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# Polypyrrole-based adsorbents for Cr(VI) ions remediation from aqueous solution: a review

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## ABSTRACT

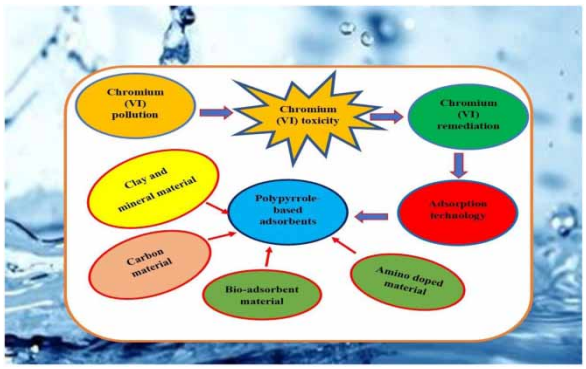
Anthropogenic activities are principally responsible for the manifestation of toxic and carcinogenic hexavalent chromium (Cr(VI)) triggering water pollution that threatens the environment and human health. The World Health Organisation (WHO) restricts Cr(VI) ion concentration to 0.1 and 0.05 mg/L in inland surface water and drinking water, respectively. The available technologies for Cr(VI) ion removal from water were highlighted with an emphasis on the adsorption technology. Furthermore, the characteristics of several polypyrrole-based adsorbents were scrutinized including amino-containing compounds, biosorbents, graphene/graphene oxide, clay materials and many other additives with reported effective Cr(VI) ion uptake. This efficiency in Cr(VI) ions adsorption is attributed to enhanced redox properties, increased number of functional groups as well as the synergistic behaviour of the materials making up the composites. The Langmuir isotherm best described the adsorption processes with maximum adsorption capacities ranging from 3.40–961.50 mg/g. The regeneration of Cr(VI) ion-laden adsorbents was studied. Ion exchange, electrostatic attractions, complexation, chelation reactions with protonated sites and reduction were the mechanisms of adsorption. Nevertheless, there are limited details on comprehensive adsorbent regeneration studies to prolong robustness in adsorption–desorption cycles and utilization of the Cr(VI) ion-laden adsorbent in other areas of research to limit the threat of secondary pollution.

**Key words:** adsorption, adsorption isotherms, chromium (VI) ions, pollution, polypyrrole, toxicity

## HIGHLIGHTS

- Hexavalent chromium sources, pollution and toxicity.
- Remediation through absorption technology.
- Polypyrrole-based adsorbents.
- Utilization of Cr(VI)-laden adsorbent waste in other areas of research.

## GRAPHICAL ABSTRACT



## 1. INTRODUCTION

Heavy industrialisation and technological advancement has culminated in the discharge of large volumes of heavy metal ions including hexavalent chromium (Cr(VI)) (Rajeev *et al.* 2019; Ahmad *et al.* 2021). The major sources of Cr(VI) are anthropogenic, besides some natural sources with the former contributing to 70% of the Cr(VI) in water (Zhitkovich 2011). This review focuses on the main sources of Cr(VI) ions and their toxic effects, as well as remediation using adsorption performance of hybrid polypyrrole-based adsorbents. Several adsorbents have been documented for Cr(VI) ion removal. However, some challenges have been encountered including tedious and expensive methods of preparation, generation of additional solid wastes, low adsorption capacities owing to the low specific surface areas and the unavailability of active functional groups (Dinker and Kulkarni 2015; Liu *et al.* 2018a; Hato *et al.* 2019; Du *et al.* 2020; Li *et al.* 2020). It is worth reviewing polypyrrole (PPy)-based adsorbents because of their unique and enhanced properties. PPy has shown great prospects in adsorption application due to its reputable environmental stability, extraordinary conductance, desirable redox properties and easiness of processing (Das and Prusty 2012; Maity *et al.* 2019). Moreover, it is inexpensive, easy to synthesize, eco-friendly and has abundant amine groups which facilitate adsorption and chelation of various organic and inorganic groups. Cationic nitrogen atoms on the PPy moiety act as adsorption sites for heavy metal ions through hydrogen bonding or electrostatic attraction (Mahmud *et al.* 2015; Hato *et al.* 2019; Maity *et al.* 2019). Consequently, the removal of Cr(VI) ions using PPy has been further enhanced by its easy acid-base doping-dedoping process, incredible stability in the environment and reversibility, exhibiting high adsorption capacities (Mahmud *et al.* 2015; Hato *et al.* 2019). Cr(VI) ions can be oxidatively reduced to Cr(III) by PPy synthesized through chemical polymerization using ammonium peroxydisulphate (APS) oxidant under acidic conditions. Great strides have been made in the synthesis of PPy in the presence of various dopants, additives and a second component to improve the adsorption efficiency. Conditions used to synthesize PPy determine the structural texture and features of the PPy materials such as surface area, porosity and the availability of binding sites (Das and Prusty 2012; Hato *et al.* 2019).

Additionally, the recovery of PPy solid adsorbent from the solution after Cr(VI) ion adsorption has posed difficulties (Jiang *et al.* 2018). Henceforth, coating PPy on other substrate materials such as cellulose, biomass, carbon materials, mesoporous materials, metals, and metal oxides among others in the synthesis of composite adsorbents is one of the strategies used to improve the cycle, adsorption efficiency and reusability. This surface modification is imperative in the preparation stage as it leads to the exploitation and application of the organic and inorganic groups, polymeric compounds, biological materials and ionic liquids in functionalization on the PPy materials. These can work as oppositely charged moieties which interact with Cr(VI) ions by electrostatic attraction.

While many adsorbents have been documented for Cr(VI) ion removal, it is worthy discussing PPy-based adsorbents. PPy-based adsorbents specifically for the removal of toxic Cr(VI) ions have not been reviewed in the published literature. So far, attempts have been made to deal with a variety of pollutants (Mahmud *et al.* 2015; Das *et al.* 2019) and general polymer-based magnetic nanocomposites for Cr(VI) ion removal (Hato *et al.* 2019). Thus, there is ample scope to review PPy-based adsorbents for Cr(VI) ion removal judging by the ever-increasing studies on PPy-based adsorbents for Cr(VI) ion removal. Furthermore, the above unique characteristics of these adsorbents make their review novel. This review gives the current literature on the adsorption of Cr(VI) ions from aqueous solution using various PPy-based adsorbents. Different pyrrole oxidation polymerization processes can produce both simple PPy and PPy-based adsorbents such as PPy-modified mats and membranes (Zhan *et al.* 2018a, 2018b), PPy-bio-adsorbents (Alsaiari *et al.* 2021), PPy-magnetic material (Chigondo *et al.* 2019), PPy-amino material (Kera *et al.* 2017), PPy-carbon material (Setshedi *et al.* 2015), PPy-modified clay composites (Ballav *et al.* 2014a, 2014b) and PPy-inorganic hybrid composites (Alzahrani *et al.* 2021). These materials exhibit potential application as PPy-based adsorbents for Cr(VI) ions.

Chromium, a transition element, is the 21st abundant element in the Earth's crust. It was discovered in 1797 by the French chemist Louis Nicholas Vauquelin (Pereira *et al.* 2021). The major chromium compound is ferric chromite ($FeCrO_4$) mainly found in South Africa, Russia, Kazakhstan, India and the Philippines (Loock *et al.* 2014) Chromium is widely used in catalysis, electroplating, chrome plating, leather tanning, glass industries, wood preservation and textile industries (Dinker and Kulkarni 2015; Zhao *et al.* 2016; Shahid *et al.* 2017; Jiang *et al.* 2018; Tumolo *et al.* 2020). Table 1 shows some industrial products containing Cr(VI) ions. This certainly demonstrates that Cr(VI) ions pose a water pollution challenge as most of these compounds are highly soluble. Humans are also highly exposed to these Cr(VI)-containing products.

