



Cite this: *Chem. Soc. Rev.*, 2025, 54, 6525

## Turning over a new leaf: innovative pest control from a materials science perspective

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The growing demand for food due to a global population increase has made the use of pesticides in agriculture unavoidable despite their various harmful side effects. Driven by stricter legislation, nations are now compelled to find alternatives. This situation led to accelerated research around the world, focusing on developing new chemistries to enhance the environmental safety of pesticides. In recent years, bioinspired strategies of pest control have emerged as alternatives to the development of new synthetic pesticides. In order to design innovative eco-friendly pest management techniques, a thorough understanding of naturally existing physical and chemical defences in plants is needed. Building upon this knowledge, material science provides innovative strategies for designing physical barriers, biomimetic adhesives, and targeted delivery systems that go beyond traditional chemical approaches. This tutorial review explores the intricate relationships between plants and insects, focusing on natural defence mechanisms such as plant cuticles, trichomes, and thigmonasty. We also review advances in synthetic pesticide use, including enhanced adhesion and controlled release formulations. In addition, we delve into advances in other integrated pest management domains, discussing the potential of bioinspired surfaces and biological control methods. This overview aims to foster comprehensive understanding and interdisciplinary approaches, highlighting the pivotal role of material science in improving sustainable pest control for the future.

Received 27th April 2025

DOI: 10.1039/d5cs00458f

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### 1. Pesticides through the ages: historical developments and emerging alternatives

Synthetic pesticides emerged after World War II as a vital means to control the spread of harmful diseases *via* insect



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vectors. Among the initial insecticides to be investigated, dichloro-diphenyl-trichloroethane (DDT), developed by Paul Mueller, proved highly toxic to a wide spectrum of insects while exhibiting relatively low acute toxicity to mammals at typical usage concentrations. This discovery further led to the development of various organophosphates and carbamates.<sup>1,2</sup> Although the initial need for insecticides was to target vectors of human diseases, their potential to control a wide range of pests led to their rapid expansion into the fields of agriculture as described by Flint and van den Bosch in 1981: “Their success was immediate. They were cheap, effective in small quantities, easy to apply, and widely toxic. They seemed to be truly ‘miracle’ insecticides”.<sup>2</sup>

Today, the term ‘pesticides’ describes a vast group of substances used as insecticides, acaricides, herbicides, bactericides, fungicides, rodenticides, nematocides, molluscicides,

and growth regulators.<sup>3</sup> These substances may act (1) protectively or curatively, (2) selectively or broadly, and (3) *via* contact or *via* uptake. Pesticide toxicity must be clearly labeled in accordance with internationally recognized hazard classifications, as either toxic, corrosive, irritating, or harmful.

Pesticides play a key role in the process of agricultural intensification – increasing yield, productivity, and quality on existing agricultural fields. Agriculture today relies heavily on pesticides to minimise plant pests and diseases, and meet the growing food demands of the ever-increasing human population.<sup>4</sup> In fact, there has been a surge in the worldwide use of pesticides over the last couple of decades, resulting in several positive and negative effects as summarised in Fig. 1.

Among these negative effects, pesticides were identified as the root cause of numerous health effects in humans. These include diseases of the skin, nerves, lungs, reproductive organs,



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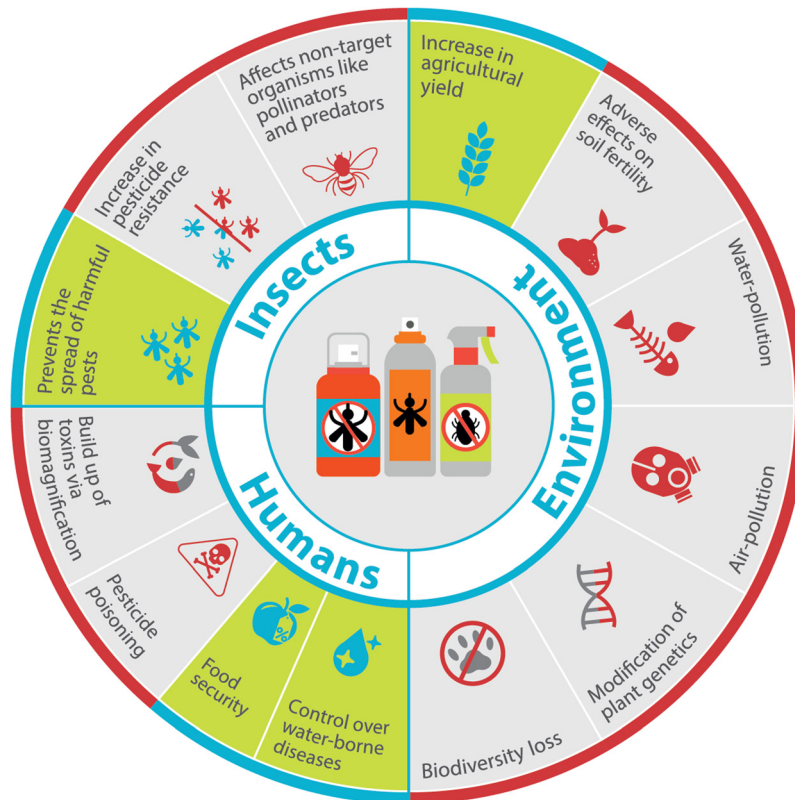


Fig. 1 Overview of desirable (green/blue panels) and undesirable (grey/red panels) consequences of synthetic pesticides on insects, environment, and humans.

and the endocrine system.<sup>5–11</sup> Pesticides may also threaten the ecosystem by harming aquatic and terrestrial life. Although soil can act as a large reservoir for storing pesticides, contamination of water bodies is often inevitable due to the close relationship of soil with surface and ground water sources.<sup>12</sup> Pesticide residues are commonly found in water bodies as a result of various processes like leaching, run-off, soil erosion, and drift.<sup>13,14</sup> Even trace residues of pesticides in these water sources can accumulate to harmful levels as the substances travel through the food chain, a process called biomagnification. In addition, pesticides can disrupt the ecological balance by harming non-target organisms in different classes like soil invertebrates (earthworms and predatory bugs), microorganisms, and pollinators (bees).<sup>12</sup> Further, undesirable consequences such as the development of pesticide resistance in target pests, can render certain pesticides ineffective, leading to the need for harsher chemicals or higher doses to kill pesticide-resistant species.<sup>15</sup>

The various harmful side effects of pesticides that emerged due to this increased usage urged researchers worldwide to search for alternatives. In the European Union, pesticides must undergo a strict admission procedure for an indication license, *i.e.*, they can be applied only to certain plant species under certain conditions. In addition, the admission period and multiple uses are very limited, to ensure rotation of different active chemical substances, thus preventing pest resistance. However, current political strategies lead to a restricted spectrum of available active chemical substances, resulting in

repeated use and, thus, increased pest resistance against pesticides. Even sublethal doses of agrochemicals along with changes in environmental temperatures contribute to the global decline of insect populations.<sup>16</sup> These trends may have severe economic consequences, particularly considering the challenges posed by invasive pests in a warming world.

A transition towards minimising and replacing toxic chemicals is not immediately feasible. For example, Aldicarb, a carbamate pesticide used on citrus plants and potatoes, was banned in the United States a decade ago because it posed “unacceptable dietary risks”. In the present day, despite being banned in over 100 countries and classified as “extremely hazardous” by the World Health Organization (WHO), Aldicarb is again being considered for use by the U.S. Environmental Protection Agency (EPA) as part of its routine pesticide review process.<sup>17–19</sup>

This highlights a pressing need to switch to more environmentally friendly pest management techniques to prevent the immediate and long-term negative effects of pesticide exposure. To develop such techniques, it is essential to recognise that there is potential not only in new chemistry but also in improving our understanding of the innate physical and chemical defences employed by plants. For instance, surface patterning observed in plant structures can effectively deter pests, inspiring material scientists to create innovative solutions.<sup>20</sup> Approaches that plants have evolved to defend themselves may be synthetically mimicked, enhanced, or reproduced.

In nature, typically, a combination of multiple defence strategies is employed. This principle is also embodied in



integrated pest management (IPM), a sustainable and large-scale approach that has been in place for about 45 years. Integrated crop management (ICM) is a broader approach that combines physical, cultural, biological, and chemical management strategies of IPM along with crop-specific strategies to grow healthy plants while minimising pesticide use.<sup>21,22</sup> Physical control considers, *e.g.*, mechanical devices that can prevent the pest from accessing the plant, such as barriers and traps. Cultural control refers to agricultural practices undertaken by farmers to make crops less favourable for pests, such as crop rotation, the use of sacrificial crops and resistant genotypes. Biological control relies on natural antagonists, such as predatory insects and microorganisms preying on target insects. Considering the current state of science and technological advances, there is still ample scope for improvement in all individual IPM domains as well as the integration of these different domains to enhance their overall effectiveness while minimising the effect on the environment. Therefore, plant biologists, agricultural scientists, microbiologists, entomologists, environmental scientists, chemists, materials scientists, and potentially other disciplines, have to combine expertise from their diverse fields.

This review aims to provide a comprehensive understanding of natural plant defence strategies and how material science can contribute to developing collaborative pest management solutions. We will discuss recent IPM developments with a particular focus on how material science can enhance chemical control, for instance, by improving the adhesion of pesticides to plants, thereby ensuring that pesticide loss and pollution is reduced. Our primary focus lies in advancing IPM, particularly against pest insects, but we will also cover some interesting examples against fungi and bacteria. This is not meant to be an exhaustive overview since there are already several specialised reviews such as on the use of nanoparticles in agriculture,<sup>23–26</sup> controlled release pesticide formulations<sup>27–29</sup> and currently employed techniques in agriculture.<sup>30,31</sup> Starting from interactions observed in nature and the resulting defence mechanisms evolved by plants to protect themselves (Sections 2 and 3), our review delves deeper into developments to improve the eco-friendliness and reduce the toxicity of chemical pesticides (Section 4). Moreover, we highlight promising strategies to control the release of synthetic pesticides (Section 5). We also draw attention to the fact that many natural defence mechanisms explored in Sections 2 and 3 remain underutilised in synthetic approaches (Sections 4 and 5), suggesting several promising, nature-inspired solutions that may be interesting to explore. Lastly, we offer insights into the combination of these emerging strategies into novel IPM approaches, suggesting synergistic combinations for enhanced effectiveness.

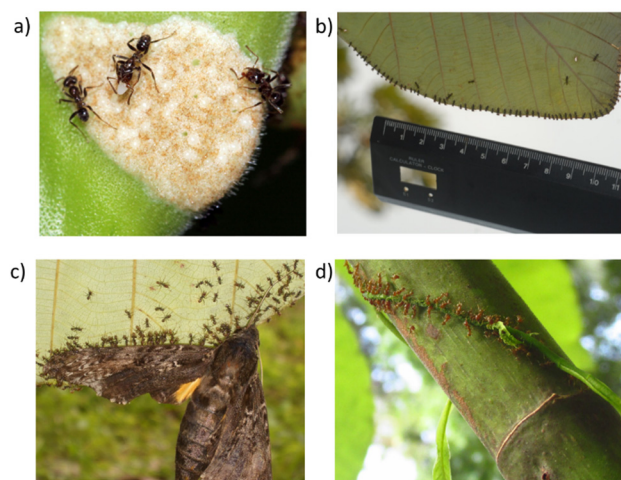
## 2. Interactions between plants and insects

Interactions between species, be it direct or indirect, form the basis for all processes in an ecosystem. Darwin already emphasised the coevolution process between insect and plant

communities.<sup>32</sup> Here, we discuss two commonly occurring types of interactions between different organisms and their relevance to plant defence and herbivorous insects. These types are mutualism and antagonism. A third type, commensalism, is not easily identifiable between plants and insects and hence, is not explored further here.

### 2.1 Mutualism

Plants and insects have mutualistic relationships mainly for pollination, seed dispersal, and protection purposes.<sup>33</sup> Mutualism, a type of symbiosis, is a cooperative interaction between two or more species, where each species benefits from the relationship. It also acts as a line of defence for plants. Ants are widely reported to have a mutualistic relationship with different plants.<sup>12,34,35</sup> For example, *Cecropia* plants<sup>36</sup> have hollow internodes which *Azteca* ants use for nesting. The internal spongy tissues lining the internodes act as a food source for the cohabitant ants (Fig. 2a).<sup>37</sup> *Cecropia* plants also produce structures called pearl bodies rich in fats to provide the ants with a balanced diet. These evolutionary features are suggested to have been solely developed by the *Cecropia* plant to provide food and shelter to *Azteca* ants. In return, the ants protect the plants against attacking insects and sometimes even slightly larger herbivores owing to their sharp mandibles (Fig. 2b).<sup>38</sup> The hook-shaped claws on the ants' feet allow them to hold on to the plant while capturing large insects (Fig. 2c), weighing over 13 000 times a single ant's body weight. Apart from protecting the plant against herbivores, these ants also prevent competing plants to grow nearby (Fig. 2d), by chewing and killing the shoot tips and tendrils of encroaching vines.<sup>39</sup> Such



**Fig. 2** Mutualistic relationship between *Azteca* ants and *Cecropia* plants. Photographs of (a) *Azteca* ants feeding on white Müllerian bodies, which are glycogen-rich food bodies located on fuzzy pads (trichilia) at the base of the plant's petiole, (b) ants hiding on the underside of the leaf with open mandibles for an ambush, (c) sphingid moth captured by the army of ants at the leaf margin, and (d) ants defending the *Cecropia* plant against an encroaching vine. (a) and (d) Reproduced under the terms of a Creative Commons Attribution License.<sup>36</sup> Copyright 2018, Springer Nature. (b) and (c) Reproduced under the terms of a Creative Commons Attribution License.<sup>38</sup> Copyright 2010, Dejean *et al.*



forms of defence provided by the ants help plants direct their energy towards growth rather than defence. These ants were also found to excrete nitrogenous wastes that act as rich nitrogen sources for the plant, thus fertilising the plant.<sup>40–43</sup> However, such mutualistic relationships are sensitive to environmental shifts. Janzen *et al.* documented how the absence of herbivores on the Caribbean islands removed the need for *Cecropia* plants to attract *Azteca* ants, which eventually led to a dissociation of their mutualistic relationship.<sup>41</sup>

## 2.2 Antagonism

Antagonistic interactions between plants and insects usually result in the insect benefitting at the expense of the plant. Unlike commensalism and mutualism, where interactions are cooperative, antagonistic relationships such as predation, parasitism, and herbivory are characterised by competition and harm to the organisms involved.

