluorinated poly (vinylidene fluoride)		$250 \mu m$	$\overline{\phantom{0}}$	$12 \text{ mm/s}$ and 15 mm/s	23	PVDF and dPVDF films underwent phase inversion in a DI water bath, replaced multiple times over 24 h.	Imtiaz et al. <b>821</b>
Waterborne polyurethane acrylate based bioink		$0.61$ mm		$6 \text{ mm/s}$	30	Samples underwent ion exchange in 4 $wt\%$ CaCl2 for 1 h	Li et al. [83]
NaOH, SiO <sub>2</sub> -sol, metakaolin and kaolin based geopolymer		$0.6$ mm			25	Curing at $60^{\circ}$ C for 7 days	Jin et al. $[84]$
Methacrylated chitosan, methacrylated gelation and chitosan based nGO based bioink	$27.1 - 46.4 \,\mu m$	$260 \mu m$	$4-6$ mm/ s	$\overline{\phantom{0}}$	10	UV irradiation followed by freeze- drying	Feng et al. [85]

<span id="page-4-0"></span>

**Fig. 4.** Schematic representations of different types of adsorption processes.

Moreover, the sips isotherm model has been formulated by contributions from both Freundlich and Langmuir models. It is used in cases where only one layer of adsorbate has affinity towards the adsorbent. This can be applied to systems where the adsorbent surface may be the same or may consist of heterogeneity. Eq. (4) is an expression that represents sips adsorption isotherm model [[88\]](#page-7-0).

$$
q_e = \frac{q_{ms}K_sC_e^{n_e}}{1 + K_sC_e^{n_e}}
$$
\n<sup>(4)</sup>

where the maximum adsorption amount is represented by  $q_{ms}$ , and both  $K_s$  and  $n_s$  are the Sips constants.

The adsorption isotherm models play a significant role in determining whether a gel is suitable for certain applications or not. If the gel exhibits an adsorption pattern that fits into the Freundlich model, then it can be inferred that the type of adsorption is chemical in nature, meaning chemical bonds are formed between adsorbate and adsorbent during the adsorption process. The different types of adsorption processes that can be determined by adsorption isotherms are previously shown in Fig. 4. Chemical bonds tend to have higher energy, they are consequently difficult to break, making the desorption process more cumbersome and affecting the reusability of gel.

Though there are semi-empirical isotherm models, such as the Volmer model, Aranovich model, and ion exchange models, the aforementioned models are extensively prevalent and frequently referenced within the academic literature.

# **5. Adsorption kinetics**

The entirety of the adsorption takes place in three steps; external diffusion is where the adsorbate gets adsorbed on the surface of the adsorbate. The subsequent phase entails the mass transfer of adsorbate molecules into the interior of the adsorbent through the network of pores it encompasses, a phenomenon commonly referred to as internal diffusion. Once the adsorbate has reached the internal active sites for adsorption, the adsorption process continues within the adsorbent bulk. Adsorption kinetics include a set of models that give information on the rate of an adsorption process through the determination of the ratedetermining step [[89\]](#page-7-0). Pseudo-first-order (PFO) and pseudo-second-order (PSO) kinetic models are generally the most commonly used models.

Pseudo-first-kinetic model is derived from the Langmuir kinetic model and assumes that external diffusion is the rate-determining step. Any adsorption process that fits the PFO model performs physisorption when the initial concentration of adsorbate is high. Eq. (5) is a rate expression for the PFO models.

$$
\frac{dq_t}{dt} = k_{p1}(q_e - q_t) \tag{5}
$$

where the adsorption capacities at equilibrium and any time *t* are expressed by  $q_e$  and  $q_t$ ,  $k_{p1}$  is the rate constant of the adsorption process under the PFO kinetic model. Similarly, the pseudo-second-kinetic model (Eq. (6)) is a simplified version of PFO and describes the nature of bonds between adsorbate and adsorbent to be chemical in nature. Chemisorption according to the PSO model is the rate-determining step, and the rate equation can be expressed as:

$$
\frac{\mathrm{d}q_t}{\mathrm{d}t} = k_{p2}(q_e - q_t)^2 \tag{6}
$$

Where  $k_{p2}$  is the rate constant of the adsorption process, which follows the PSO kinetic model.

The pivotal properties for assessing the practicality of a gel in an adsorption process revolve around its adsorption capacity and efficiency. Certain gels may exhibit distinctive affinities for specific pollutants, while others can demonstrate comparable adsorption capabilities across various pollutants. Another key aspect to note is the preparation method used, which also influences the adsorption behavior of gels. [Table](#page-5-0) 2 presents the adsorption properties and preparation method of a few gels.