**Table 1** | Products that contain hexavalent chromium (Perry 2021)

| Product | Types of hexavalent chromium chemicals |
|---|---|
| Pigments in paints, inks and plastics | lead chromate, chrome green, molybdenum orange, zinc chromate, calcium chromate, potassium dichromate, sodium chromate |
| Anti-corrosion coatings (spray plating and spray coating) | Chromic trioxide (chromic acid), zinc chromate, barium chromate, calcium chromate, sodium chromate, strontium chromate |
| Stainless steel and other high chromium alloys | Hexavalent chromium (when cast, or torch cut) |
| Textile dyes | Ammonium dichromate, potassium chromate, potassium dichromate, sodium chromate |
| Wood preservation | Chromium trioxide |
| Leather tanning | Ammonium dichromate |

Chromium exists as Cr(II), (III) and (VI), with Cr(II) being unstable. Trivalent and hexavalent forms in aqueous solution are biologically significant (Qiu *et al.* 2014; Dinker and Kulkarni 2015; Shariati *et al.* 2017). However, Cr(VI) is 500 times more toxic than Cr(III). Cr(III) is mostly insoluble and is a micronutrient which is biologically important. Cr(VI) is extremely soluble and mobile (1,680 g/L) over a wide pH range (Dinker and Kulkarni 2015; Prepared by Federal-Provincial-Territorial Committee 2015; Zhao *et al.* 2017; Borthakur *et al.* 2019; Swaidan *et al.* 2019; Wei *et al.* 2020; Jing *et al.* 2021). Depending on the pH, it occurs in numerous forms comprising $H_2CrO_4$, $HCrO_4^-$, $CrO_4^{2-}$ and $Cr_2O_7^{2-}$. Figure 1 shows the relative distribution of different species of Cr(VI) in aqueous solution. At pH more than 6 the $CrO_4^{2-}$ is dominant, whereas at below pH 6 Cr(VI) exists as $H_2CrO_4$ and $HCrO_4^-$, with $HCrO_4^-$ being predominant. At very high Cr(VI) concentrations, $HCrO_4^-$ dimerises to $Cr_2O_7^{2-}$ (IARC Monographs-100C 1990; Dinker and Kulkarni 2015; Tran *et al.* 2019; Hato *et al.* 2019) Subsequently, Cr(VI)-containing compounds are highly soluble and mobile in aqueous environments leading to potential Cr(VI) pollution.

## 2. HEALTH AND ENVIRONMENTAL EFFECTS OF Cr(VI)

Inappropriate disposal of the Cr(VI) from aqueous solution or wastewater leads to considerable environmental problems and jeopardize human health. Humans come into contact with Cr(VI) through dermal exposure, inhalation and ingestion (Zhitkovich 2011; Loock *et al.* 2014; Hammud *et al.* 2015; Mahmud *et al.* 2015; Fan *et al.* 2017; Maleh *et al.* 2020).

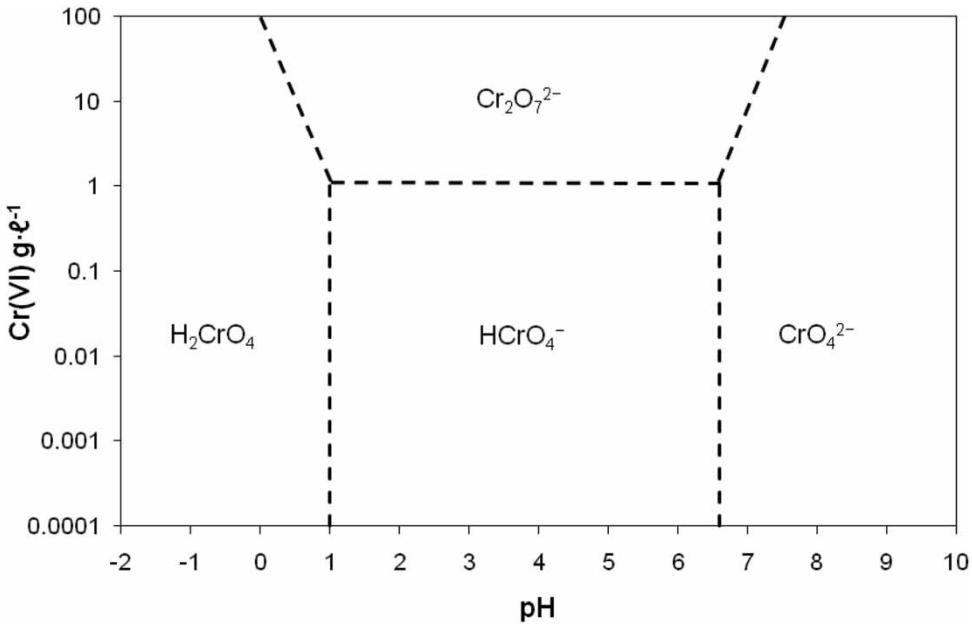



**Figure 1** | The relative distribution of different species of Cr(VI) in aqueous solution as function of pH (adapted from Dinker and Kulkarni 2015).

The effects of Cr(VI) toxicity include mutagenic, teratogenic, carcinogenic and genotoxic on living organisms as well as bioaccumulation. Cancer and mutation take place through damage of the DNA–protein cross-links as well as single-stranded breakage in live cells. Furthermore, Cr(VI) toxicity can include skin irritation, pulmonary congestion, hepatopathy and lung cancer (Zhitkovich 2011; Sun *et al.* 2014; Dinker and Kulkarni 2015; Federal-Provincial-Territorial Committee 2015; Fan *et al.* 2017; Chigondo *et al.* 2019; Maleh *et al.* 2020; Tumolo *et al.* 2020; Jing *et al.* 2021). The presence of high concentrations of Cr(VI) ions in the soil causes disruption of soil organisms through the destruction of the natural soil enzymes that help preserve good soil quality (Hato *et al.* 2019). Furthermore, Cr(VI) ions can disrupt aquatic life through free movement in marine and biological species (Zhitkovich 2011).

A grave case is the fate of chromite mine workers in Sukinda in the Jajpur and Orisha state where it was reported that 70% of the surface water and 60% of drinking water contains Cr(VI) ions (Walsh 2007) at levels above the internationally stipulated. Infertility, birth defects and still births were predominant while 84.75% and 86.42% deaths were reported at the mine and surrounding villages, respectively. Gastrointestinal problems, tuberculosis and asthma were reported as common ailments around the mine as a result of water contaminated with Cr(VI) ions (Walsh 2007; Bae *et al.* 2009). Consequently, its levels in drinking and surface water as well as industrial wastewater are regulated (Sutton 2010; Dinker and Kulkarni 2015). The acceptable standards of Cr(VI) by Bureau of Indian Standards (BIS-2012), World Health Organisation (WHO) and USA Environmental Protection Agency (EPA) are 0.05 mg/L and 0.1 mg/L for drinking and for surface water, respectively (Chromium (VI) Handbook 2004; Sutton 2010; Saha *et al.* 2011; WHO Chron. 2011; Loock *et al.* 2014; Dinker and Kulkarni 2015). This makes it fundamental to remove or reduce Cr(VI) ions from water bodies to acceptable levels. A review aimed at critically examining the extent to which PPy-based adsorbents have been utilized for Cr(VI) ions removal is thus important if the Cr(VI) ions environmental mitigation is to be clearly understood.

## 3. METHODS OF REMOVING Cr(VI) IONS FROM WATER

Due to severe health effects of Cr(VI), it is essential to treat water and wastewater containing Cr(VI) ions before release into the environment or modify it into less toxic forms. A variety of well-established methods are available namely chemical precipitation (Tumolo *et al.* 2020; Mdlalose *et al.* 2020), electrochemical (Dinker and Kulkarni 2015), ion exchange resin (Mahmud *et al.* 2015), coagulation-flocculation (Jiang *et al.* 2018), reverse-osmosis (Dinker and Kulkarni 2015; Aigbe & Osibote 2020), membrane filtration (Maleh *et al.* 2020; Mdlalose *et al.* 2020), electrocoagulation (Rimu & Rahman 2020), bioremediation (Maleh *et al.* 2020), electrokinetics (Dinker & Kulkarni 2015), reduction (Jiang *et al.* 2018) and adsorption (Muhammad & Bilal 2020). Figure 2 gives a summary these methods for removing Cr(VI) ions from water. These well documented methods, have been extensively utilized and quite a number of them are still used to date. However, their application still pauses various environmental challenges ranging from being uneconomic, generation of large volumes of secondary pollutants, fouling, high energy requirements, low efficiency for the removal of trace levels of pollutants, requirement of large volumes of chemicals, pH sensitivity as well as pre- and post-treatment procedures (Zhao *et al.* 2016; Jiang *et al.* 2018; Chigondo *et al.* 2019; Hato *et al.* 2019; Maleh *et al.* 2020; Soni *et al.* 2020). Adsorption technology has however attracted much attention due to its simplicity in design, cost–effectiveness, high removal efficiency, wide choice of adsorbents, easy operational conditions and environmental friendliness (Dinker & Kulkarni 2015; Ghosh *et al.* 2020; Maleh *et al.* 2020; Wang *et al.* 2020; Mdlalose *et al.* 2020). Even though it also has its limits like tedious post-treatment processes, needed for hybridized adsorbents to improve their capacity, rapid saturation, expense of regeneration and loss of material, it is more preferable than all the other methods for Cr(VI) ion remediation.