Predation refers to one organism (predator) killing and consuming another organism (prey) for food. For example, carnivorous plants have evolved various attributes that help them capture and digest prey insects to supplement their nutrient needs.<sup>44</sup> What differentiates carnivorous plants from each other are their specialised active or passive traps to attract and capture prey.<sup>45,46</sup> Some plants employ active moving traps that shut quickly, capture and absorb the prey upon contact such as that of bladderworts.<sup>47</sup> A typical example of snap traps is the Venus flytrap (*Dionaea muscipula*) (Fig. 3a), which emits over 60 volatile compounds to attract prey insects. When the prey insect explores the trap, their movement can set off the sensory hairs that trigger the closure of the trap, thus ensnaring the prey.<sup>48</sup> In contrast, plants employing passive traps do not rely on moving plant parts but on innate features such as slippery and sticky surfaces and their hierarchical cascade arrangement.<sup>49–52</sup> For example, pitfall traps employed by different families of pitcher plants (Fig. 3b) attract prey through various means, including secretion of sweet-smelling nectar, appealing patterns, and coloured veins. Once attracted, the prey loses its grip on the rim and inner pitcher wall as it encounters slippery surfaces arising from anisotropic epidermal cell curvatures and two layers of epicuticular wax crystals.<sup>50,53–56</sup> The pitcher also contains a pool of viscoelastic biopolymer digestive fluids at the base, that break down the prey's soft tissues, releasing essential nutrients like nitrogen and phosphorus for the plant.<sup>57</sup>

Parasitism, in contrast, does not kill the host immediately. Instead, the parasitic organism draws nutrients from the host and slowly weakens it over time.<sup>62,63</sup> For example, the adult females of gall-forming insects belonging to the Cynipidae (gall wasps, order Hymenoptera) and Cecidomyiidae (gall midges, order Diptera) families (Fig. 3c) inject eggs along with a secretion into their host plant tissues. This results in the death of the plant cells adjacent to the eggs, causing neighbouring cells to create a growing tumour-like mass called gall. After the larvae emerge, their feeding activity, along with oral secretions they produce, stimulate further gall growth, thus draining energy from the plant.<sup>64</sup>

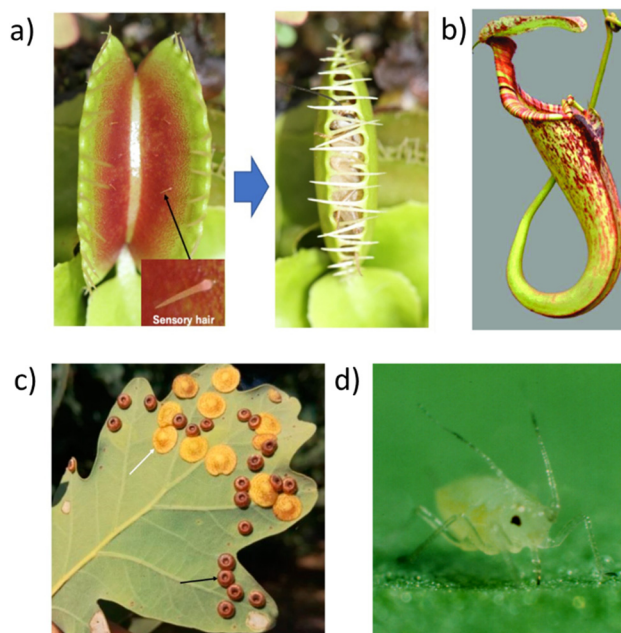


Fig. 3 Antagonistic plant-insect relationships. Photographs of (a) snap trap of the Venus flytrap, (b) pitfall trap of the pitcher plant, (c) galls of two different species of *Cynipidae* wasps on the underside of an oak leaf, and (d) an aphid feeding by penetrating its slender mouthparts (stylets) into the plant tissues. (a) Reproduced with permission from National Institute for Basic Biology.<sup>58</sup> Copyright 2020, Mitsuyasu Hasebe. (b)–(d) Reproduced under the terms of a Creative Commons Attribution License.<sup>59–61</sup> Copyright 2020, Schwallier *et al.*, Copyright 2021, Jankiewicz *et al.*, and Copyright 2014, Lohaus and Schwerdtfeger respectively.

Herbivory concerns insects that feed on plants by chewing on plant parts like roots, stems, and leaves, sucking out the plants' cell contents, injecting fluids into the plant cells, or transmitting diseases.<sup>65</sup> For example, aphids have slender specialised mouthparts called stylets, which they use to penetrate plant tissues, after which they secrete digestive enzymes directly into the tissue and suck out the sugary phloem sap (Fig. 3d). Aphids can also inflict damage on plants by the sticky waste they secrete called honeydew, which causes leaf loss.<sup>66</sup>

To defend themselves against attacking species, plants have evolved a number of morphological and chemical defence mechanisms, leading to an ongoing co-evolutionary race between plants and herbivores. Although in this review we focus on interactions between plants and insects, antagonistic relationships between different insects, mainly herbivore pests and their natural enemies, have also been exploited in recent years in the form of biological control with beneficial insects in IPM.<sup>67–69</sup>

## 3. Structural natural defence in plants

Plant defence mechanisms can be classified into different categories, such as constitutive *vs.* induced. Constitutive defence refers to preformed plant traits that are always present in the plant irrespective of the presence of a pest,<sup>70</sup> while induced defence refers to temporary plant traits that develop



rapidly in response to an attack, for example, when foreign molecules or damaged cells activate an immune response.<sup>71,72</sup> Since most attacks on plants are unforeseeable and quite unpredictable to an extent, many plants express low levels of constitutive defence to conserve energy and repurpose these resources during an infestation as a form of induced defence.<sup>73</sup>

Another classification uses the distinction between direct and indirect defence mechanisms. Direct defence refers to plant attributes that negatively affect the attacking pest, including morphological characters like thorns, spines, trichomes, *etc.*, and chemical compounds such as toxins that interfere with the pest's metabolic activities.<sup>74,75</sup> Conversely, indirect defence acts on undesirable pests by involving other organisms that can attack and remove plant enemies. Since a defence mechanism can fall under multiple categories of constitutive *vs.* induced, direct *vs.* indirect, or morphological *vs.* chemical attributes, we discuss the mechanisms individually in this section, focusing on morphological features. Natural chemical defence mechanisms involving secondary metabolites, toxins, digestive inhibitors, and recruitment of predatory insects with volatiles also play an equally important part and have been reviewed in detail elsewhere.<sup>76–79</sup>

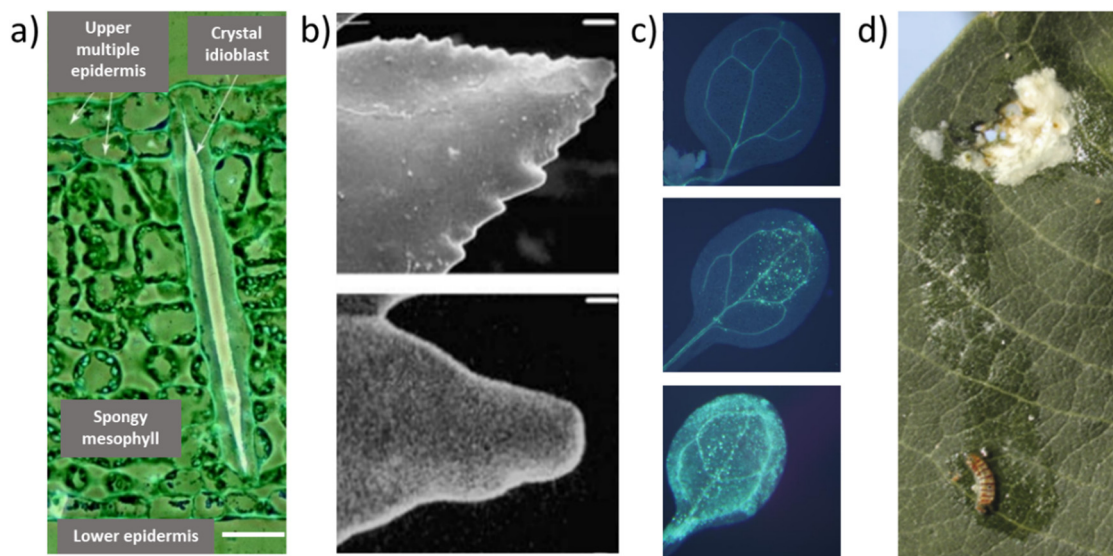
### 3.1 Plant cell attributes

The plant cell wall typically contains a complex mixture of components like cellulose, hemicellulose, lignin, and pectin, which may play essential roles in cell wall fortification as a response to external stresses (induced defence).<sup>80,81</sup> In addition, plants absorb dissolved calcium and silicon from the soil

*via* the root system.<sup>82–85</sup> Coordinated mineralisation processes lead to the deposition of microscopic solids such as cystoliths (calcium carbonate), idioblasts (calcium oxalate), and phytoliths (silicon), that act as toxic antinutrients and physical deterrents against herbivores.<sup>83,86,87</sup>

Calcium oxalate crystals are the most widespread solid minerals across the plant kingdom, reaching 3–80% plant dry mass mineral content. They perform a number of functions, such as providing structural support for tissues, storing essential substances, and regulating mineral content within the plant.<sup>88</sup> This type of plant defence is typically more effective against chewing insects compared to sucking insects. When offered a calcium oxalate-rich wild type and a mutant calcium-oxalate defective line of the legume species *Medicago truncatula* (Fig. 4a), the beet armyworm *Spodoptera exigua* displayed clear feeding preferences for the mutant. The larval teeth remained sharply pointed along with a slightly serrated edge while feeding on the mutant, similar to the control group fed with an artificial diet. In contrast, larvae that fed on the wild type ended up with smoothed teeth and a blunt point displaying the abrasive effects of these crystal idioblasts (Fig. 4b).<sup>83,89</sup>

High silicon contents (>4%) have been observed in grasses (Poaceae), horsetails (Equisetae), and sedges (Cyperaceae), where they frequently strengthen plant cell walls.<sup>83,84</sup> Rice, for example, stores up to 10–15% of its dry mass in silicon. Apart from acting as a structural support for these plants, silicified cell walls are closely associated with reduced blast disease since they protect the plant cells from being penetrated by attacking fungi.<sup>93,94</sup> Phytoliths occur within and between the



**Fig. 4** Plant cell attributes acting as a natural defence including (a) calcium oxalate crystal idioblast visible in the leaf cross-section of a mature *Claoxylon sandwicense* plant. Scale bar = 400  $\mu\text{m}$ , (b) scanning electron microscopy (SEM) images showing smoothing of a *Spodoptera exigua* larvae tooth (bottom) due to abrasive effects from calcium oxalate crystals in *Medicago truncatula* in comparison to a sharp tooth from larvae on an artificial diet (top). Scale bar = 10  $\mu\text{m}$ , (c) callose deposition highlighted using epifluorescence microscopy with wounded (middle) and bacterial peptide treated (bottom) *Arabidopsis thaliana* cotyledons in comparison to unwounded control seedlings (top). (d) Monarch caterpillar succumbed after contact with released latex after initial larval feeding on *Asclepias syriaca* leaves. (a) Adapted with permission.<sup>90</sup> Copyright 2001, Elsevier Science Ltd. (b) Reproduced with permission.<sup>89</sup> Copyright 2006, American Society of Plant Biologists (c) Adapted under the terms of a Creative Commons Attribution License.<sup>91</sup> Copyright 2018, Keppler *et al.* (d) Reproduced with permission.<sup>92</sup> Copyright 2019, Springer Science + Business Media, LLC, part of Springer Nature 2019.



plant cells and wear down the mandibles of herbivorous insects due to their abrasive nature, impeding feeding.<sup>95</sup> The African armyworm *Spodoptera exempta* fed with silica-rich grasses (*Deschampsia caespitosa*, *Festuca ovina*, *Lolium perenne*) struggled to digest the leaves and showed rapid mandible wear. It could not easily adapt to the physical defence and lost fitness.<sup>96</sup> In addition to a physical barrier, silicon can trigger systemic plant defence mechanisms by inducing defensive enzymes such as peroxidases and polyphenol oxidases, as observed after adding silicon to soil or nutrient solution.<sup>94,97,98</sup> The exact mechanism of how silicon triggers the activation of defensive enzymes is still unclear. However, there is evidence that silicon boosts activity of various antioxidant enzymes like peroxidases, which help mitigate the cytotoxic effects of excess reactive oxygen species, typically generated during herbivore attacks.<sup>98,99</sup>

Callose also plays a role in the induced fortification of cell walls, as shown in Fig. 4c. In contrast to silicon, callose is a linear  $\beta$ -glucan polysaccharide synthesised by the plant itself. When a plant faces a pathogen attack, it responds by depositing callose between the plasma membrane and the cell wall at the locations where the pathogen has struck.<sup>100</sup> Callose is also an important defence against larger insects, making it more difficult for them to penetrate the plant tissues.<sup>101</sup> After herbivory attacks, the deposition of callose can help seal plant wounds, restricting further access to feed from other plant parts and preventing infections with microorganisms.<sup>102</sup>

Similarly, laticifers contain a sticky viscous emulsion called latex, serving as a defence in most plants.<sup>103</sup> When herbivores damage plant parts, the tubular network of laticifers release latex locally at the site of attack thereby sealing the wound.<sup>104</sup> This exudate contains secondary metabolites like proteins, alkaloids, flavonoids, and terpenoids that act as toxins for attacking pests, as observed in milkweeds (*Asclepias* spp.) containing cardiac glycosides, toxic to many herbivores.<sup>105</sup> After monarch butterflies, *Danaus plexippus*, attach their eggs reliably on the underside of the milkweed leaves, the hatched larvae start feeding on leaves for survival. While chewing the plant tissues, latex gets released and solidified in the presence of air, forming a sticky glue hindering the feeding process and potentially killing the caterpillar (Fig. 4d).<sup>92</sup>