## **6. Applications of 3D-printed gels in effluent treatment**

Industrial discharge in the textile industry consists of dyes, such as methylene blue and rhodamine B. They are soluble in water and may present an imminent environmental danger, due to their inherent toxicity [[92,93](#page-7-0)]. Gels from Ref. [[33\]](#page-6-0) have been used for the removal of dyes from wastewater, but their adsorption capacity is limited. By harnessing DIW, highly ordered and layered gels can be obtained with extensive porosity for exposure to additional internal adsorption sites

#### <span id="page-5-0"></span>**Table 2**

Adsorption properties of gels and their preparation methods.

Gels	Preparation method	Adsorption capacity/efficiency	References
MMTN based hydrogel	<b>DIW</b>	134 mg/g (Pb <sup>+2</sup> )	1721
CelloZIF gel	<b>DIW</b>	85 % (RhB) 98 % (MeB) 101.2 mg g $(Cu^{+2})$ 33.5 mg/g $(Co^{+2})$	[77]
PVA/MMT- based hydrogel	freeze-thaw method	94.4 % at 50 °C.	[90]
<b>TOCNF</b> based aerogel	Ammonia-induced solid- state polymerization	35 % (MeB)	[91]

[[72\]](#page-7-0). In petroleum and chemical industries, one of the key pollutants detected are oils [\[94](#page-7-0)], which are immiscible with water, and pose a significant threat by potentially interfering with the functions of critical equipment employed in effluent treatment processes. Cellulosic gels have been studied for the separation of oil from water, out of which CelloZIFs are currently being synthesized with DIW to increase their adsorption capacity and efficiency [[77\]](#page-7-0).

Heavy metals such as lead, cobalt, and copper undergo ionization in water. The ions are extremely toxic at low doses, due to their ability to anchor to DNA and stall protein-affiliated functions [\[95](#page-7-0),[96\]](#page-7-0). These are often found in electrochemical industrial wastewater and can be removed through adsorption by gels. Effluents in conventional treatment plants emit various greenhouse gases out of which carbon dioxide and methane are the most common [\[97](#page-7-0)]. Large quantities of these gases are harmful to the environment and contribute to significant global warming [[98,99](#page-7-0)]. Efforts have been made to synthesize gels to adsorb these toxic gases to reduce concentration in the overall atmosphere.

#### **7. Concluding remarks and future scope**

This paper has comprehensively reviewed the application of 3Dprinted gels for effluent treatment. Gels are particularly studied for this purpose due to their unique interpenetrating structure, which provides additional internal sites and enhances adsorption capacity. Moreover, a critical examination of conventional gel preparation methods reveals several limitations, necessitating the search for viable alternatives. Direct Ink Writing (DIW), an additive manufacturing process, has the potential to overcome these drawbacks and offers benefits such as easier scale-up of production, cost-effectiveness, and the creation of higher-quality gels with adjustable porosity. These advantages collectively underscore the transformative potential of DIW in effluent treatment, indicating a progressive shift towards more efficient and sustainable methodologies. The innovative application of DIW for gel preparation is gaining momentum and recognition, showing promising potential for use in gels designed for effluent treatment. Based on the available literature, a general method for gel preparation using DIW is provided, followed by a brief description of important parameters such as adsorption isotherms and adsorption kinetics. There is an apparent research gap necessitating deeper exploration of the adsorption properties of gels, an aspect inadequately covered in existing literature.

Extensive research on gels for effluent treatment and the preparation of gels using DIW highlights the need for comprehensive studies addressing the adsorption properties of these 3D-printed gels for efficient contaminant removal from effluent. In 2022, the polymer gel market was valued at USD 34.50 billion and is projected to grow at a compelling CAGR of 6.6 % over the next decade. Consequently, a vital discourse is imperative regarding the optimal gel structure to provide products with the highest adsorption capacity and efficiency. It is noteworthy that the references cited in this review predominantly focus on the selective adsorption of a single type of pollutant from effluent. Future research should concentrate on the adsorption of multiple

pollutant types and explore the use of advanced functional gels, extending beyond pollutant removal to unlock additional benefits. Such research initiatives are not only desirable but also vital to propel further advancements in the field of effluent treatment.

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# **Code availability**

Not applicable.

# **Ethics approval**

The submitted article complies with the journal's ethical guidelines and does not contain the results of studies involving humans and/or animals.

## **Consent to participate**

Not applicable.

### **Consent for publication**

The authors consent to publish the article on acceptance.

#### **CRediT authorship contribution statement**

**Apsara Panchapakesan:** Writing – original draft, Methodology, Investigation, Data curation, Conceptualization. **Priyanka Anil Dalave:** Data curation, Formal analysis, Investigation, Writing – review  $\&$  editing. **Balasubramanian Kandasubramanian:** Writing – review & editing, Visualization, Validation, Supervision, Resources, Conceptualization. **Sikiru O. Ismail:** Writing – review & editing, Validation, Investigation, Data curation.

### **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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