### 3.1. Adsorption process

The adsorption procedure encompasses the accumulation of material (adsorbate) liquid or gas on the surface of a solid phase material (adsorbent) (Wang *et al.* 2015) in batch or column mode. Figure 3 summarises some basic adsorption concepts. The adsorption process comprises the build-up or adherence of gas, liquid or dissolved solid molecules ions on the surface of a solid such as carbon, biochar, chitosan and polymer composite (Wang *et al.* 2015; Hato *et al.* 2019). The adsorbate becomes attached on the surface of the adsorbent by physical or chemical means. As a result, the adsorption process is a mass transfer system (diffusion, migration and convection) from a liquid or gaseous phase to solid phase. Adsorbate molecules from bulk solution migrate to the active sites available on the surface of the adsorbent. Adsorbents are distinguished by active sites which are able to interact with particles from bulk solution as a result of their specific electronic and spatial properties. These active sites might have the similar or dissimilar energy, depending on the type of material surface. The opposite of

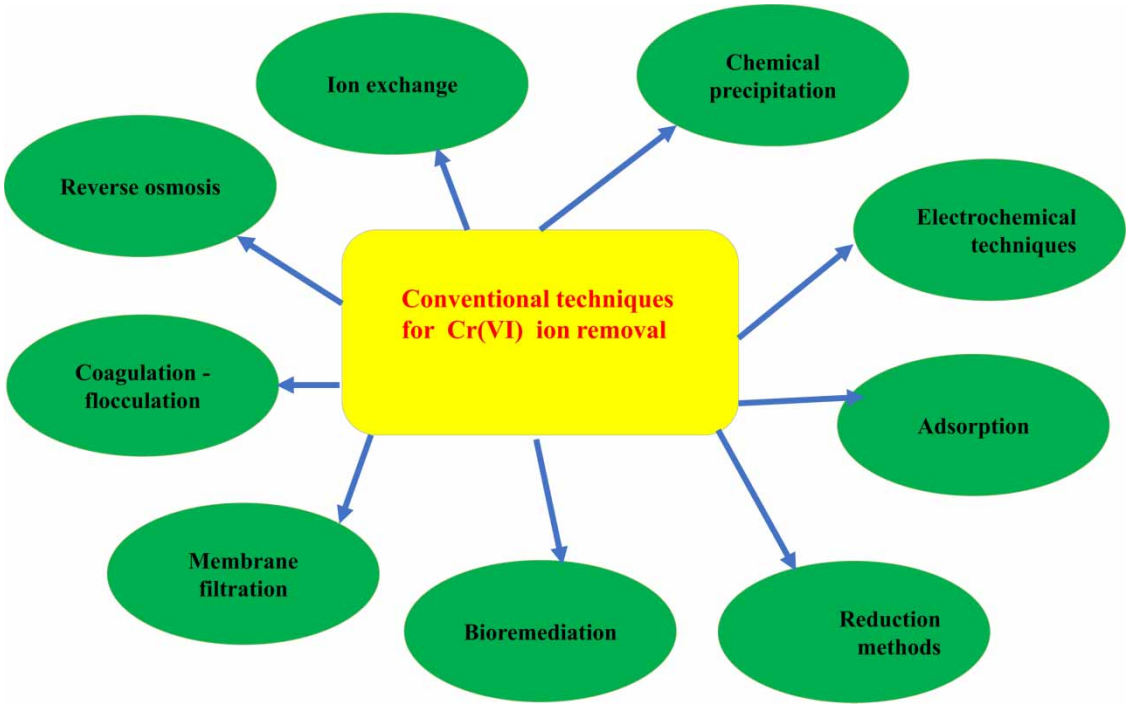



**Figure 2** | Conventional methods of Cr(VI) ion removal.

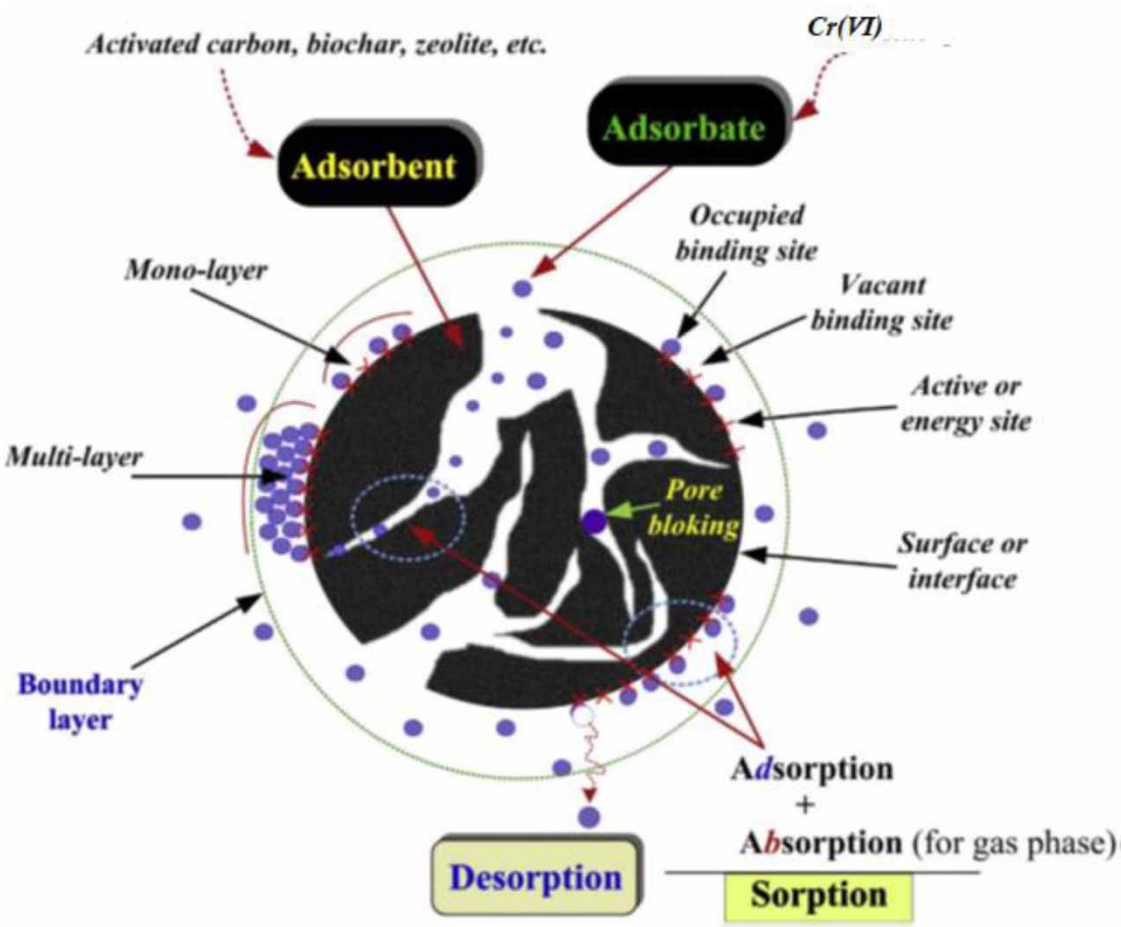



**Figure 3** | Summary of the basic adsorption technology concepts (adapted from Tran *et al.* 2017).

adsorption is called desorption, which is the release of adsorbed species from the adsorbent surface, back into the bulk solution which happens during regeneration of the adsorbent. The adsorption process could be monolayer (surface coverage of the adsorbate onto an adsorbent surface where all the adsorption active sites have the same energy) or multi-layer where the quantity of adsorbed molecules is added for all active sites with discrete bond energy, with the stronger binding sites occupied first (Tran *et al.* 2017; Hato *et al.* 2019).

To thoroughly understand the properties of adsorbents and to interpret the adsorption phenomenon and mechanisms, a variety of physico-chemical techniques can be utilized to characterize an adsorbent. These various characterization techniques and the adsorbent information availed are illustrated in Figure 4. The process of adsorption mostly considered as physisorption and chemisorption plays a major part in sorbate attraction to the sorbent (Bajpai and Rajpoot 1999; Ali and Gupta 2007; Hua *et al.* 2012; Chanakya and Mahindra 2017; Hato *et al.* 2019; Aigbe & Osibote 2020). During physisorption the sorbate is reversibly bonded to the adsorbent surface by van der Waals forces at low enthalpy values of about 20 kJ/mol, low temperature, multi-layered sorption and low activation energy. In chemisorption, the adsorbent is bound to the sorbent through covalent bonding or electrostatic attraction characterized by irreversible sorption with a high sorption enthalpy from −80 to −400 kJ/mol, monolayer sorption and high activation energy. Adsorption is affected by various factors such as charge of the adsorbent and adsorbate, pH of the aqueous solution, temperature of the solution, adsorbent concentration, dosage and surface area (Hato *et al.* 2019; Aigbe & Osibote 2020).

To date, researchers have attempted to produce suitable adsorbents with high adsorption capacity and selectivity for the rapid removal of Cr(VI) ions from water and wastewater. Numerous adsorbents have been utilized for this cause including activated carbon (Lal *et al.* 2020; Ugwu and Agunwamba 2020), zeolites (Mthombeni *et al.* 2015), biomass (Maleh *et al.* 2020), fly ash (Farooqi *et al.* 2021), polymers (González-López *et al.* 2020; Rimu & Rahman 2020; Sheng *et al.* 2021), metal and metal oxides (da Silva Neto *et al.* 2019), carbon nanotubes (Anastopoulos *et al.* 2017), graphene (Zhao *et al.* 2016), clay minerals (Bentchikou *et al.* 2017), polymers and polymer-inorganic hybrid adsorbents (Mahmud *et al.* 2015; Jiang *et al.* 2018; Wang *et al.* 2020).