A similar plant defence is the presence of resin ducts, which are intercellular spaces filled with resin under internal pressure. Typically present in most conifers, resins are a mixture of monoterpenes, sesquiterpenes, and diterpene resin acids. When stem-boring insects break into these networks of ducts, they get expelled out due to the pressure from the resin flow. Upon contact with air, volatile compounds in the resin mixture evaporate, resulting in the insects getting solidified in resin acids. Further, this reaction upon exposure with air also ensures that the wounded site in the plant is sealed off by solid resin. The breached resin duct system is subsequently fixed by the formation of new resin ducts (induced plant response).<sup>106</sup>

### 3.2 Plant cuticle

Plant surfaces above the ground have a hydrophobic covering composed of cutin and intracuticular wax, referred to as the

cuticle, acting as an extracellular interface with the environment.<sup>107–109</sup> This biopolymer has important mechanical properties for the plant, providing structural stability and maintenance of its physiological health.<sup>108</sup> The chemical composition and microstructure of the cuticle may differ profoundly between plant species and developmental stages.<sup>110</sup> This is important since cuticular folds can influence the leaf blade and flower petal stability, as well as plant surfaces' optical and tribological properties.<sup>111</sup> For example, it has been shown that leaf beetles and pollinators slip away when walking on flat substrates with nm-sized folds, while  $\mu\text{m}$ -sized folds on epidermal convexities support insect foothold.<sup>112</sup>

Being the interface for biotic interactions, the cuticle can affect adhesion, host recognition, and mechanical prevention of microbes and arthropods.<sup>109</sup> Apart from acting as a first line of defence for most plants against various pests and pathogens, the cuticle also plays a significant role in protecting against UV radiation, high temperatures, and water loss.<sup>113</sup>

**3.2.1 Plant epicuticular wax crystals.** Epicuticular waxes crystallise on the molecular wax layer of the outer plant cuticle and self-assemble into diverse shapes, chemistries, and clusters. Commonly, they are mixtures of aliphatic hydrocarbons and their derivatives. The chemical composition varies between plant species, within the organs of one species, or during organ development.<sup>109,110</sup> Dense wax coverages provide the plant surfaces with superhydrophobic and self-cleaning properties, which repel watery fluids and prevent infestation of pathogens and parasites.<sup>114</sup>

Effects of epicuticular plant waxes on insect feeding and behaviour, especially for insect-host selection, have been reported extensively.<sup>115</sup> Alkanes of epicuticular waxes were identified to serve as insect deterrents in sorghum and maize; wax esters increased aphids resistance in alfalfa, and wax alcohols in concert with reduced hydrocarbon chain length on sugarcane reduced the sugarcane stalk bore larvae survival. Moreover, aromatic wax constituents were found to promote resistance of various plants such as the *Rhododendron* species to the azalea lace bug.<sup>116</sup>

Wax crystals on plant surfaces have been studied for over a century and were found to hinder insect attachment by influencing factors such as their composition, structure, size, abundance, and distribution.<sup>117</sup> Gorb and Gorb proposed and tested four possible mechanisms involved in weak insect attachment on plant surfaces covered with crystalline epicuticular wax: (1) roughness, (2) contamination, (3) fluid-adsorption, and (4) wax-dissolution.<sup>117,118</sup> The roughness mechanism refers to the nanoscopic to microscopic roughness caused by wax crystals decreasing the real contact area between the plant surface and the insect attachment pad. The contamination mechanism causes insects to lose foothold due to wax crystals detaching from plant surfaces. The fluid-adsorption mechanism refers to highly porous, lipophilic plant epicuticular wax coverage absorbing the fluid responsible for adhesion released by the insect attachment pads. Finally, the wax-dissolution mechanism involves plant epicuticular wax crystals dissolving by lipids and lipophilic substances in the adhesion-mediating



fluid of insect attachment pads. However, this mechanism is based on indirect evidence and has not been experimentally proven.<sup>117,118</sup>

### 3.3 Trichomes

Trichomes are hair-like structures present naturally as an extension of the epidermis on some plants.<sup>119</sup> They perform several functions in plants, such as protecting against UV radiation, preventing excess water loss from transpiration, regulating temperature, facilitating gas exchange, and acting as a natural defence.<sup>119</sup> Most trichomes are inherently present, meaning they are a type of constitutive defence. However, it is also very likely that some plants can induce them by increasing the density of trichomes defending against predator attacks.<sup>120–122</sup>

Sticky exudates of glandular trichomes can trap or hamper the movement of pests (physical defence), or produce antagonising volatiles or toxins that can deter and harm the insect when detected, contacted or ingested (chemical defence).<sup>123</sup> For example, the wild potato *Solanum berthaultii* resists the attack of pest beetles, leafhoppers, and aphids owing to the presence of two types of glandular trichomes; elongated cone-shaped with non-covered glandular heads (type B) and short capitate cutin-covered four-celled glandular heads (type A). When insects attack plants, they usually encounter type-B trichomes first, which continuously release an adhesive viscoelastic exudate, thereby coating the body of the pests. The insect struggles to free itself and gets in contact with the shorter, stiffer type-A trichomes, which release a two-compound adhesive consisting of polyphenol oxidase enzymes and a phenolic substance, chlorogenic acid. Their reaction produces a quinone-based brown polymer, which hardens and immobilises the pest. Additionally, the exudate from type-B trichomes contains sesquiterpenes, repellent to pests settling on the plants.<sup>124,125</sup> A similar mechanism is observed in the trichomes of *Sicana odorifera* where aphids rupture the heads, leading to the deposition of a sticky exudate on the insect.<sup>126</sup>

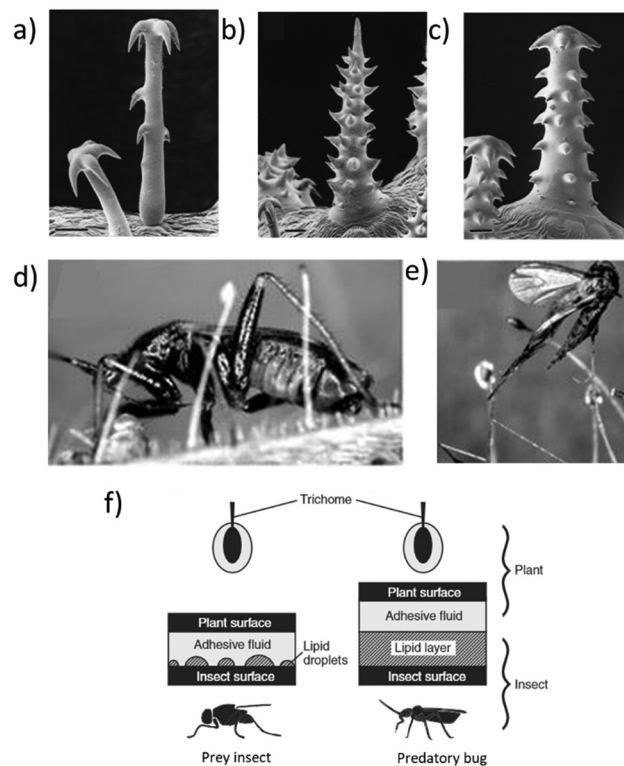
Murungi *et al.* studied different African nightshades (*Solanum* sp.) in which glandular trichomes prevented oviposition by tomato spider mites *Tetranychus evansi* (Acari, Tetranychidae). This was attributed to the unsaturated fatty acids present in these exudates, interfering oviposition through volatile chemical signals.<sup>127</sup> Transferring the exudate of the glandular trichomes from *Solanum sarrachoides* onto *Solanum scabrum*, void of these trichomes, exhibited a 70% reduction of placed mite eggs. Similarly, potato tuber moths laid 97% fewer eggs on potato crop *Solanum tuberosum*, when exudates of the wild potato *Solanum berthaultii* were manually transferred to the susceptible cultivar.<sup>128</sup>

Non-glandular trichomes are mainly physical barriers, preventing pests from reaching the leaf surface.<sup>129</sup> For example, field beans *Phaseolus vulgaris* are equipped with tapered hook-shaped trichomes, impaling, *e.g.*, potato leafhoppers *Empoasca fabae* and leafminers *Liriomyza trifolii*, particularly on the lower leaf side.<sup>130</sup> Once trapped, the leafhoppers immediately try to free themselves and get stabbed by neighbouring trichomes.

The trapped leafhoppers cannot feed and die from starvation and/or dehydration.<sup>130,131</sup> Similar effects have been observed with hook-shaped non-glandular trichomes in prickled herbs, belonging to the family Loasaceae (Fig. 5a–c), which are known for reinforced trichomes with incorporated biominerals (calcium phosphate, silica) in tips and barbs, providing mechanical defence.<sup>132</sup>

Trichomes can also have a detrimental effect on non-target organisms, including predatory insects.<sup>133,135</sup> The hook-shaped field bean trichomes of the previous example are also known to impale and kill acariphagous ladybird beetles.<sup>136</sup> Similarly, the long erect tomato trichomes have been observed to impale larvae of the two-spotted lady beetle attempting to forage green peach aphids.<sup>137</sup> In addition, trichome exudates on glandular hairy tomato plants also hindered omnivorous bugs, reducing their prey searches and forcing them to groom more often.<sup>138</sup>

Some insects have evolved morphological and behavioural characteristics that help them to overcome trichome defences.<sup>139</sup> For example, while resins secreted by the glandular



**Fig. 5** Trichomes acting as a natural defence mechanism: SEM images of (a) hook-shaped, (b) tapered conical-shaped and barbed, and (c) cylindrically shaped and barbed trichomes of *Mentzelia pumila*. Photographs showcasing (d) an adult mirid bug *Pameridea roridulae* in motion on the surfaces of carnivorous *Roridula gorgonias* leaves covered with glandular trichomes and (e) a trapped fly on *R. gorgonias* trichomes. (f) A thick, greasy epicuticular lipid layer equipping *P. roridulae* with sloughing-off surface properties and enabling the bug to navigate across the sticky plant surface unlike the stuck prey insects. (a)–(c) Reproduced with permission.<sup>133</sup> Copyright 1998, The National Academy of Sciences. (d)–(f) Reproduced under the terms of The Company of Biologists Publication Agreement.<sup>134</sup> Copyright 2008, The Company of Biologists Limited.



trichomes of the carnivorous *Roridula gorgonias* plants normally capture insects, mirid bugs (*Pameridea roridulae*) use their body strength and a thick lipoid greasy layer on the integument to prevent getting stuck (Fig. 5f).<sup>134,140</sup> Other mirid bugs living on pubescent plants use long slender legs to cling to trichomes while keeping their body away from the plant surface.<sup>140</sup> On other glandular plants, adhering prey insect corpses are known to attract predatory insects, thus indirectly defending by herbivore suppression.<sup>141</sup>

### 3.4 Spines, thorns, and prickles

Robust, sharp structures like spines, thorns, and prickles are physical deterrents against large herbivores.<sup>142,143</sup> Spines (Fig. 6a) contain vascular bundles and are a modified form of leaf tissues. They are stiff and slender and typically replace photosynthetic leaves in plants to prevent water loss and protect them from herbivores. Cactus spines further aid in directing water drops toward the plant body.<sup>144</sup> Thorns (Fig. 6b) also contain vascular bundles but are a modified form of the stem and are quite tough and woody. Prickles are not vascularised and are breakable, short extensions of the epidermis (Fig. 6c).<sup>145,146</sup>

### 3.5 Thigmonasty

Thigmonastic defence refers to non-directional plant movements in response to an external stimulus.<sup>149</sup> When *Mimosa pudica*

*pudica* ('touch-me-not' plant) leaves were disturbed by an external trigger, the water-filled cells were observed to lose turgor pressure due to the redistribution of potassium, sodium, and calcium ions.<sup>150–152</sup> Leaflets almost instantly folded up and petioles dropped (Fig. 6d and e). In this way, the plant reduces the visible amount of foliage and exposes its thorny stem to deter herbivores.<sup>153</sup> Specialised swollen structures, called pulvini, present at the base of the leaflets and along the stems function as rigid supports to maintain the structure and hold the mass of the leaflets.

### 3.6 Camouflage

Camouflage as a natural defence is observed in passion flowers *Passiflora* sp. to deter Heliconiine butterflies.<sup>148</sup> Female Heliconiine butterflies avoid laying eggs on passion flowers *Passiflora* sp. plants covered with existing butterfly eggs to reduce competition, because certain *Heliconius* sp. larvae exhibit cannibalistic behaviour.<sup>148,154</sup> *Passiflora* plants defend themselves from being damaged by these caterpillars by having structures mimicking the yellow eggs of butterflies on their leaves, which are swollen ends of stipules (Fig. 6f). Visual cues arising from the yellow-coloured eggs or egg-mimicking stipules are critical for butterflies' oviposition site decision.<sup>155</sup> When artificially coloured green eggs were introduced on the plant, butterflies laid eggs nearby, yet yellow eggs resulted in a drastic reduction in ovipositional frequency.<sup>155</sup>

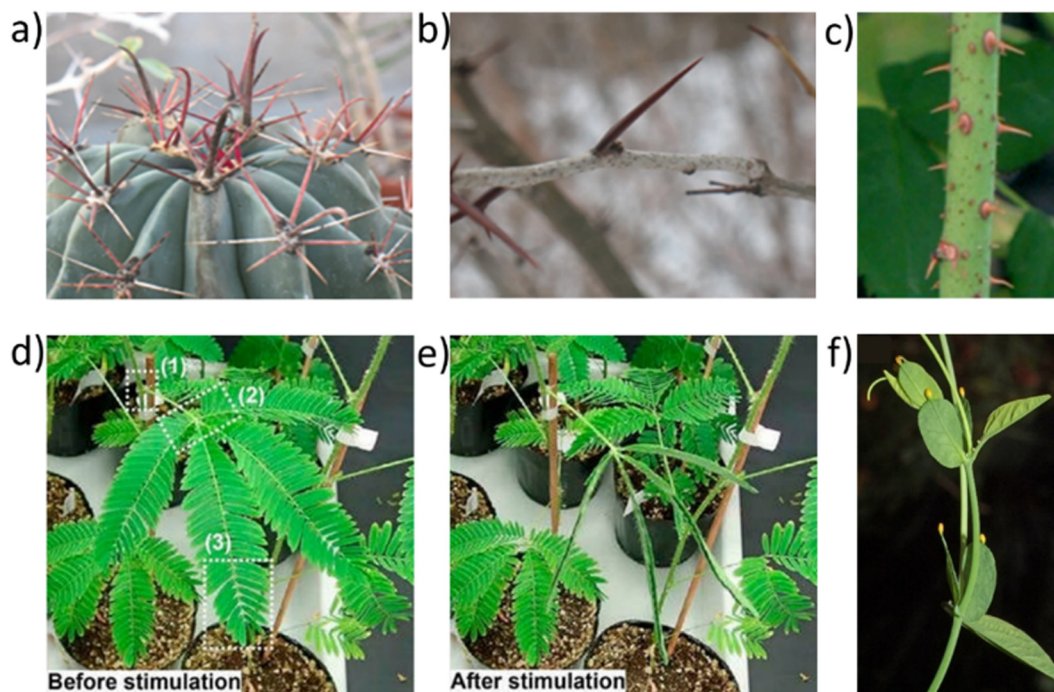


Fig. 6 Natural defences, including (a) spines on California barrel cactus *Ferocactus cylindraceus*, (b) thorns on honey locust *Gleditsia triacanthos*, and (c) prickles on rose *Rosa floribunda* stems. (d) Camouflage in *Mimosa pudica* before mechanical stimulation and (e) after mechanical stimulation leading to folded leaves. (f) Yellow stipules on *Passiflora* sp. resembling eggs of *Heliconius* butterflies. (a)–(c) Adapted with permission.<sup>146</sup> Copyright 2013, Nature Education. (d) and (e) Reproduced under the terms of a Creative Commons Attribution License.<sup>147</sup> Copyright 2020, Hagihara and Toyota. (f) Reproduced with permission.<sup>148</sup> Copyright 2017, Cambridge Philosophical Society.



### 3.7 Morphological features contributing to indirect defence

Plant morphology has evolved to support indirect defences by attracting and hosting predatory insects that help control pests. For example, hollow internodes in *Cecropia* plants house *Azteca* ants to protect the plant (see Section 2.1). Similarly, domatia, small cavities found on the underside of leaves, provide shelter for beneficial arthropods like predatory mites.<sup>156</sup> In return, they protect the plant from herbivores and pathogens.<sup>157</sup> Another morphological feature contributing to indirect defence are extrafloral nectaries on various plant parts. They secrete a sweet nectar solely employed to attract predatory insects like ants and lady beetles that can defend the plant against herbivores.<sup>158</sup>

In summary, nature employs a range of structural natural defences in plants to protect them against pests, including both constitutive and induced mechanisms. The natural plant defences discussed in this review and their classification are summarised in Table 1. Specialised structures like calcium oxalate crystals, silicon-rich cell walls, and callose act as morphological barriers, while plant cuticle and epicuticular waxes prevent pest attachment. Other defence mechanisms like trichomes play a dual role by acting as both physical and chemical defences. These mechanisms, which have evolved to counteract various environmental threats, are foundational in exploring sustainable pest control alternatives.

## 4. Advances in the usage of synthetic pesticides

Currently used commercial pesticides predominantly work as neurotoxins by interfering with the insect's nervous system after ingestion, inhalation, or upon contact. They are categorised based on their chemistry as detailed in Table 2.

Current economic, social, and technical circumstances necessitate the continued use of these pesticides, despite their impact to the environment and human health. However, there appears to be ample room to reduce their use. It is estimated that about 99.9% of the total pesticides applied on plants are wasted due to various processes like evaporation, degradation, and surface run-off, resulting in about 0.1% of the initial volume being effective against target pests (Fig. 7).<sup>165–167</sup>

Hence, the efficacy of synthetic chemical pesticides needs to be optimised through approaches such as enhancing their retention and using controlled-release formulations.

### 4.1 Improving pesticide adhesion on plants

Pesticide application procedures comprise spraying, fogging (creating a fine mist), pouring, powder release, fumigation (using gaseous pesticides), and seed dressing.<sup>168</sup> Accordingly, synthetic pesticides are available in different formulations, ranging from solid powders to liquid solutions. Solid formulations include ready-to-use varieties such as granules (*e.g.*, aldicarb from the carbamates group) and pellets that need to be sprinkled on target areas, and powders (*e.g.*, DDT from chlorinated hydrocarbons) that should be mixed in water before application. Liquid formulations are available as (1)

aqueous solutions of hydrophilic active substances (*e.g.*, imidacloprid from neonicotinoids), (2) concentrates of oil-soluble (*i.e.*, hydrophobic) active substances that emulsify when mixed in water (*e.g.*, chlorpyrifos from organophosphates), and (3) suspension concentrates that have to be diluted with water before application (*e.g.*, carbaryl from the carbamates group).<sup>169</sup> Spraying is the most practical technique used commercially to apply these pesticide formulations on crops since it can quickly and easily cover a large area. However, this technique often results in a large amount of chemicals ending up around the plants, thus contaminating the environment.

The wetting of plants is challenging because of their diverse three-dimensional, hierarchical anatomy, structures, and low cuticle surface energy.<sup>170</sup> Several superhydrophobic plant species are naturally self-cleaning due to their waxy nature and roughness arising from ordered micro- and nanoscale cell and cuticle sculptures.<sup>114,170,171</sup> Consequently, droplets tend to bounce and splash upon application, while also drifting or leaching from the plant due to environmental forces like wind and rain. A droplet hitting a hydrophobic plant surface goes through four distinct phases: (i) initial impact, (ii) spreading, controlled by inertial forces, (iii) receding, controlled by surface tension, and (iv) final state, which can either be a complete detachment from the plant, or the drop sitting on the non-wetting leaf surface with a high contact angle (Fig. 8a).<sup>172–175</sup>

Whether a drop bounces off or not depends on parameters such as the plant's surface energy and texture, but also the volume, viscosity, and surface tension of the drop. Plant surface wetting is often inhomogeneous or affected by aggregating droplets on trichomes and other structures, and/or domains of varying surface properties on the same plant.<sup>180</sup>

Most common attempts to enhance droplet adhesion to foliar surfaces rely on additives that alter the fluid properties of the spray product. For example, surfactants reduce the surface tension by the formation of micelles.<sup>181,182</sup> Li *et al.* studied the properties of the cationic surfactant didecyltrimethylammonium bromide (DDAB),<sup>175</sup> showing that it migrates rapidly from the bulk to the gas-liquid interface, thus reducing the surface tension. Apart from solely increasing retention, this also improves spreading on a hydrophobic leaf surface due to the fast adsorption of the DDAB molecules at the interface. Field experiments using the herbicide glyphosate IPA to control weeds support this hypothesis, revealing improved inhibitory herbicide effects at increased concentrations of DDAB (0.01–0.1%). Another additive used in pesticide applications is glycyrrhizic acid, a surfactant with low surface activity and viscosity.<sup>183</sup> Its ability to delay the bounce-off of pesticide-containing watery drops is due to surfactant molecules self-assembling into one-dimensional nanofibres that pin the droplets to a rough leaf surface (Fig. 8b).<sup>177</sup>

In general, however, a drawback for all surfactants is that they can lead to smaller droplets, which are more susceptible to evaporation and wind drift.<sup>184,185</sup> Surfactants may also induce changes in leaf micromorphology. For example, a rapid deterioration was observed for cabbage *Brassica oleracea* epicuticular wax crystals, which could impact plant fitness.<sup>186</sup>





**Table 1** Overview of mechanical natural defences discussed in this review

Category	Types	Constitutive <i>vs.</i> induced	Direct <i>vs.</i> indirect	Morphological <i>vs.</i> chemical	Ref.
Plant cell attributes	Phytoliths and cell wall fortification (silicon-related) Idioblasts (calcium-related) Laticifers	The cell wall is a first line of constitutive defence, while fortification is mostly induced.  Constitutive defence.  Constitutive defence.	Direct defence against pests.  Direct defence against herbivores.  Latex acts as a direct defence due to its toxins and sticky nature.  Resins add to direct defence.	Physical barriers against pests accessing the plant cell contents.  Morphological features acting as an irritant for chewing insects.  Latex can act as a physical and chemical defence. The sticky fluid can seal wounds and the mouthparts of feeding pests. It also contains several toxins that are toxic for insects once ingested. Resin flows act against stem-boring insects by physically expelling them. Further solidification of the resin occurs upon being exposed to air.	83,84,94,95  82,83,89  92,103–105
Plant cuticle	Resin ducts	Typically preformed and part of the constitutive defence. However, breached resin ducts can be replenished with the formation of new ones as an induced response to wounding by the plant. Constitutive defence.	Direct defence.	Physical barrier against invading pathogens and parasites.	106
Trichomes	Epicuticular wax crystals Glandular and non-glandular, <i>etc.</i>	Most trichomes are a part of the constitutive defence. Some plants can increase their density and/or glandular activity during an attack.	Glandular trichomes directly affect the pest owing to mechanical robustness or the sticky secretions that trap them or toxins that can be ingested. Some trichomes can also secrete volatile compounds to attract predators of the target pests, acting as an indirect defence mechanism. Affect the herbivore directly.	Physical barriers for pests, restricting access to the plant surface. They also contain chemical secretions or biomaterials aiding the defence mechanisms.	120–123
Spines, thorns, and prickles		Constitutive defence.	Affect the herbivore directly.	Morphological and mechanical defence.	142–146
Thigmonasty (plant movements)		Typically induced by an external stimulus such as touch or feeding.	Rapid movements act as a direct defence against target pests.	Plant movements like folding or drooping constitute a morphological defence.	149,153
Camouflage		Constitutive defence.	Camouflage could be classified as an indirect defence since it reduces the likelihood of being discovered by herbivores. Indirect defence by providing incentives for predatory insects to visit the plant for pest control.	Primarily morphological since it uses pigments	148
Morphological features contributing to indirect defence	Hollow internodes, extrafloral nectaries are mostly induced in response to herbivory. domatia	Although most form a constitutive defence mechanism, extrafloral nectaries are mostly induced in response to herbivory.		Morphological defence structures.	157–159

Table 2 Pesticide classes of active compounds, mechanisms of action and adverse side effects<sup>14,160–164</sup>

Group	Examples	Composition	Mode of pesticide action	Side effects on humans and animals	EU legislation
Chlorinated hydrocarbons	DDT, lindane, aldrin, endosulfane, methoxychlor and heptachlor	Non-polar and lipophilic molecules containing C, H, and Cl atoms.	They bind to sodium ion channels, inhibiting the flow of sodium ions and thus, impeding the nerve impulse transmission.	Potentially carcinogenic, affecting the kidney, liver, immune system, and reproductive organs over long-term exposure.	Several, such as DDT, lindane, and aldrin, are banned.
Organophosphates	Parathion, malathion, chlorpyrifos	Alkyl or aromatic phosphoric acid esters.	Acetylcholinesterase is inhibited, which leads to an accumulation of the nerve-stimulating chemical, acetylcholine in insects.	Acute exposure can cause poisoning and neurological effects.	Several, such as parathion and dimethoate, are banned, while malathion is one of the oldest and most widely used.
Carbamates	Carbaryl, aldicarb, carbofuran	N-Methyl carbamates are derived from carbamic acid and are mechanistically similar to organophosphates.	They function similar to organophosphates by (reversible) inhibition of acetylcholinesterase.	Similar to, but considered less toxic than organophosphates.	Several, such as aldicarb, carbaryl, and carbofuran, are banned.
Pyrethroids	Permethrin, bifenthrin, cypermethrin	Pyrethroids are the more light-stable synthetic analogues of the naturally occurring pyrethrins from plant sources ( <i>Chrysanthemum cinerariifolium</i> ).	Once ingested, they attach to the sodium channel, inducing over-stimulation of the nervous system, which causes pests to lose their coordination (paralysis).	Comparatively low mammalian toxicity, although acute exposure to high doses can induce adverse effects on the nervous system and potential allergic reactions. Also particularly toxic to aquatic organisms.	Permethrin, bifenthrin, and resmethrin are banned from agricultural use.
Neonicotinoids	Imidacloprid, acetamiprid	Compounds containing a negatively charged cyano or nitro group chemically similar to nicotine.	They bind to the nicotinic acetylcholine receptor in insects, blocking them and thus, causing paralysis.	It is highly toxic to bees and other pollinators and can accumulate in pollen and nectar.	Clothianid, imidacloprid, and thiamethoxam are restricted to indoor use.