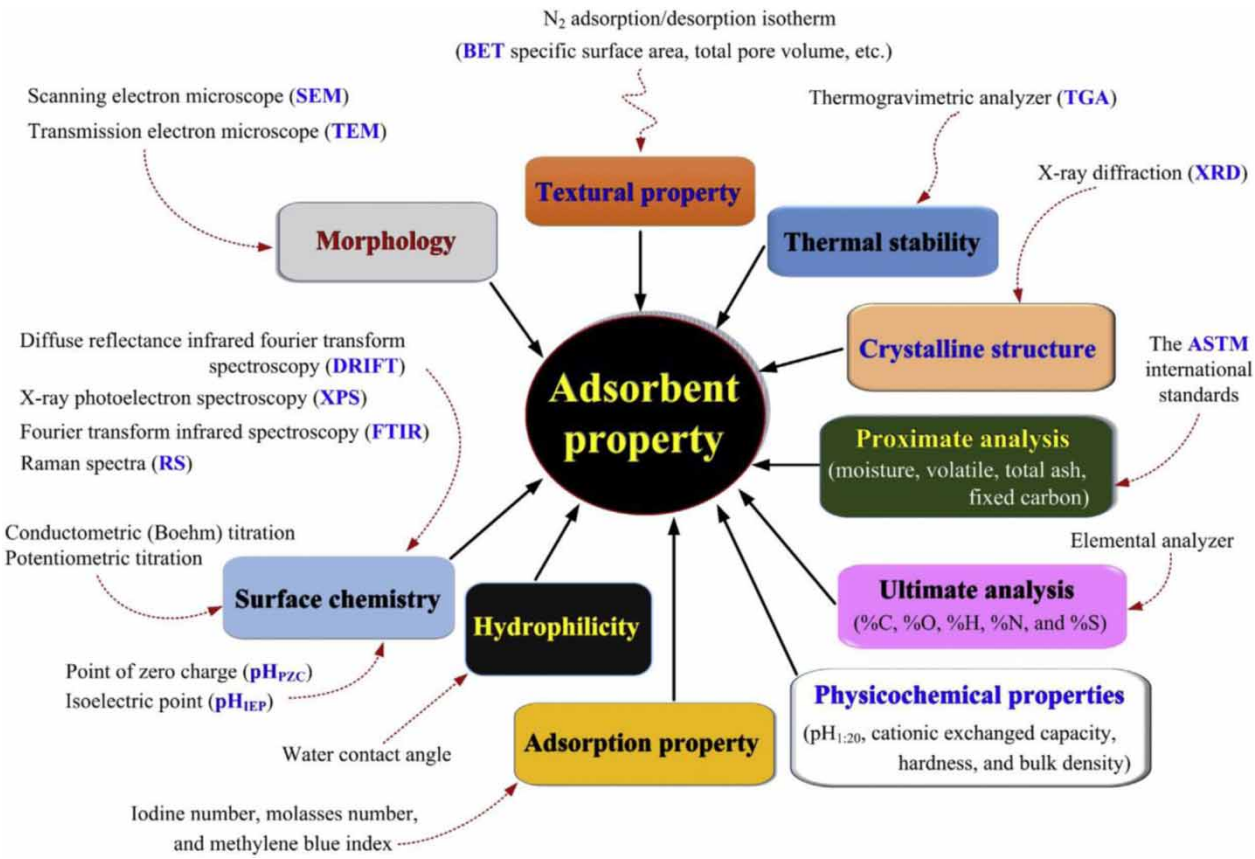



**Figure 4** | Physico-chemical techniques that can be utilized to characterize an adsorbent (adapted from Tran *et al.* 2017).

## 4. POLYPYRROLE-BASED ADSORBENTS

Conducting polymer(CP)-inorganic hybrid adsorbents have received enormous consideration in many applications owing to their simplicity in synthesis, satisfactory electrical conductivity, excellently biocompatible, fascinating electronic and redox properties, eco-friendliness and low cost (Ates *et al.* 2012; Huang *et al.* 2014; Dinker and Kulkarni 2015; Mahmud *et al.* 2015; Jiang *et al.* 2018; Chigondo *et al.* 2019; Hato *et al.* 2019). One such polymer whose composites have attracted much attention for Cr(VI) remediation is polypyrrole (PPy) (Bhaumik *et al.* 2012; Mahmud *et al.* 2015; Hato *et al.* 2019; Aigbe & Osibote 2020).

### 4.1. Polypyrrole conducting polymer

PPy is a conducting polymer. Its conductivity trait originates from minor modification of alternating double single bonds along major polymer chain overlapping the pi-bonds in their structure. This enables free electron shift and transfer in their bound atom space. These synthetic polymers have conjugated π-electron moiety exhibiting exceptional electronic properties, for instance truncated energy, optical transition and ionisation potentials, in addition to high electron affinities (Krishnani *et al.* 2013; Mahmud *et al.* 2015; Hato *et al.* 2019; Taghizadeh *et al.* 2020). CP conductance stems from their ease of oxidation or reduction, a characteristic that is not found in traditional polymers.

The most popular methods of preparing PPy involves chemical oxidative polymerization of pyrrole and electrochemical polymerization (Ballav *et al.* 2012; Krishnani *et al.* 2013). Chemical oxidative polymerization takes place with a variety of dopants under different conditions (Figure 5), since the adsorption efficiency largely depends on the preparation conditions of PPy (Huang *et al.* 2014; Mahmud *et al.* 2015). The two methods for the process of doping in chemical polymerization of CPs are p-doping where the polymer becomes oxidized with counter anions and n-doping where the polymer is reduced with countercations (Hato *et al.* 2019; Taghizadeh *et al.* 2020). The chemical oxidants used in the preparation of PPy are aqueous APS and anhydrous iron (III) chloride (Hato *et al.* 2019).

PPy has shown a worthy prospect in adsorption application due to its reputable environmental stability, extraordinary conductance, redox properties and easiness of processing (Das and Prusty 2012; Maity *et al.* 2019). PPy is inexpensive, easy to synthesize, eco-friendly and has abundant amine groups which facilitate adsorption and chelation. During complexation cationic nitrogen atoms on the PPy moiety act as adsorption sites for heavy metals ions through hydrogen bonding or electrostatic attractions (Mahmud *et al.* 2015; Hato *et al.* 2019; Maity *et al.* 2019). Consequently, the use of PPy for the removal of Cr(VI) has benefited much from this behaviour coupled by its ease acid–base doping–dedoping process, incredible stability in the environment and reversibility (Mahmud *et al.* 2015; Hato *et al.* 2019). Direct reduction of adsorbed Cr(VI) to Cr(III) on sites can be accomplished through donation of electrons by O, S, and N atoms of dopants (Rodríguez *et al*. 2000;