Damak *et al.* described the potential incorporation of polyelectrolytes in chemical pesticides to increase retention on hydrophobic surfaces.<sup>178</sup> In their proof-of-concept study, two oppositely charged polyelectrolyte solutions were sprayed simultaneously on a superhydrophobic surface, forming solid precipitates of polyelectrolyte complexes, which led to a 10-fold increased retention in comparison to pure water. In contrast, spraying just one of these solutions results in droplets rolling off the leaf surface similar to water (Fig. 8c). Presumably, the combination of two oppositely charged precipitates causes surface defects that pin the drops to the hydrophobic substrate.<sup>178</sup>

The rheological properties of spray products can also be altered using flexible polymers. Bergeron and coworkers showed that the addition of a small quantity of the hydrophilic polyethylene oxide (PEO) substantially increased retention of sprayed solutions on (super)hydrophobic surfaces, even without considerably changing their surface tension and viscosity under shear flow.<sup>187</sup> The suppression of droplet rebound was due to the significant reduction of the retraction velocity, attributed to non-Newtonian properties like the extensional viscosity (*i.e.*, resistance to stretching) of the polymer solutions.<sup>178,187,188</sup> In particular, the authors proposed that this effect resulted from the significant elongational characteristics of the fluid inside the receding droplet. As the fluid in the droplets undergoes expansion and retraction, high-molecular-weight polymers stretch out due to a velocity gradient, resulting in energy dissipation, which can effectively inhibit droplet rebound. While some authors supported this interpretation,<sup>189,190</sup> others remain unconvinced. For example, Smith *et al.* argued that the anti-rebound effect is due to an additional force at the contact line. This force, known as contact line friction, occurs when the polymer chains stretch as the droplet moves, resisting its retraction.<sup>191</sup> Evidently, the effects of polymer additives require further study, also concerning their environmental and food safety. Nevertheless, the positive effect of these additives is undeniable, with proof-of-concept studies demonstrating that they enhance fluid retention by over tenfold compared to water alone, achieving a plant surface coverage up to 80%.<sup>178</sup>

Taking a completely different path to increased pesticide efficacy, Schwinges *et al.* functionalised soybean plant leaves to curb the spread of the fungi *Phakopsora pachyrhizi*, which causes the Asian soybean rust (Fig. 8d).<sup>179</sup> A bifunctional peptide composed of an antimicrobial and anchoring part was employed for this purpose. Since the outer membrane of microbes is composed of lipids, certain peptides can destabilise this lipid membrane, thereby killing the microbes.<sup>192,193</sup> Thanatin, an amphiphilic peptide, was used to adhere dermaseptins, a class of antimicrobial peptides, on soybean leaves. Although the exact chemical compounds that participate in the binding are unknown, hydrophobic interactions between the lipophilic epicuticular leaf waxes and the peptides were thought to be responsible for the strong adhesion on the leaf surface. The bifunctional peptide combining thanatin and dermaseptins reduced rust infection symptoms in soybean by



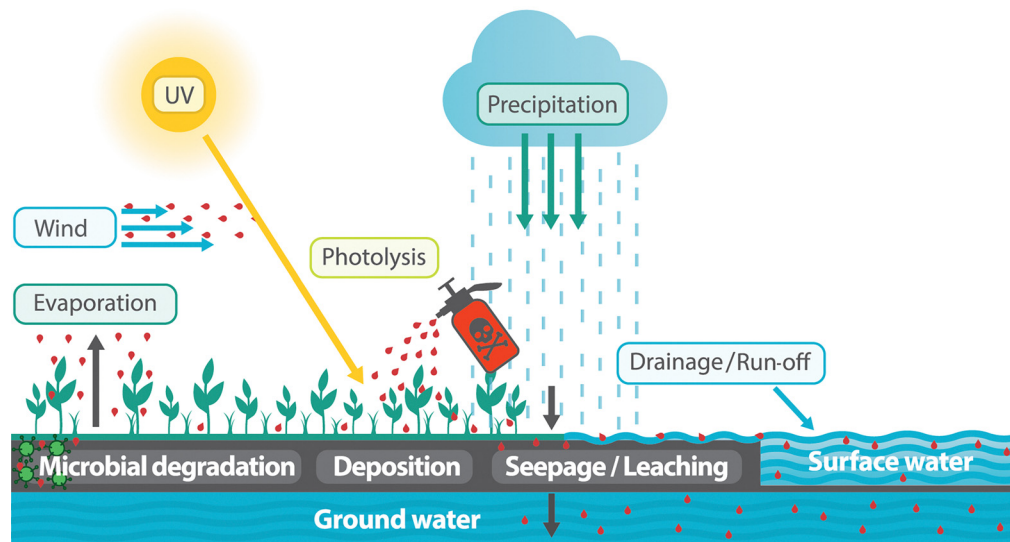


Fig. 7 Illustration depicting various pathways by which pesticides get lost from the target plants and infiltrate the surrounding environment.

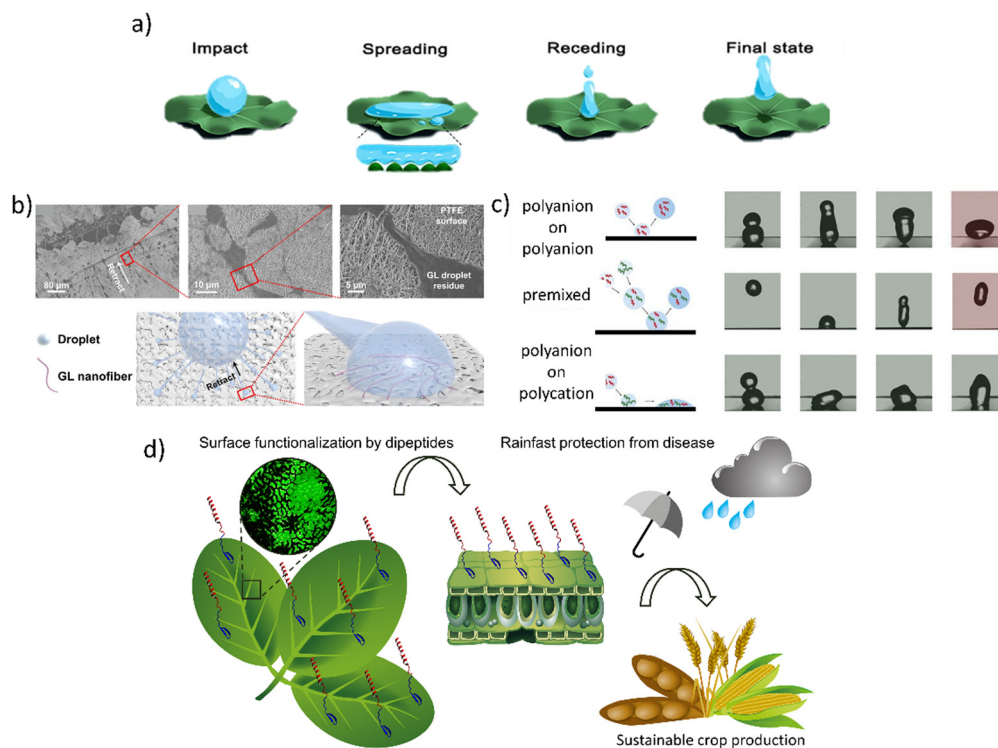


Fig. 8 (a) Four distinct phases of a droplet impinging on a hydrophobic leaf surface. (b) SEM images of droplets with glycyrrhizic acid after impact show filamentous residues, indicating one-dimensional nanofibres pinning the droplet to a polytetrafluoroethylene (PTFE) surface. (c) Snapshots of negatively (polyanions) and positively (polycations) charged polymers impacting a superhydrophobic surface, indicating high retention when they combine and form precipitates directly on the surface (bottom panel). (d) Illustration of soybean leaves functionalised with dermaseptin–thanatin dipeptide, showing the potential of anchoring antimicrobial peptides on the leaf surface. (a) Adapted with permission.<sup>176</sup> Copyright 2023, Elsevier B.V. (b) Adapted under the terms of a Creative Commons Attribution License.<sup>177</sup> Copyright 2020, American Chemical Society. (c) Adapted under the terms of a Creative Commons Attribution License.<sup>178</sup> Copyright 2016, Springer Nature. (d) Reproduced under the terms of a Creative Commons Attribution License.<sup>179</sup> Copyright 2019, The Royal Society of Chemistry.

up to 30% compared to separate application of thanatin and dermaseptin. Presumably, the dipeptides on the leaf surface protruded from the epicuticular wax rosettes, which ensured

peptide interaction with the fungi at very early developmental stages, preventing the fungi from infecting the plant cells.<sup>179,192,193</sup>

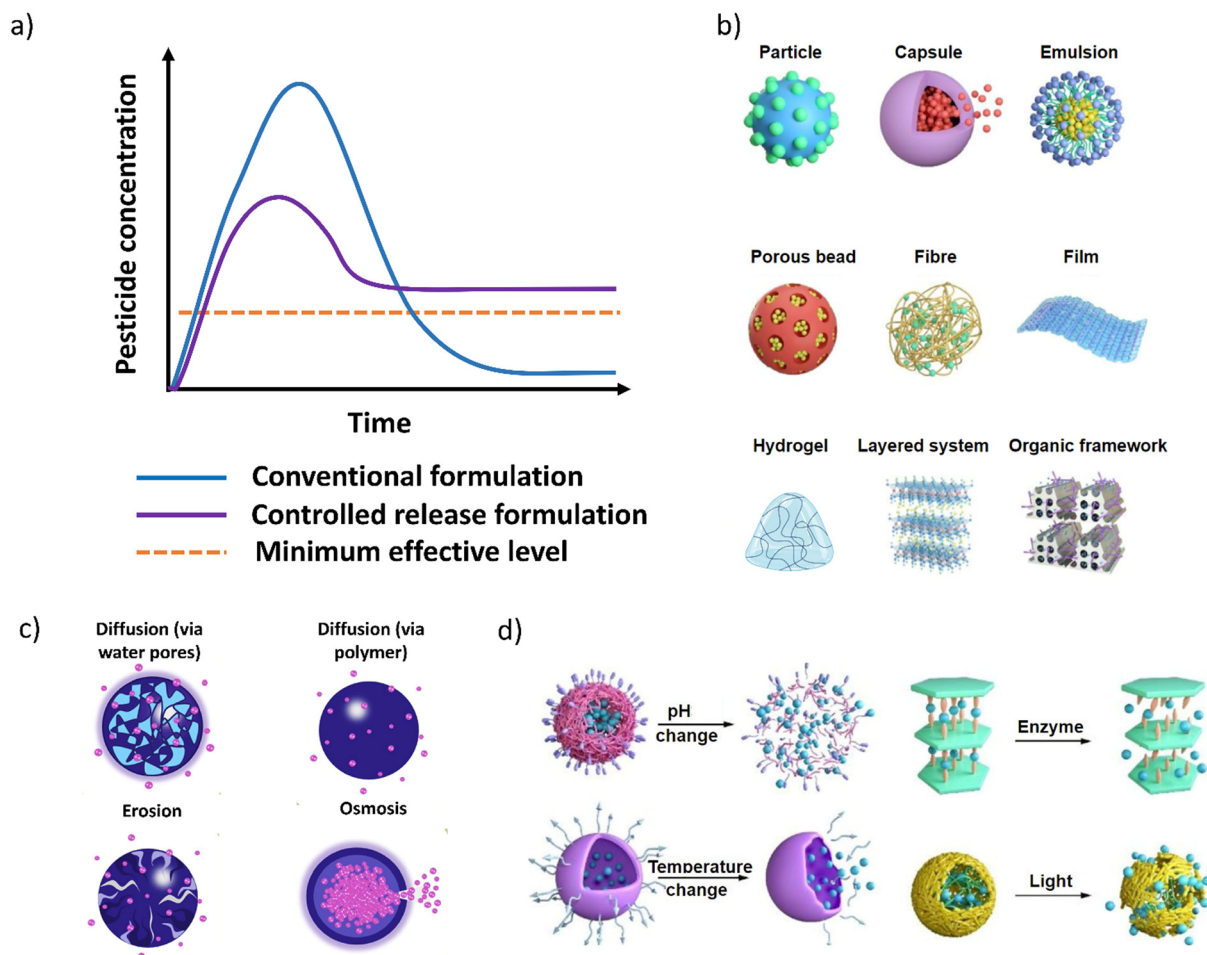


## 4.2 Controlled release

Controlled-release formulations involve the customised release of compounds (*e.g.*, drugs, proteins, fertilisers, nutrients, and other biologically active agents) after a certain time or in response to external stimuli (*e.g.*, pH, temperature, enzymes, UV light, magnetic fields, osmosis).<sup>194</sup> By controlling the pesticide release in this way, less organic solvents and dispersing agents may be needed, and leaching of the sprayed product may be reduced.<sup>29</sup> Controlled-release formulations are widely researched in the medical field to facilitate targeted drug delivery. Similar formulations are being developed to enhance the efficacy of pesticide delivery in agricultural settings. These formulations serve to keep the concentration of the active pesticide ingredient above a critical effective level for a longer period of time (Fig. 9a). This reduces the number of applications needed, preventing side effects from excessive concentrations, and overall, minimising waste and toxicity.<sup>29</sup> These delivery systems can be formed from organic, inorganic, or

hybrid compositions and vary from the more straightforward cases of (nano)particles, capsules, emulsions, and porous beads to more complex and extended configurations such as fibres, films, hydrogels, layered and framework materials (Fig. 9b).<sup>27</sup> Controlled-release systems can be distinguished based on whether their performance is a passive or dynamic process.

Traditional controlled-release formulations are typically passive or sustained-release systems where a continuous, stable release of the loaded pesticide concentration is achieved through inherent processes. It is predominantly a consequence of passive diffusion and osmotic pressure or gradual carrier breakdown without external triggers (Fig. 9c).<sup>195</sup> The controlled-release formulations belonging to this category are advantageous in situations where pesticide action is required equally throughout a large part of the crop growth cycle. Examples of such passive delivery systems are sorption-based materials characterised by high porosity.<sup>196</sup> For example,



**Fig. 9** (a) Pesticide release concentration for conventional pesticides (blue line) and controlled-release formulations (purple line) as a function of time after application. The dashed line indicates the minimum level for effectiveness. (b) Different types of controlled-release pesticide systems. (c) Various sustained-release mechanisms, namely diffusion through water-filled pores or directly through the polymer, release due to erosion/degradation of the polymer carrier, and release due to differences in osmotic pressures. (d) Various 'smart release' mechanisms triggered by external stimuli, namely pH, temperature, enzymes, and light. (b) and (d) Adapted with permission.<sup>29</sup> Copyright 2021, American Chemical Society. (c) Adapted with permission.<sup>27</sup> Copyright 2020, Elsevier B.V.



metal–organic frameworks (MOFs) are crystalline materials composed of metal ions and organic ligands, forming a highly porous three-dimensional network. In 2017, Yang *et al.* first incorporated biodegradable MOFs in agricultural contexts by preparing an eco-friendly MOF that exhibited good uptake and release kinetics of the pesticide *cis*-1,3-dichloropropene. These MOFs consisted of non-toxic  $\text{Ca}^{2+}$  ions bridged by naturally occurring L-lactate and acetate linkers. The pesticide-loaded MOFs achieved a 100-fold increase of the time the pesticide is present compared to the plain, volatile liquid product, as well as good degradability, illustrating the potential of MOFs as sustained-release carriers in agriculture.<sup>196</sup> Following this invention, many more sustained-release porous framework materials have been reported,<sup>197–199</sup> and similar performance has been reported for other material designs (Fig. 9b).<sup>29,195</sup>

Controlled release systems relying on dynamic, stimulus-responsive processes have been established by drawing inspiration and using theoretical foundations from biomedicine.<sup>200,201</sup> These ‘smart-release’ systems respond to external signals and undergo physicochemical changes, resulting in the release of the loaded pesticides. These signals include changes in pH, temperature, presence of specific enzymes, or light irradiation (Fig. 9d). This approach aims to make the application of pesticides more targeted, safe, and efficient.<sup>195,202</sup> For example, the commercially available pesticide, Seltima, uses an encapsulation technology that allows for the fungicide, pyraclostrobin, to be released onto rice crops while simultaneously restricting it from being released into groundwater.<sup>203</sup> The key to this double action is the sensitivity of the microcapsule wall to humidity, which cause the capsules to release the fungicide when applied on rice leaves. If the microcapsules fail to adhere to the crop and end up into nearby water bodies, they sink to the bottom while remaining intact having the toxic ingredient trapped.<sup>203</sup> The microbes also present inside are then expected to degrade the active ingredients.

### 4.3 Smart solutions

Synergistically combining the passive and active types of controlled-release systems results in innovative formulations that enhance adhesion to leaf surfaces and release the active chemicals in a controlled fashion, thus minimising environmental impact without compromising efficacy.

Song *et al.* explored one such system by using folate/zinc supramolecular hydrogels loaded with a herbicide called dicamba.<sup>185</sup> Folic acid and zinc, which are important elements of plant growth activities, form a hydrogel with a nanofibre network, which aids in the encapsulation of dicamba. The folate/zinc supramolecular hydrogels display apparent shear-thinning properties, indicating that they can be sprayed through a small nozzle, after which the nanofibre network is quickly re-established. Since the surface tension of these hydrogels is not very different from that of water, a retention mechanism similar to the one discussed in Section 4.1 with PEO addition is hypothesised (Fig. 10a). All liquids spread instantly upon impact due to inertial forces, up to a maximum spreading diameter.<sup>7,8</sup> Once the surface energy starts coming

into play, the droplet tries to retract. While liquids like water experience a large surface energy when impacting a hydrophobic surface, causing them to bounce off, the folate/zinc supramolecular hydrogels, akin to PEO as an additive, can securely hold on to the surface owing to the dynamic nanofibre network, which initially spreads up to the maximum diameter, dissipating most of its energy due to its viscous nature and from surface friction losses. Although the focus of the study by Song *et al.* was solely on increasing retention, these hydrogels may also influence the release kinetics.

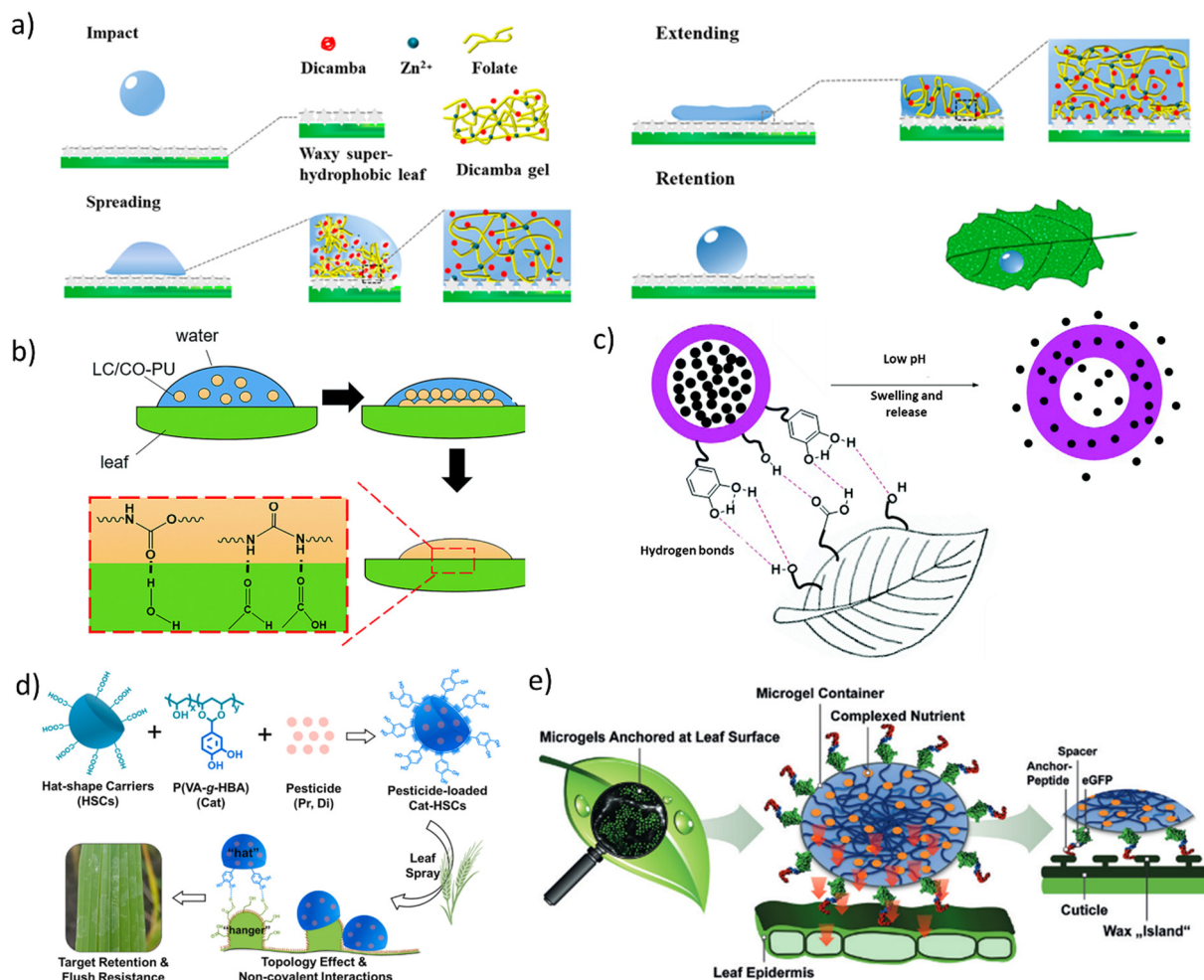
Nanocapsules also offer a smart solution by combining controlled release, improved retention, and enhanced efficiency. Zhu *et al.* studied the retention of nanocapsules loaded with  $\beta$ -cypermethrin, which is a hydrophobic pesticide.<sup>207</sup> The nanocapsules were synthesised using complexes of oppositely charged biopolymers, *i.e.* gelatin and acacia gum, in an oil-in-water microemulsion. The resulting system is hypothesised to increase deposition on a leaf surface owing to its small size, although small droplets may also increase loss through pesticide drift.<sup>207</sup>

Zhang *et al.* used a similar formulation and combined it with the concept of spraying oppositely charged polymers discussed earlier.<sup>178</sup> Azadirachtin, a biopesticide, was incorporated into the core of anionic and cationic polyurethane core-shell structures synthesised from castor oil.<sup>208</sup> The increased retention of the solutions on the hydrophobic surface is attributed to surface precipitation arising from simultaneously spraying oppositely charged particles, as discussed earlier, in addition to reduced surface tension effects from the added Tween-80 surfactant. This formulation includes controlled release and the added advantages of heat and light protection for sensitive encapsulated pesticides.

Qin *et al.* explored a castor oil-based polyurethane carrier system by incorporating lambda-cyhalothrin (LC) in a nanoemulsion formulation without surfactants.<sup>165</sup> The LC nanoemulsions adhered much better to leaf surfaces than a commercial emulsifiable concentrate and wettable powder formulation after washing with water. However, all three systems showed similar deposition behaviour before washing. After spraying these nanoemulsions, the liquids spread on the leaf surface owing to their surface tension ( $34.9\text{--}40.3\text{ mN m}^{-1}$ ) being significantly lower than the critical surface tension of the tested crops (cotton:  $63.3\text{--}71.8\text{ mN m}^{-1}$ , corn:  $47.4\text{--}58.7\text{ mN m}^{-1}$ ), without the use of any surfactants or emulsifiers (Fig. 10b). Subsequently, the droplets of the nanoemulsion coalesced, and evaporation of water led to the formation of solid films on the leaf surface, increasing contact between the LC residues and the plant surface. Better adhesion to plants was also attributed to hydrogen bonding between urea and urethane groups of pesticide emulsions and the leaf surface functional groups, like hydroxyl and aldehyde.<sup>165</sup>

Chen *et al.* combined the concept of hydrogen bonding for increased retention with controlled-release nanocapsules (Fig. 10c).<sup>204</sup> They utilised catechol compounds, which are known for facilitating strong underwater adhesion in mussels.<sup>209</sup> Acidity-controlled nanocapsules were covered with





**Fig. 10** (a) Schematic mechanism of the dicamba-in-hydrogel droplet forming a cross-linked nanofibre network when it impacts a super-hydrophobic leaf. (b) Nanoemulsion droplets containing castor oil-based polyurethane (CO-PU) and lambda-cyhalothrin (LC) spread well due to their low surface tension followed by strong adhesion due to the coalescence of the nanoparticles and hydrogen bonding between nanoemulsion and leaf surface. (c) Mechanism of pesticide release and leaf surface adhesion of pH-responsive adhesive nanocapsules. (d) Formation and retention mechanism of catechol-modified hat-shaped carriers loaded with pesticides. (e) Schematic of loaded microgels whose outer surface is decorated with anchor peptides to facilitate strong binding to the leaf surface. (a) Adapted under the terms of a Creative Commons Attribution License.<sup>185</sup> Copyright 2020, American Chemical Society. (b) Adapted under the terms of a Creative Commons Attribution License.<sup>165</sup> Copyright 2017, The Royal Society of Chemistry. (c) Adapted with permission.<sup>204</sup> Copyright 2021, The Royal Society of Chemistry. (d) Reproduced with permission.<sup>205</sup> Copyright 2020, Elsevier B.V. (e) Reproduced with permission.<sup>206</sup> Copyright 2020, Wiley-VCH Verlag GmbH & Co.

catechol groups in order to form hydrogen bonds with the alcohols, acids, and aldehydes present on a leaf's waxy surface, thereby increasing pesticide retention on the plant. Under acidic conditions ( $\text{pH} < 6.5$ ), protonation of amino groups from  $\text{NH}_2$  to  $\text{NH}_3^+$  in the nanocapsules led to an increase in the positive charge, which resulted in swelling due to electrostatic repulsion and swelling of the channels, thus promoting diffusion and release of the encapsulated pesticide. Although such pH-responsive materials are promising, most of these systems are still in the proof-of-principle stage, and not yet optimised for real-world settings. For example, a more plausible trigger was proposed with an alkaline pH-responsive pesticide system, developed by encapsulating the insecticide LC in *O*-carboxymethyl chitosan (*O*-CMCS) and covering it with polyurethane (PU).<sup>210</sup> This system was designed to release the active

ingredient in an alkaline environment ( $\text{pH} 8.0\text{--}9.5$ ), which is the pH condition found inside the gut of some pests. When taken up by dew drops present on the plant, the acidic nature of these drops ( $\text{pH} 5.3\text{--}6.8$ ) significantly slowed down the release of LC, thereby ensuring that the pesticide is active mostly when ingested by the pest.<sup>210</sup>

While most techniques for improving retention focus on the properties of the incoming droplets for better adhesion, as discussed up until now, one can also consider the leaf surface. Leaves can have a number of structures on their surface, such as nanosplinters and micropapillae. Zhao *et al.* were among the first to create pesticide carriers that took into account both surface modification of the incoming particles and the leaf surface topology.<sup>188,205</sup> Emulsion interfacial polymerisation allowed the preparation of hat-shaped carriers (HSCs) loaded



with pesticide, which have a complementary shape to the micropapillae on the leaf surface, provoking a hanger-hat effect to enable better adhesion (Fig. 10d). So-called Janus particles were used for this purpose. In their follow-up work, adding catechol compounds improved this hanger-hat effect. Comparing HSCs with and without catechol groups, the retention of the fungicide on the leaf surface improved when catechol groups were added, which was attributed to a synergistic effect of the hanger-hat topology and non-covalent interactions arising from the catechol groups. An added value of functionalising the HSCs with catechol groups is the faster pesticide release for a prolonged period of 15 days compared to the unmodified HSCs. This acceleration was attributed to the difference in synthesis techniques where the modified particles were loaded with pesticide on a fully swollen polymer, facilitating quick release. In contrast, the unmodified particles were synthesised along with the presence of the pesticide, resulting in a tightly bound structure and thus, slower release rates.

Antimicrobial peptides, as discussed in Section 4.2, are of particular interest due to their ability to interact with microbial membranes. They have been previously attached to leaf surfaces using adhering peptides.<sup>179</sup> Similarly, Meurer *et al.* used these peptides to attach hydrophilic microgels loaded with nutrients to leaf surfaces (Fig. 10e).<sup>206</sup> Poly(allylamine) microgels were synthesised using a water-in-oil emulsion polymerisation reaction, and modified with a catechol derivative, 2,3-dihydroxybenzoic acid (DHBA) to enhance the uptake of Fe<sup>3+</sup> micronutrients. The adhering peptide lantarin A was used to ensure reliable retention on hydrophobic plant surfaces. The peptides adhere on small islands of hydrophobic wax-like regions on the leaf surface. These Fe<sup>3+</sup>-loaded microgels were tested on iron-deficient cucumber plants, and results indicated positive re-greening of the application sites in contrast to the chlorotic spots with iron deficiency in the leaves. Although this system has been designed to deliver micronutrients to targeted locations by increasing retention and reducing wastage on the leaves, it may be extended into the fields of pesticides and insecticides.<sup>211</sup> Research along similar lines was conducted by Mai *et al.* who developed an alginate gel modified by catechol-based compounds that could form strong non-covalent interactions with the waxy leaf surface.<sup>212</sup> Subsequently, Fe<sup>3+</sup> ions were introduced into the polymer network to form a dense 3D crosslinked network with a high resistance to washing off. This significantly improves pesticide retention on leaf surfaces and enhances resistance to rainwater while facilitating controlled release of the active ingredients when irradiated by light.