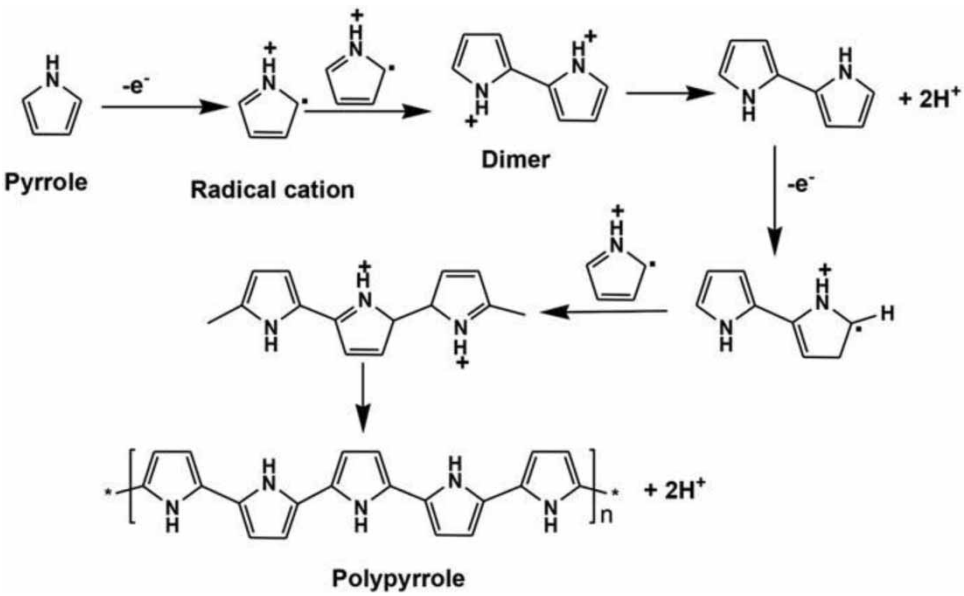



**Figure 5** | Chemical polymerization of pyrrole monomer (adapted from Hato *et al.* 2019).

Ates *et al.* 2012; Tran *et al.* 2019). Nevertheless, PPy tends to agglomerate owing to π–π interactions between the chains, culminating in reduction of surface area and lowering number of binding sites for Cr(VI) ions (Kera *et al.* 2017; Chigondo *et al.* 2019). Chain modification with dopants in the course of polymerization can overcome these restrictions (Ballav *et al.* 2012; Amalraj *et al.* 2016a, 2016b; Das *et al.* 2019). Immense studies have been conducted on the synthesis of PPy with various dopants and additives to increase its adsorption efficiency. Large numbers of modifications, aimed at improving PPy composite adsorptive performance towards Cr(VI) have been studied (Bhaumik *et al.* 2012; Hammud *et al.* 2015; Mahmud *et al.* 2015; Aigbe & Osibote 2020). Moreover, PPy-based adsorbents turn into electron donors for the reduction of Cr(VI) to Cr(III) under acidic conditions as illustrated in Equations (1)–(3) (Fang *et al.* 2018; Chigondo *et al.* 2019). This occurs through electron transfer from a neutral state ($PPy^0$) to Cr(VI). These adsorbents also offer adsorption sites for Cr(III):

$$PPy^+ + e^- \rightarrow PPy^0 \quad (1)$$

$$3PPy^0 + 7H^+ + HCrO_4^- \rightarrow Cr^{3+} + 4H_2O + 3PPy^+ \quad (2)$$

$$3PPy^0 + CrO_4^{2-} + 4H_2O \rightarrow Cr^{3+} + 8OH^- + 3PPy^+ \quad (3)$$

## 5. POLYPYRROLE-BASED ADSORBENTS FOR CR(VI) REMOVAL

Great strides have been made in synthesizing PPy in the presence of various dopants and additives with the second components improving the adsorption efficiency as modelled by the Langmuir adsorption capacity under given conditions (Hato *et al.* 2019). Table 2 gives a summary of the latest investigations of PPy-based composites and the Langmuir adsorption capacities and experimental conditions for the removal of Cr(VI) ions which is impressive for one type of adsorbent backbone (PPy). It is noticeable that the adsorption of Cr(VI) ions is more effective at low pH in agreement with the introduction discussion focusing on species of Cr(VI). The nature and properties of the dopant or additive in the PPy composite influences the adsorption efficiency of the adsorbent. This is so because different adsorbents have different surface areas, active sites, selectivity, stability, generatability and rapidness of the adsorption process (Hato *et al.* 2019). According to a study done by Zhan *et al.* (2018a, 2018b) bamboo-like PPy nanofibrous mats nanocomposite prepared by non-emulsion electrospinning and in-situ polymerization was the most effective adsorbent with a maximum uptake of 961.5 mg/g at 25 °C. The Cr(VI) adsorption by bamboo-like polypyrrole nanofibrous mats was dictated by electrostatic attractions, anionic exchange and reduction mechanisms owing to the special porous structure, high surface area and abundant adsorption active sites (Zhan *et al.* 2018a, 2018b). This was marked considering the Cr(VI) ion concentration range of 5–250 mg/L in comparison to other materials outlined in Table 2 falling within the same concentration range. However, the challenge of a complex fabrication procedure may limit its applicability. Equally, capsular polypyrrole hollow nanofibers (PPy-HNFs) fabricated *via in situ* polymerization of pyrrole on an organic–inorganic template, followed by acid etchings showed remarkable performance towards Cr(VI) in aqueous solution with a maximum adsorption capacity of 839.30 mg/g at pH 2 (Zhao *et al.* 2015) but its concentration range (50–600 mg/L) is higher than bamboo-like polypyrrole nanofibrous mats. It was reported that the adsorption process took place under very acidic pH of 2 in most cases owing to stronger electrostatic attractions of hydroxyl (OH) groups to Cr(VI) ions and protonated amine groups. The adsorbents PPy/$NiFe_2O_4$ (Sun *et al.* 2017a, 2017b) and PPy-TiP (Baig *et al.* 2015) exhibit less effectiveness in the removal of Cr(VI) ions considering their concentration ranges. In some studies, it is difficult to assess the adsorbent capacity due to lack of adequate data like temperature of adsorption and Cr(VI) concentration range. Most (98%) of the adsorption processes using various adsorbent were better modelled by the Langmuir isotherm with all the kinetics studies being pseudo-second-order modelled.

### 5.1. Amino doped polypyrrole adsorbents

The ease of protonation of the amino (-NH) group of PPy under acidic conditions is beneficial to the adsorption of Cr(VI) through ion exchange and electrostatic attraction. Conversely, the deprotonation may be through simple solution pH change, signifying its exceptional regeneration in adsorption. To this end, several studies had been done aimed at increasing the number of amino groups within the PPy composite moiety by using amino-based dopants. Studies (Ballav *et al.* 2012; Bhaumik *et al.* 2012; Chávez-Guajardo *et al.* 2015; Amalraj *et al.* 2016a, 2016b; Kera *et al.* 2016; Kera *et al.* 2017; Sall *et al.* 2017; Kera *et al.* 2018; Chigondo *et al.* 2019) utilized amino dopants to enhance PPy adsorption of Cr(VI) successfully. Amalraj *et al.* (2016b) prepared agglomerated spherical particles of threonine-doped polypyrrole (Thr-PPy) *via in situ*

**Table 2** | Adsorption capacities and experimental conditions of polypyrrole-based adsorbents for the removal of Cr(VI) ions

| Adsorbent | Langmuir adsorption capacity, qmax (mg/g) | Temperature (°C) | pH | Concentration range (mg/L) | Ref. |
|---|---|---|---|---|---|
| Bamboo-like PPy nanofibrous mats | 961.50 | 25 | 2.0 | 50–250 | Zhan *et al.* (2018a, 2018b) |
| Capsular PPy hollow nanofibers (PPy-HNFs) | 839.30 | 25 | 2.0 | 50–600 | Zhao *et al.* (2015) |
| PPyPANI@RHA) | 769.15 | 30 | 2.0 | 50–100 | Dutta *et al.* (2021) |
| PPy/Ca-REC composites | 714.29 | 25 | 2.0 | 300–1500 | Xu *et al.* (2019b) |
| PPy/REC | 689.70 | 25 | 2.0 | 300–1500 | Xu *et al.* (2019a) |
| PPy-$NH_2$ | 675.23 | 25 | 2.0 | 150–300 | Liu *et al.* (2018b) |
| PPy–GO NC | 625.00 | 25 | 2.0 | 25–100 | Setshedi *et al.* (2015) |
| GO-$\alpha$CD-PPY NCs | 606.06 | 25 | 2.0 | 100–700 | Chauke *et al.* (2015) |
| PPy/BC | 555.60 | 25 | 2.0 | 100–200 | Shao *et al.* (2021) |
| PPy-mPD/$Fe_3O_4$ | 555.60 | 25 | 2.0 | 100–600 | Maponya *et al.* (2020) |
| PPy-OCNT NC | 555.56 | 25 | 2.0 | 200–600 | Omwoyo *et al.* (2015) |
| PANI + PPy | 510.90 | 25 | 2.0 | 50–350 | Janmohammadi *et al.* (2021) |
| PPy/graphene oxide composite nanosheets | 497.10 | nr | 3.0 | nr | Li *et al.* (2012a, 2012b) |
| PPy-c-CS | 401.00 | nr | 2.0 | nr | Ji *et al.* (2018) |
| GO/$MnO_2$/PPy | 374.53 | 25 | 2.0 | 150–300 | Liu *et al.* (2018a) |
| PPy/rGO aerogel EPGA | 361.00 | 25 | 2.0 | 5–100 | Chen *et al.* (2020) |
| PMMA/RHA/PPy | 360.50 | 19 | 2.0 | 10–70 | da Rocha *et al.* (2020) |
| Graphene/$Fe_3O_4$@PPy | 348.40 | 25 | 2.0 | nr | Yao *et al.* (2014) |
| MZ-PPy | 344.83 | 25 | 2.0 | 100–300 | Mthombeni *et al.* (2015) |
| PPy/MLS | 343.64 | 25 | 2.0 | 25–75 | Du *et al.* (2020) |
| SP/PPy | 336.70 | 25 | 2.0 | 100–400 | Tan *et al.* (2017) |
| $Fe_3O_4$@PPyArg | 322.58 | 25 | 2.0 | 50–450 | Chigondo *et al.* (2019) |
| Gg-g-poly (Am)/PPy | 312.50 | 25 | 2.0 | nr | Goddeti *et al.* (2020) |
| PPy) hydrogels | 312.00 | nr | 2.0 | nr | Li *et al.* (2015) |
| PPy/DABSA composite | 303.03 | 25 | 2.0 | nr | Kera *et al.* (2017) |
| PPy-PANI/$Fe_3O_4$ | 303.00 | 25 | 2.0 | nr | Kera *et al.* (2016) |
| PPy-sepiolite nanofibers | 302.00 | 25 | 2.0 | 200–400 | Chen *et al.* (2014a, 2014b) |
| $\gamma$-$Fe_2O_3$@Chi@PPY | 301.20 | nr | 2.0 | 1–500 | Reis *et al.* (2021) |
| PPy/$Fe_3O_4$/$SiO_2$ | 298.00 | nr | 2.0 | 25–300 | Alzahrani *et al.* (2021) |
| PPy/OMWCNTs NCs | 294.00 | 25 | 2.0 | 100–500 | Bhaumik *et al.* (2016) |
| (Ppy-$Fe_3O_4$/rGO | 293.30 | 30 | 2.0 | nr | Wang *et al.* (2015) |
| PPy/$MoS_2$ | 257.73 | 25 | 2.0 | 50–200 | Xiang *et al.* (2021) |
| PPy/PANI | 256.41 | nr | 7.0 | 5–100 | Thao *et al.* (2019) |
| PPy-N membranes | 250.31 | 35 | 2.0 | nr | Li *et al.* (2012a, 2012b) |
| $Fe_3O_4$@gly-PPy NC | 238.09 | 25 | 2.0 | 50–150 | Ballav *et al.* (2014a, 2014b) |
| PPy-PANI | 227.00 | 25 | 2.0 | 100–400 | Bhaumik *et al.* (2012) |
| AHNSA | 224.00 | nr | 2.0 | nr | Sall *et al.* (2017) |
| PPy-gly | 217.39 | 25 | 2.0 | 50–100 | Ballav *et al.* (2012) |
| $Fe_3O_4$/PPy | 209.20 | 25 | 2.0 | 5–70 | Wang *et al.* (2012) |
| GCS@PPy/L-cys | 209.18 | - | 2 | 10–200 | Li *et al.* (2020) |
| PPy/$Fe_2O_3$ MNC | 209.00 | nr | | 2.5–100 | Chávez-Guajardo *et al.* (2015) |