In summary, recent advances in synthetic pesticides focus on improving pesticide adhesion on plant surfaces, aiming to prevent premature wash-off and thereby increase effectiveness. This has led to the development of surfactants and polyelectrolyte additives that help maintain pesticide retention. In parallel, controlled-release systems have gained attention, as they can regulate the pesticide release over time, minimising environmental impact and reducing toxicity. Convergence of innovations in these areas have resulted in smart delivery solutions, using systems based on hydrogels, antimicrobial

peptides, and nanocapsules that combine both improved adhesion and controlled release to create more efficient and sustainable pest control strategies.

## 5. Integrated pest management domains beyond chemical control

While significant advances in improving the efficacy of chemical control strategies in IPM are underway, as discussed in the previous sections, efforts to entirely eliminate synthetic chemical pesticides from contemporary agriculture are still scarce. In the following sections, we highlight some ideas in the physical, cultural, and biological control domains of IPM, offering glimpses of a possible future where agriculture is completely free from synthetic chemical interventions.

### 5.1 Mineral powders

In olden times, stored grains were commercially mixed with minerals like silica to prevent infestation of the common grain weevil.<sup>213</sup> One of the first non-chemical pest management strategies to be explored by scientists was the use of dust particles. Since the 1930s, research has been conducted to study the exact mechanism of action of these inert dusts. Although it was initially hypothesised that weevils died after ingesting the dust, it was later confirmed that the main cause of death was increased rates of water loss due to friction between their cuticle and the dust particles.<sup>213</sup> Abrasion is necessary for hard, non-sorptive particles to remove the insect's epicuticular grease, leading to death by desiccation.<sup>214</sup> Other small inorganic particles made from materials like clay and silica interfere with target pests in different ways. Spraying kaolin (clay mineral) shields plant surfaces from aphid attacks since these phloem-feeders tend to settle on foliage based on a sensitivity to colour. Spraying kaolin as a film on citrus plants led to a whitish appearance, thus affecting the host-finding abilities of aphids, reducing pest colonisation.<sup>215,216</sup> Glenn *et al.* first studied insect and disease suppression by applying a porous and hydrophobic layer of kaolin mineral particles.<sup>217</sup> The kaolin particles were modified to become hydrophobic by coating them with an undisclosed synthetic hydrocarbon. Although kaolin is relatively soft and non-abrasive compared to other commonly studied particle layers, pear psylla *Psylla pyri* feeding and ovipositional activities were found to be affected. Adults constantly cleaned themselves to remove the tiny kaolin particles adhered to their bodies, neglecting their regular activities and eventually dying due to starvation. In addition to these effects, minerals also affect pests by means of physical hindrance and their repelling hydrophobic nature. For example, several bacteria and fungi require water to propagate their species. The hydrophobic mineral particles ensure that water is not available for this purpose, and also prevents the propagules from coming into contact with the plant surface (Fig. 11a). An unexpected advantage of these particle films is the improvement in plant photosynthesis by reducing the heat stress on the leaf surface and allowing photosynthesis for a



longer part of the day.<sup>218</sup> However, the most recognisable disadvantage of such particle films comes from the application point of view, where a perfect coverage of foliage is required for the particles to curb the spread of an infestation effectively. This is restricted by the fact that these particles cannot adhere strongly to the leaf surface and drift could lead to reduced effectiveness. Also, the particles are not as effective with rainfall in open fields. More recently, researchers studied these particle films with different pests, proposing strategies to improve their functionality.<sup>219–222</sup> Faliagka *et al.* tried to utilise the same concept of desiccation caused by abrasion of the insect cuticles with a textile impregnated with silica dust.<sup>223</sup> Although the dust-impregnated fabric nets effectively restricted the entry of aphids, concerns regarding reduced ventilation inside a greenhouse persist. Further discussion is omitted since such nets are not directly applied to plants and, hence, are out of the scope of this review.

It is also interesting to note that the mechanism of action of these mineral powders closely resemble the roughness and contamination hypotheses of epicuticular wax crystals described in Section 3.2.1 highlighting the promise that bioinspired strategies hold to change the future of pest management, as discussed in the next section.

## 5.2 Bioinspired alternatives

Nature's vast array of defence mechanisms could serve as valuable inspiration for creating synthetic pesticides that are both effective and environmentally friendly. Developing bioinspired pesticides could also potentially achieve targeted pest control methods that minimise harm to non-target organisms in concert with nature's own strategies.<sup>226</sup>

Taking a step in this direction, Schifani *et al.* described the potential of artificial nectaries designed to mimic extrafloral nectaries in order to attract predatory ants as discussed in Section 3.7.<sup>227</sup> By simply using a sugar solution of sucrose in water, they demonstrated a significant reduction in typical pear orchard pests, along with an increase in predatory arthropods. This relatively simple strategy highlights the potential of leveraging natural plant defence mechanisms for developing bioinspired alternatives.

Similarly, Szyndler *et al.* studied the hook-shaped trichomes of bean leaves to fabricate surface replicas that hinder bed bugs.<sup>224</sup> Their inspiration came from a historical practice where bean leaves trapped bed bugs owing to a physical entanglement mechanism between the trichomes and the legs of the bed bugs (Fig. 11b).<sup>228</sup> To fabricate synthetic trichomes, a double moulding process was used where a negative mould was applied to replicate the leaf surface, followed by a polymeric positive mould to create the test substrate (Fig. 11c). For comparison, they also fabricated hybrid trichomes, by breaking off the tips of natural trichomes in the negative mould, leading to a hybrid variation with natural tips and synthetic stalks. The synthetic trichomes were observed not to pierce any of the bed bugs in the study, while the natural trichomes trapped 90% of the bed bugs within seconds on average. The hybrid trichomes,

although expected to function similar to natural trichomes, also performed poorly in terms of piercing the insect feet.

The reason for this result was attributed to the differences in terms of the material's flexural and torsional stiffness. For synthetic trichomes, the entire structure (tip, stalk, and base) is composed of a solid material, while natural trichomes consist of solid tips and hollow cylindrical stalks set on flexible bases. Thus, the hollowness of the stalk could give the natural trichomes enough flexibility to graze along the cuticle of the bed bug till it gets stuck eventually piercing the feet, whereas synthetic and hybrid trichomes might end up bending instead. Such replication approaches and synthetic surfaces serves as excellent models to study biological surfaces *via* comparative persistent models.<sup>229,230</sup>

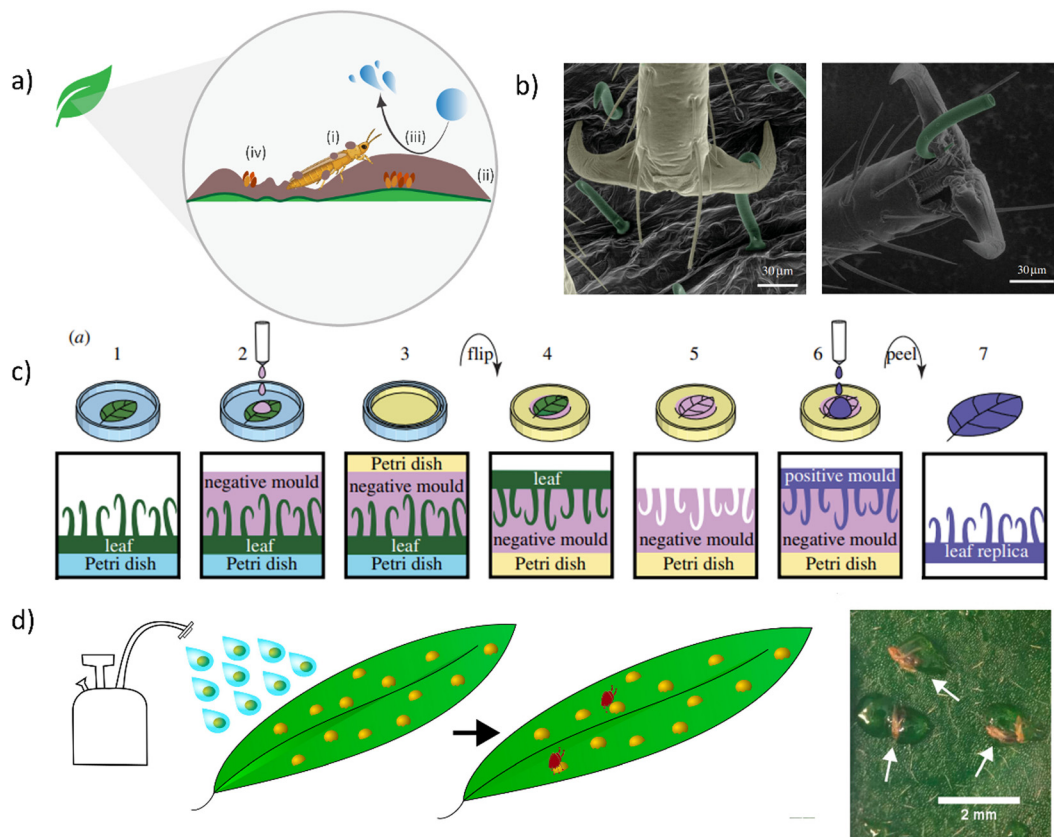
Exploring the potential behind mimicking trichomes further, an innovative physical pesticide was developed by Zwieter *et al.* whereby adhesive particles made from oxidised vegetable oils imitated the defence mechanism arising from glandular trichomes. An aqueous suspension of these adhesive particles was sprayed on plants, leaving the sticky particles behind after water evaporation. They acted as miniature glue traps, physically immobilising target pests similar to the sticky exudates of glandular trichomes as discussed earlier (Fig. 11d).<sup>225,231</sup> Being trapped, mortality of western flower thrips *Frankliniella occidentalis* increased approximately three-fold due to lack of food supply as compared to the pure control.<sup>232</sup> A water-based variation of this strategy was undertaken in our own work, where *Drosera* trichomes were mimicked using sugar-based natural deep eutectic solvents.<sup>233</sup> These recent developments highlight the potential of the diverse defences found in nature to pave the way for bioinspired eco-friendly pest management solutions. It is important to note that such advances still require significant research to study their impact in real-world settings, including any side effects arising from their accumulation in the environment.

## 5.3 Pest repellence

Physical pest control can be through mechanical, thermal, optical, and acoustic procedures, mainly repelling herbivores. One well-known strategy is to manipulate pest behaviours such as host feeding, host plant detection, and mating.<sup>234,235</sup> In the 'push-pull' strategy introduced by Pyke *et al.*, pests are 'pushed' away from the host plant and 'pulled' towards an alternate attractive source to entice them away from the target field/crops. This strategy was tested with neem tree extracts which repelled, while sacrificial crops attracted *Heliothis* away from cotton plants.<sup>236</sup> Various kinds of push-pull strategies, such as visual cues, pheromones, and trap cropping, have been summarised in detail elsewhere.<sup>237</sup>

Plants that secrete sticky fluids have been experimentally shown to act as dead-end trap crops to protect nearby plants. Unlike traditional trap crops that simply attract pests away from the plants of interest, dead-end trap crops lure pests towards them but do not allow them to reproduce or survive long-term.<sup>238,239</sup> For example, a recent greenhouse trial found





**Fig. 11** (a) Mechanisms of action of hydrophobic particle films, namely (i) adhering to the insect to hinder feeding and locomotion, (ii) interrupting colour signalling and presenting a physical barrier from the leaf surface, (iii) preventing water access for propagation, and (iv) preventing propagules from reaching the plant surface. (b) SEM images of hook-shaped trichomes of bean leaves interlocking with bed bug's claws (left) and impaling the pretarsus (right). (c) Double-moulding microfabrication of biomimetic leaf surfaces. (d) Physical pesticide consisting of a sprayable aqueous suspension of adhesive particles to immobilise target pests upon contact. White arrows indicate Western flower thrips trapped in the trichome mimic particles on a detached leaf. (b) and (c) Adapted with permission.<sup>224</sup> Copyright 2017, The Royal Society. (d) Adapted under the terms of a Creative Commons Attribution License.<sup>225</sup> Copyright 2024, National Academy of Sciences.

that a special laboratory strain of tobacco (*Nicotiana benthamiana*) was as effective as commercial sticky traps in killing whitefly and thrips. Such dead-end trap crops offer a sustainable alternative to sticky traps as they do not rely on non-biodegradable plastics and provide the added advantage of minimal negative effects to predatory insects.<sup>238,240</sup>

Experimenting with another type of behavioural manipulation technique, Polajnar *et al.* used mechanical vibrations to cause mating disruptions in the invasive leafhopper pest *Scaphoideus titanus*. In these insects, the mating sequence involves a series of pulses from the male with short occasional pulses as a reply from the female, resulting in a characteristic duet between the two. The team used continuous mechanical vibrations that acted as noise, to block the communication between the male and the female leafhoppers with a disruption efficiency of around 90% male-female pairs for one day. To save energy, the mechanical vibrations can also be tuned down during specific time periods, where the target pests are unlikely to mate.<sup>241</sup> This behavioural manipulation technique is part of the field of bioacoustics or applied biotremology, which is attracting increasing attention in phytomedical research.