(*Continued.*)

**Table 2** | Continued

| Adsorbent | Langmuir adsorption capacity, qmax (mg/g) | Temperature (°C) | pH | Concentration range (mg/L) | Ref. |
|---|---|---|---|---|---|
| Magnetic PPy/$Fe_3O_4$ | 208.77 | 25 | 2.0 | 200–700 | Aigbe *et al.* (2018) |
| PPy/$Fe^0$ NC | 202.00 | 25 | 2.0 | nr | Katata-seru *et al.* (2020) |
| PPy-coated on cellulose sulfate fibers | 198.00 | nr | 2.0 | nr | Hosseinkhani *et al.* (2020) |
| PPy/SBA-15 | 194.17 | 25 | 2 | nr | Wang *et al.* (2021) |
| Threonine/PPy | 185.50 | 25 | 2.0 | nr | Amalraj *et al.* (2016b) |
| PPy-mPD | 183.20 | 25 | 2.0 | 100–600 | Kera *et al.* (2018) |
| Asp/PPy | 176.67 | 30 | 2.0 | nr | Amalraj *et al.* (2016b) |
| PPy-$Fe_3O_4$ | 176.00 | 25 | 2.0 | 100–400 | Bhaumik *et al.* (2013) |
| PPy/MMT | 166.70 | 30 | 2.0 | 150–350 | Chen *et al.* (2015) |
| PPy/$Fe_3O_4$/AgCl | 166.70 | 20 | 2.0 | 100–500 | Sun *et al.* (2017b) |
| Sulfonated poly(arylene ether nitrile)/ PPycore/shell | 165.30 | 25 | 2.0 | nr | Zhan *et al.* (2017) |
| PPy/SCB | 156.00 | 25 | 2.0 | 25–100 | Chen & Pan (2021) |
| PPy-HNTs NC | 149.25 | 25 | 2.0 | 25–100 | Ballav *et al.* (2014a, 2014b) |
| NCPPy | 147.30 | 30 | | nr | Shahnaz *et al.* (2020) |
| PPy – $Fe_3O_4$ – SW | 144.93 | 30 | 2.0 | nr | Sarojini *et al.* (2021) |
| Ppy@x%MgFe2O4 | 138.60 | 25 | 2.0 | nr | Karthikeyan *et al.* (2021) |
| PPy-OMMT NC | 119.34 | 25 | 2.0 | 250–800 | Setshedi *et al.* (2013) |
| PPy–$Fe_3O_4$ NC | 119.00 | 25 | 2.0 | 50–150 | Muliwa *et al.* (2016) |
| MSEP/PPy | 108.85 | 25 | 2.0 | 50–100 | Zhou *et al.* (2018) |
| PPy@magnetic chitosan | 105.00 | 25 | 2.0 | nr | Alsaiari *et al.* (2021) |
| PANI/PPy) | 91.60 | 25 | 2.0 | 100–200 | Wang *et al.* (2013) |
| PPy/$Ti(HPO_4)_2$ | 86.84 | 15 | 3.4 | nr | Qi *et al.* (2016) |
| UFB-PPy | 85.00 | 30 | 2.0 | 20–100 | Zhang *et al.* (2020) |
| PPy-modified natural corncob-core sponge | 84.70 | 25 | 3.5 | 50–200 | Zhang *et al.* (2016) |
| CS/PPy | 78.60 | 30 | 4.2 | 25–200 | Karthik and Meenakshi (2015) |
| PPy-LDHs | 76.21 | 25 | 5.0 | 10–50 | Sahu *et al.* (2019) |
| PPy/PG | 72.81 | 30 | 5.0 | 10–200 | Yao *et al.* (2012) |
| MSFA/PPy. | 66.93 | 25 | 2.0 | 25–100 | Zhou *et al.* (2016) |
| PPy/$NiFe_2O_4$ | 50.00 | 20 | 2.0 | 100–1000 | Sun *et al.* (2017a, 2017b) |
| PPy/ATP | 48.45 | 25 | 2.0 | 10–100 | Chen *et al.* (2014a, 2014b) |
| PPy/$Fe_3O_4$/ATP | 43.48 | nr | 2.0 | 100–500 | Sun *et al.* (2020a, 2020b) |
| PPy@poly(St-co-DVB) | 35.00 and 16.00 | nr | 2.0 | nr | Chaleshtari and Foudazi (2020) |
| PPy-TiP | 31.64 | 30 | 2.0 | 200–1000 | Baig *et al.* (2015) |
| MBC/PPy | 19.23 | 25 | 5.3 | 20–60 | Yang *et al.* (2018) |
| Gel/CS/PPy. | 15.00 | nr | 2.0 | nr | Xing *et al.* (2020) |
| PPy/RCC activated carbon | 8.80 | 30 | 2.0 | 2–10 | Thamilarasu *et al.* (2012) |
| PPy/SD | 3.40 | nr | 2.0 | 10–120 | Ansari and Fahim (2007) |
| PPy cellulose fiber | - | - | 2.0 | 100–700 | Lei *et al.* (2012) |
| Ppy/$Fe^0$ NC | nr | nr | 2.0 | nr | Mdlalose *et al.* (2020) |
| PPy/$Fe_3O_4$ | nr | nr | 2.0 | 50–250 | Mirrezaie *et al.* (2014) |

nr, not reported.

polymerization of pyrrole with threonine for the Cr(VI) uptake from aqueous solutions. The adsorbent was characterized using Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy/energy dispersive X-ray spectroscopy (FESEM/EDS), high resolution-transmission electron microscopy (HR-TEM), Braunauer–Emmett–Teller (BET) method and X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD) techniques. The adsorption experiments were carried in the batch mode and modelled using Langmuir, Freundlich, Dubinin–Radushkevich and Temkin adsorption isotherm. It was found that the adsorption was best described by Langmuir isotherm model with a maximum adsorption capacity of 185.5 mg/g and the process was spontaneous and endothermic. The kinetic studies revealed that pseudo-second-order and intra-particle diffusion models best described the process. Adsorbents of high adsorption capacity for Cr(VI) ions removal were reported from these studies. Nevertheless, comprehensive studies on the adsorbent regeneration are still limited. Complicated fabrication procedures and the rupture of the polymer chain by a repeated reaction of oxidation with highly oxidizing Cr(VI) species could decrease the mass sorption sites in the spent adsorbent, which could account for the decrease in the adsorption capacity.

### 5.2. Polypyrrole modified bio-adsorbents

The application of bio-adsorbents gives a green alternative for heavy metals removal because they are biodegradable, low cost, biocompatible and non-toxic (Karthik and Meenakshi 2015; Jiang *et al.* 2018; Alsaiari *et al.* 2021). Such biosorbents like cellulose (Hosseinkhani *et al.* 2020), corncob (Zhang *et al.* 2016), sisal pulp (Tan *et al.* 2017), rice husks (da Rocha *et al.* 2020), sawdust (Ansari and Fahim 2007) and chitosan (Ji *et al.* 2018) have been combined with PPy to improve the adsorption performance on aqueous Cr(VI) ions as they possess exceptional functional groups which facilitate adsorption (Melah *et al.* 2020; Liu *et al.* 2021). These are effective as they are eco-friendly, renewable, easy and inexpensive to synthesize. Hosseinkhani *et al.* (2020) synthesized polypyrrole coated on cellulose sulfate fibres which were characterized by EDS, FTIR, BET and thermogravimetric analyses (TGA). The as-synthesized adsorbent was assessed on the effect of pH, contact time, adsorbent dose and initial concentration of Cr(VI) ions. The removal percentage of Cr(VI) was 99.9% under the optimised conditions at initial concentration of Cr(VI), 200 mg/L, pH 2; and 200 minute contact time. The adsorption process was described by the Freundlich, Langmuir, Temkin, Redlich–Peterson, Radke–Prausnitz, Dubinin–Radushkevich and UT models with a Langmuir model maximum adsorption capacity of 198 mg/g being reported. Furthermore, the adsorption process followed the intra-particle diffusion model and was endothermic and spontaneous. The adsorbent could be regenerated in four cycles and was selective towards Cr(VI) ions as $Cu^{2+}$, $Ni^{2+}$ and $Zn^{2+}$ did not interfere with the removal percentage of Cr(VI) ions considerably.

### 5.3. Polypyrrole-modified carbon material

Carbon nanomaterials exist in various forms including carbon nanotubes (CNTs) (Anastopoulos *et al.* 2017), graphene, activated carbon and bio char. CNTs have been extensively applied for the removal of heavy metal ions due to their small size, respectable electrical conductivity, hollow/layered structures and high specific surface area (Bhaumik *et al.* 2016). Graphene oxide (GO) is a recent novel nanostructure form of carbon materials with a large specific surface area, good mechanical strength and flexibility (Chauke *et al.* 2015). Activated carbon (AC) adsorption is widely used in the removal of heavy metal ions in wastewater. It has a large specific surface area for adsorption but commercial AC is typically expensive hence cheaper and renewable agricultural raw materials have been utilized for the fabrication of AC and biochar. Due to the outstanding adsorption properties (Ghosh *et al.* 2020) they can be used in PPy doping to produce Cr(VI) ions exceptional adsorbents and several studies have been reported to this end (Thamilarasu *et al.* 2012; Wang *et al.* 2013; Omwoyo *et al.* 2015; Chen *et al.* 2020; Li *et al.* 2020; Reis *et al.* 2021). Furthermore, dispersed GO is capable of providing highly active PPy-based nanocomposite with remarkable Cr(VI) ions removal efficiency (Setshedi *et al.* 2015). Subsequently, GO exploits the advantage of the capability of cyclodextrins to self-assemble with numerous pollutants through inclusive complexation. Chauke *et al.* (2015) reported the oxidative synthesis of PPy functionalized with both graphene oxide and $\alpha$-cyclodextrin ($\alpha$CD) to afford GO-$\alpha$CD-PPy NCs which was characterised by FTIR, FESEM, HR-TEM, BET and XRD techniques. Batch adsorption experiments were performed and the determined optimum conditions were temperature of 25 °C, pH of 2, and contact time of 30–200 min at 200 mg/L of Cr(VI) concentration. The Langmuir isotherm best described the adsorption with a maximum adsorption capacity of 606.06 mg/g which was endothermic in nature and the adsorption kinetics followed the pseudo-second-order model. The effect of co-existing ions studies exposed a very selective adsorbent which was regenerated in three cycles.

### 5.4. Polypyrrole-modified clay and mineral

Clay materials are hydrated aluminium-silicate-bearing minerals sheet layers held together by van der Waals forces or hydrogen bonds (Xu *et al.* 2019a). They are widely applied to adsorption removal of heavy metal ions and adsorbent supported with clay minerals has been widely researched for the Cr(VI) ions removal due to its special surface area, high exchange capacity, and enriched removal ability of heavy metal ions. Adsorption on clays takes place through hydroxyl, oxygen and particles edge on the surface of clays and thus they are very useful in adsorption technology. PPy-clay based adsorbents have been studied yielding good results as already shown in Table 1 (Setshedi *et al.* 2013; Ballav *et al.* 2014a, 2014b; Zhou *et al.* 2018; Olad *et al.* 2019; Sarojini *et al.* 2021). Xu *et al.* (2019b) prepared semi-spherical agglomerated as polypyrrole/calcium rectorite exfoliated sheets (PPy/Ca-REC) composites for aqueous solution Cr(VI) ions adsorption, via *in situ* polymerization of pyrrole monomer. The as-synthesized adsorbent was characterised by XRD, FTIR spectroscopy, SEM and XPS. The adsorption of Cr(VI) onto the PPy/Ca-REC adsorbent was extremely pH dependent and the adsorption kinetics obeyed the pseudo-second-order kinetic model attaining equilibrium in 30–180 min. The adsorption isotherm data fitted well to the Langmuir isotherm model giving a maximum adsorption capacity of 714.29 mg/g at 25 °C. The composite was revived for three consecutive adsorption–desorption cycles and showed high selectivity towards Cr(VI) ions. Through XPS results, electrostatic interactions, ionic interaction as well as reduction were postulated as the adsorption mechanisms for Cr(VI) removal.

## 6. REGENERATION OF PPY-BASED ADSORBENTS

The regeneration and reusability of an adsorbent is necessary to evaluate its feasibility and cost–effectiveness for application in the large scale treatment of industrial wastewater (Kera *et al.* 2018). Most studies reviewed conducted regeneration studies of the spent adsorbents including arginine-doped polypyrrole ($Fe_3O_4$@PPyArg) (Chigondo *et al*. 2019), polypyrrole-polyaniline coated rice husk ash (PPyANI@RHA) (Dutta *et al*. 2021), waste plastic filter modified with polyaniline and polypyrrole (PPF@PANI + PPy) (Janmohammadi *et al*. 2021), magnesium ferrite-reinforced polypyrrole hybrids (Ppy@x% $MgFe_2O_4$) (Karthikeyan *et al*. 2021), m-phenylenediamine-modified polypyrrole (PPy-mPD) (Kera *et al*. 2018), polypyrrole and montmorillonite clay (PPy-MMT) (Mdlalose *et al*. 2020), $Fe_3O_4$ and attapulgite-doped polypyrrole (PPy/$Fe_3O_4$/ATP) (Sun *et al*. 2020a, 2020b) and polypyrrole-coated molybdenum disulfide (PPy/$MoS_2$) (Xiang *et al*. 2021). Numerous studies have reported on various regeneration methods using acids, bases or salts aqueous solutions (Mdlalose *et al.* 2018) with the most popular desorbing solutions being 0.05 M or 0.1 M NaOH while 2 M HCl was used for adsorbent regeneration. NaOH accelerates the deprotonation of $-NH_3^+$ groups on adsorbent surfaces resulting in the decrease of electrostatic attraction between these groups and Cr(VI) species ($HCrO_4^-$) as well as OH groups out competing $HCrO_4^-$ (Mdlalose *et al.* 2018; Dutta *et al.* 2021; Janmohammadi *et al.* 2021). Nevertheless, such a more comprehensive study of the adsorbent regeneration is still limited as described in most literature. These are necessary if meaningful information is to be derived from adsorption studies and have potential in large-scale industrial water treatment. The number of adsorption–desorption cycles ranged from three to six. The rupture of the polymer chain by a repeated reaction of oxidation with highly oxidizing Cr(VI) species could decrease the mass and sorption sites in the spent adsorbent, which could account for the decrease in the adsorption capacity. Hence, further studies are necessary to investigate alternative desorption and regeneration treatments which will minimise deterioration of the structure of the CP composites and increase their lifespan. Methods to improve the structural integrity of the CP composites should also be investigated as robust adsorbents are attractive for real field applications. Mdlalose *et al.* (2020) conducted a detailed and informative study of adsorption–desorption cycles using pristine NaOH and $NH_4OH$ as well as with HCl, $NH_4Cl$, $HNO_3$ combinations to establish the stability of polypyrrole-montmorillonite clay composite. Improved regeneration efficiencies were observed for regeneration using $NH_4Cl$ as some of the reagents used became dopants which improved the process.

## 7. THE Cr(VI) ION REMOVAL MECHANISMS

To evaluate the removal efficiency of PPy-based adsorbents, the elucidation of the conceivable mechanisms of the adsorption process is desirable. The adsorption behaviours of PPy-based adsorbents are associated with the adsorption factors of the solution namely initial Cr(VI) ion concentration, pH, temperature, co-existing ions and contact time (Kera *et al.* 2017; Xiang *et al.* 2021). Furthermore, the adsorption mechanisms of the particular composite adsorbent hinges on the properties of PPy and various substrates. However, there are certain shared characteristics for all PPy-based adsorbents for the uptake

of Cr(VI) ions from aqueous solution or wastewater. Lower pH typically demonstrates an improved adsorption capacity attributable to robust electrostatic attractions between aqueous Cr(VI) ions and protonated amine groups of the PPy moiety. The reduction in adsorption capacity as the original solution pH increases was largely a result of the waning electrostatic interactions between adsorbent and Cr(VI) ions as well as their competitive adsorption of Cr(VI) ions and $OH^-$ on PPy-based adsorbents adsorption sites (Amalraj *et al.* 2016a; Li *et al.* 2020; Shao *et al.* 2021). Chemical redox reaction occurrence during the Cr(VI) ions adsorption processes is validated by application of FTIR spectroscopy and XPS spectroscopy, X-ray adsorption near edge structure (XANES) analysis techniques for the adsorbent before and after Cr(VI) ion adsorption (Mdlalose *et al.* 2018; Chigondo *et al.* 2019; Tran *et al.* 2019). For example XPS and XANES N 1s core-level spectra of PPy-based adsorbents before and after Cr(VI) ions adsorption with deconvoluted peaks at specific binding energies and their percentage intensities would show a slight shift to the higher binding energies and reduced peak intensities were observable and documented indicating the involvement of N atoms in adsorption. Furthermore, XPS Cr 2p core level spectra usually show bands typical for Cr(III) and Cr(VI) species on adsorbent surfaces (Kera *et al.* 2017; Fang *et al.* 2018; Mdlalose *et al.* 2018; Chigondo *et al.* 2019; Tran *et al.* 2019; Wang *et al.* 2020; Wei *et al.* 2020; Karthikeyan *et al.* 2021) thus helping to explain the adsorption mechanism. Quite a number of studies explained the mechanism using XPS analysis.

The removal of Cr(VI) ions by PPy-modified materials was mainly dependent on the dopant groups besides the amine groups of PPy. Nevertheless, the nature of the PPy-based adsorbents affected the adsorption efficiency and adsorption mechanisms as this depended on the nature of the substrate material. Overall, the adsorption mechanisms of PPy-based adsorbents appeared to have taken place by the reduction of Cr(VI) species to Cr(III) species under acidic conditions. In the meantime, the amine group (−NH−) of PPy is partially oxidized to the positively charged species (−NH•+) which can attract Cr(VI) ions (Li *et al.* 2020). Thus, the adsorption process was associated with ion exchange, electrostatic attractions, complexation, chelation reactions with protonated sites and reduction (Tran *et al.* 2019; Liu *et al.* 2021; Mdlalose *et al.* 2020). Thus the adsorption process can be divided into three portions dependent on the features of the adsorbent: surface complexation under the acidic conditions between negatively charged aqueous Cr(VI) ions and protonated amine groups by electrostatic attractions or ion exchange between aqueous Cr(VI) ions and $OH^-$ on adsorbent surface. Some Cr(VI) ions are reduced to Cr(III) ions while amines are oxidized. Cr(III) are then chelated onto amino substituents on amino dopants and other possible functional groups on various substrates (Wang *et al.* 2013; Zhang *et al.* 2016; Wei *et al.* 2020). The difference in the adsorption experiment conditions, unique adsorbent properties, and adsorbent preparation methods may lead to the different adsorption mechanisms (Tran *et al.* 2019). In this regard some researchers went further to elucidate the Cr speciation in adsorption, by utilising IC-ICP-MS to determine the concentrations of Cr(III) and Cr(VI) filtrate samples from the study of the effect of pH on Cr(VI) ions removal (Setshedi *et al.* 2013; Kera *et al.* 2018; Chigondo *et al.* 2019; Rajeev *et al.* 2019). At pH 2, the concentration of Cr(III) species was found to be high in the filtrate and no Cr(VI) ions were detected. Conversely, at pH 3–12, Cr(VI) ions were increasingly detected. At higher pH, $CrO_4^{2-}$ dominates and since it has a low redox

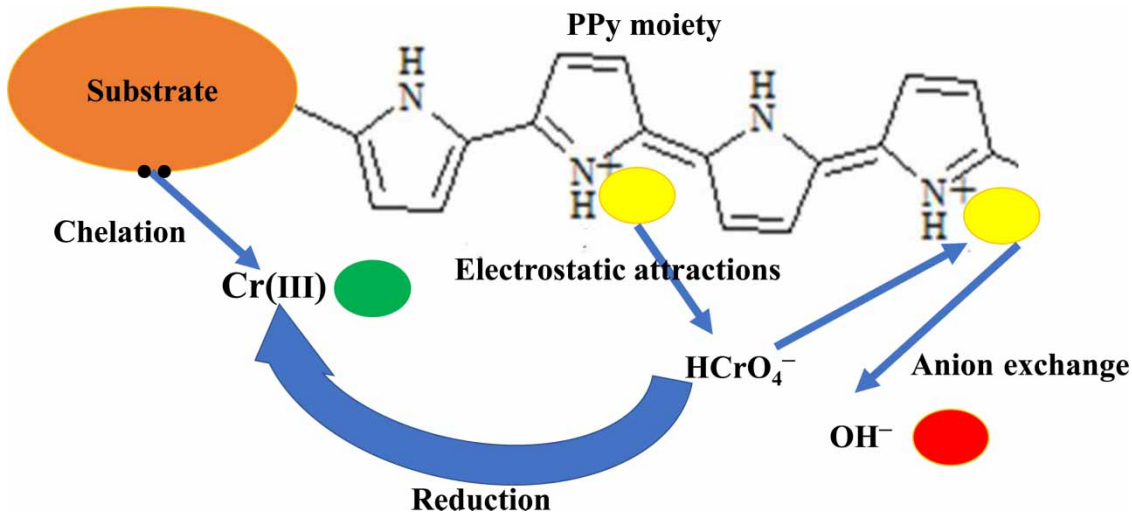



**Figure 6** | Plausible mechanisms of Cr(VI) ion removal by PPy-based adsorbents.

potential (−0.26 V), it was not easily reduced to Cr(III). However, the removal mechanisms of PPy-modified substrate materials remain to be studied further. The pathway of the removal mechanisms of Cr(VI) is summarised in Figure 6.

## 8. CONCLUSION AND FUTURE PERSPECTIVES

This review covers the major anthropogenic sources of Cr(VI), the major regular products containing these toxic ions and their toxicity effects. It further explored the methods of Cr(VI) ions mitigation with adsorption technology being found to be more appropriate due to low execution costs and easy to operate. A plethora of adsorbents is available including PPy-based composites which have proven to be effective in Cr(VI) ions removal and several adsorption parameters influence have been investigated including the effect of pH, initial concentration, temperature and co-existing ions. On the basis of these parameters, it was found that the functionalized PPy materials are quite useful and hence are widely studied for Cr(VI) adsorption. They display numerous advantages such as fast kinetics, high capacity and preferable sorption toward Cr(VI) ions in water. However, to further inspire the practical application of PPy-based polymers in the removal of Cr(VI) ions some technical limitations need to be resolved. To date, from the commercial point of view, no greater achievements have been attained using PPy-based adsorbents. Extensive research is necessary to commercialise these adsorbents which would give a new dimension for adsorption technology towards mitigation of the environmental pollution problems.

The Langmuir and Freundlich models have been found to be most prevalent adsorption isotherms models used to describe the adsorption process with the Langmuir maximum adsorption capacity being used to compare the different adsorbents reviewed. The adsorption efficiency might be considerably different from laboratory-scale bench experiment solutions. Moreover, a variety of PPy-based composite should be developed. Comprehensive study of the adsorbent regeneration is still limited in most literature. This is necessary if meaningful information is to be obtained from adsorption studies and have potential in large-scale industrial water treatment and to reduce the costs. The rupture of the polymer chain by a repeated reaction of oxidation with highly oxidizing Cr(VI) species could decrease the mass sorption sites in the spent adsorbent, which could account for the decrease in the adsorption capacity. Hence, further studies are necessary to investigate alternative desorption and regeneration treatments which will minimise deterioration of the structure of the CP composites and increase their lifespans. Methods to improve the structural integrity of the CP composites should also be investigated as robust adsorbents are attractive for real field applications. In some reviewed studies inadequate information was provided and in others comprehensive, energy consuming preparatory methods were reported which cannot be reproduced on a commercial scale in a cost-effective manner. The utilization of Cr(VI)-laden waste materials in other sectors of research in order to limit the risk of secondary pollution as a result of the adsorption process is imperative.

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## CONFLICT OF INTEREST

We declare that there are no conflicts of interest.

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## DATA AVAILABILITY STATEMENT

All relevant data are included in the paper.

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