Species-specific 'semiochemicals' (physical cues) can be generated to interfere with Aleyrodidae white flies (Hemiptera), Mycetophilidae fungus gnats (Diptera), Pentatomidae true bugs (Heteroptera), moths (Lepidoptera), and various beetles (Coleoptera) in greenhouses, fields, orchards, vineyards, and forests, reducing the pest population densities.<sup>242,243</sup>

#### 5.4 Biopesticides

Another approach to pest control involves the exploitation of natural pest control measures such as releasing the natural predators of target pests. This type of biocontrol is summarised in numerous overviews.<sup>69,244,245</sup> Here, we review pesticides isolated from natural sources, such as microorganisms, animals, and plants.<sup>246,247</sup> These biopesticides have emerged as viable alternatives to synthetic pesticides and, in recent years, comprise approximately 10% of the international pesticide market.<sup>248</sup> They match to an extended degree the profile of an 'ideal pesticide' due to their biodegradability, frequent target-specific action, and high efficiency even at low concentrations.<sup>246,249</sup> Additionally, reports have shown that using some natural pesticides not only affects pests but also



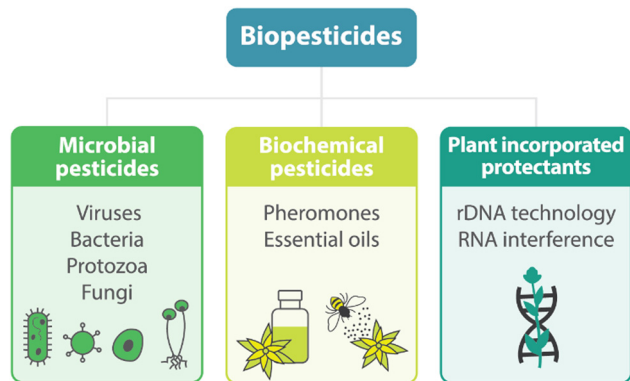


Fig. 12 Overview of the three different biopesticide categories that are recognised by the U.S. Environmental Protection Agency (EPA).

promotes soil biodiversity and helps plants build up tolerance to environmental conditions such as droughts.<sup>248,250</sup> Biopesticides are classified into three main categories by EPA: (1) microbial pesticides, (2) biochemical pesticides, and (3) plant-incorporated protectants (PIPs) (Fig. 12).<sup>247,251</sup>

Microbial pesticides are pesticides consisting of microorganisms, including viruses, bacteria, protozoa, and fungi that enter the host through ingestion or contact, and kill the host by multiplying and releasing toxins. *Bacillus thuringiensis* (Bt) has been credited as the most successful microbial pesticide in the market owing to its fast and host-specific action that leaves other organisms mainly unaffected. The bacterium produces parasporal crystal proteins called  $\delta$ -endotoxins, also known as 'Cry' and 'Cyt' proteins, that exhibit toxicity towards a broad spectrum of insect pests, including Lepidoptera, Coleoptera, and Diptera. Around one thousand toxin genes encoding entomopathogenic protein toxins have been discovered and studied in Bt strains collected from various geographic areas.<sup>252</sup>

Another important example of microbial pesticides, also approved by the EPA, is the entomopathogenic fungus *Metarhizium anisopliae*.<sup>249</sup> It has a broad spectrum of activity against arthropod hosts while remaining safe for the crops and the environment.<sup>253,254</sup> A wide range of strains and isolates of *M. anisopliae* can be found in moist soil environments that promote filamentous growth and the generation of infectious spores known as conidia.<sup>254</sup> The infection begins with the adherence of conidia to the insects residing in the soil upon direct contact, followed by conidia germination. Subsequently, the generated germ tubes differentiate to form the appressorium (highly specialised infection cell), used to penetrate the host cuticle. Once the fungus overcomes the epidermis, it colonises the insect's hemolymph (body fluids), extrudes hyphae, and sporulates, killing the host. This whole process is completed in about five days under optimal conditions.<sup>255,256</sup>

Biochemical pesticides are mostly designed to work through non-toxic mechanisms, although this category can include natural toxins. In contrast to conventional pesticides, this type of pest control does not rely on harming the pests but rather on repelling or attracting them into traps. For example, more than 1600 insect pheromones are currently used as 'semiochemicals'

(chemical signals used between organisms), to affect the mating patterns of insects, either by disrupting them or by triggering them to search for a sexual partner instead of laying eggs and aggregating.<sup>249,257</sup> This mode of diverting insects away from crops has several benefits, like lower costs, ease of use, and high selectivity and sensitivity.<sup>254</sup>

Essential and vegetable oils sourced from plants have been used as insect repellents, attractants, and contact pesticides since ancient times because they are widely accessible, affordable, rapidly biodegradable, and safe for mammals.<sup>258</sup> However, their mode of action is not fully understood. For example, eggs of the two-spotted spider mite *Tetranychus urticae*, when covered with vegetable oil, did not suffocate as commonly supposed, but hatching larvae were hampered.<sup>259</sup>

Commercially available botanical pesticides are mainly isolated from neem *Azadirachta indica*, chrysanthemum *Tanacetum cinerariifolium*, tobacco *Nicotiana tabacum*, ryania *Ryania speciosa*, and sabadilla *Schoenocaulon officinale*. They primarily target insects and plant parasites like nematodes, fungi, bacteria, and viruses.<sup>258</sup>

Plant-incorporated protectants (PIPs) are classified as the third category of biopesticides by the EPA, but remain unrecognised by most international authorities.<sup>251</sup> PIPs refer, in particular, to genetically modified (GM) crops that can produce pesticide substances by themselves through rDNA technology. This method relies on the insertion of genetic material endowed with the capability to introduce substances for natural defence into the designated plant's genome. Dating back to the 1980s, the first reported PIPs were Cry proteins expressed in GM crops containing Bt transgenes. Ever since, many Bt crops have been established, the majority of which are cotton and corn genotypes.<sup>249,260</sup> Additionally, a new generation of PIPs has recently been registered, consisting of GM crops that protect themselves by expressing double-stranded RNA (dsRNA).<sup>261</sup> This method is called host-induced gene silencing (HIGS) and is based on RNA interference (RNAi), a form of post-transcriptional gene silencing described initially by Fire *et al.* in 1998.<sup>262</sup> The mode of action is as follows: dsRNA molecules enter the insect's body *via* the plant, where an endoribonuclease enzyme, Dicer, cleaves the dsRNA into smaller RNA fragments. These fragments are then incorporated into the RNA-induced silencing complex (RISC) by the protein Argonaute. RISC is directly responsible for silencing essential genes for pest survival.<sup>261,263</sup> HIGS is a transgenic delivery system that can also improve inherent plant defence qualities.<sup>264</sup> The first RNAi crop that was approved by EPA, in 2017, SmartStax PRO by Bayer AG, targets the corn rootworm *Diabrotica virgifera* by expressing dsRNA that interferes with the synthesis of one of its essential vacuolar sorting proteins.<sup>260,265</sup>

RNAi-based pest control was first studied in beetles and moths, where the genes responsible for insect development and survival were targeted for suppression (Fig. 13).<sup>266,267</sup> However, most earlier experiments injected dsRNA into insects to study the resulting gene expression.<sup>268–271</sup> In terms of commercial pest control, it is more practical if the pest takes up the dsRNA autonomously.<sup>272</sup> Spray-induced gene silencing (SIGS) is a



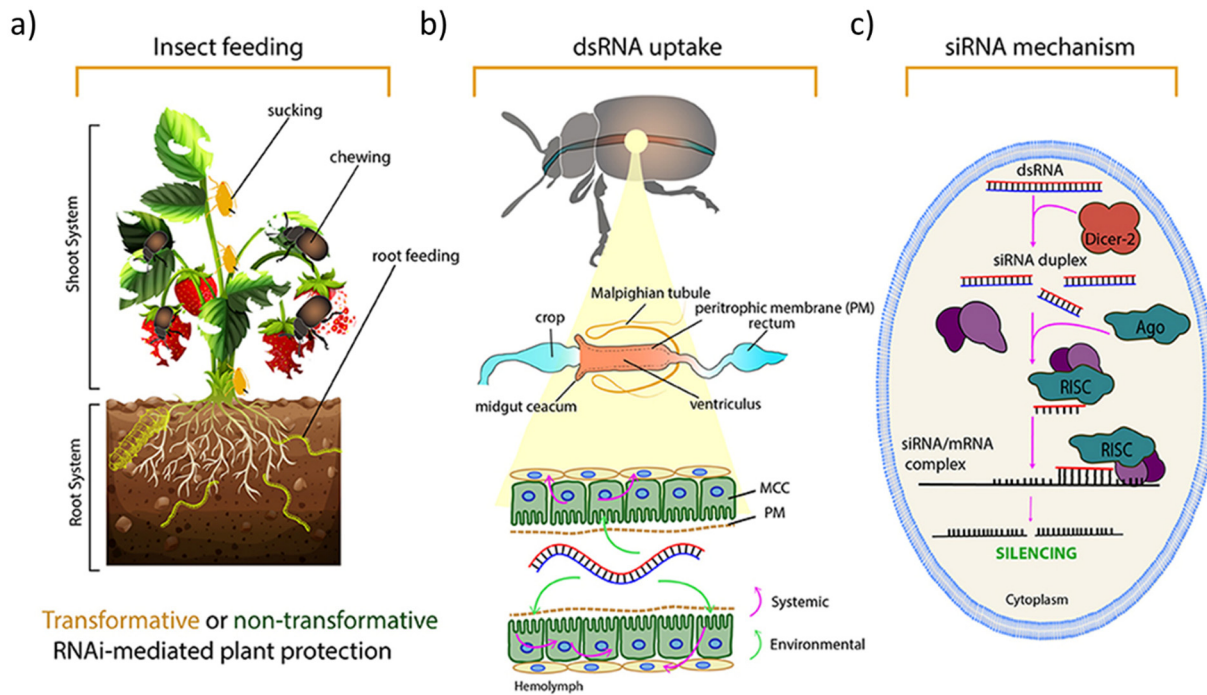


Fig. 13 The steps involved in RNAi-based pest control. (a) Ingestion of dsRNA by insects. (b) Uptake of dsRNA by the microvilli of the columnar cells (MCC) in the insect midgut. (c) Mechanism of gene silencing. Reproduced under the terms of a Creative Commons Attribution License.<sup>276</sup> Copyright 2016, Joga *et al.*

non-transgenic strategy for delivering dsRNA *via* a foliar spray, root irrigation, trunk injections, or seed dressings, whereby insects acquire it through plant feeding and chewing.<sup>264,273</sup> Oral delivery of dsRNA has been successful in a number of organisms, such as the western corn rootworm, striped flea beetle, and cotton bollworm.<sup>272</sup> Although uptake by oral ingestion shows great potential, the efficiency of RNAi may be heavily influenced by the environment it has to travel through, such as the pH and the presence of enzymes in the insect gut region, depending on the insect species.<sup>274</sup> In a study with locusts and small mottled willow moths, dsRNA strands were incubated in the digestive fluids. While the dsRNA degraded quickly in the fluid from locusts, it was successfully incorporated in moths fluid. Although the pH of both fluids varies in locusts and moths (pH 6.8 *vs.* 8.8), it was hypothesised that the degradation of the dsRNA strands is due to the nuclease enzymes present in the locust fluids. A deactivation of these enzymes by heating resulted in a significant reduction in the degradation of dsRNA.<sup>274</sup> In the case of lepidopteran insects where RNAi oral ingestion was previously unsuccessful due to the gut enzymatic activity, Parsons *et al.* developed inter-polyelectrolyte polymer-dsRNA complexes to protect the dsRNA strands in the gut.<sup>275</sup> Poly-[*N*-(3-guanidinopropyl)methacrylamide] (pGPMA), a synthetic cationic polymer, was shown to form complexes through electrostatic interactions with the negatively charged RNA backbone. Apart from enhancing the stability of the RNA strands, these complexes also protect them from enzymatic degradation since pGPMA is a weak acid, which prevents dissociation of the complexes in an alkaline gut environment (pH 10–11) of the insects.<sup>275</sup>

Further research in RNAi has revealed many other novel dsRNA delivery strategies, such as the usage of modified viruses (virus-induced gene silencing: VIGS), or *via* modified microorganisms like bacteria, yeast, and fungi.<sup>276–278</sup> A bottleneck regarding such pest control techniques is the necessity of substantial quantities of dsRNA for field applications. Being an evolving field of research, an engineered bacterium was developed by biotechnology company RNAgri (formerly Apse), called RNA Containers™ (ARCs) which can mass produce dsRNA for target applications.<sup>276</sup>

In summary, there is a wide range of non-chemical methods of pest control, such as mineral powders like kaolin, which work by desiccating pests, and bioinspired surfaces that mimic natural plant defences, like trichomes, to trap pests. Pest repellence strategies include mechanical, thermal, and acoustic methods, while biopesticides can be derived from natural sources like microorganisms, plants, and animals. All these innovations contribute to environmentally friendly and bioinspired pest control approaches, offering potential strategies to replace traditional chemical solutions.

## 6. Future perspectives

While navigating the complexities of modern agriculture, it is evident that substantial efforts are necessary to transition towards optimised innovative pest management to ensure food safety and compliance with stricter legislation surrounding the currently used synthetic pesticides. IPM (and ICM) are key



concepts towards creating a sustainable agriculture. Despite much progress, more remains to be done.

The future of chemical strategies in IPM looks promising as researchers continue to explore environmentally friendly solutions. There has been notable research and advances to reduce the loss of synthetic pesticides and to control release rates over time. For instance, the humidity-responsive pesticide Seltima demonstrates how controlled-release formulations can improve efficacy while minimising environmental impact.

Physical, cultural, and biological control strategies are also being judiciously explored. Traditional methods continue to evolve alongside novel techniques. New research domains are focusing on developing pesticides that are selectively toxic to target pests. One such promising concept is chemical genetics, where small molecules are used to elicit biological action. After this concept initially emerged in biology and therapeutics, it is now explored in targeted pesticide development.<sup>279,280</sup> It is known that one of the various mechanisms that pesticides use to control pathogens is the disruption of key proteins that are vital for their growth, reproduction, or metabolism.<sup>281</sup> Hence, investigating ligand binding and other active sites of these essential proteins is an important step toward understanding the common molecular target structures that could be exploited when designing new pesticides.<sup>280</sup> Computational modelling is also an upcoming field in agriculture, with potential for predicting environmental impact and toxicity of organic pesticides include pesticide loss and drift.<sup>282</sup> However, its use in material design for plant protection, such as for screening novel compounds, is still in its early stages.<sup>283</sup>

In parallel, there are several promising commercial products entering the market which have similarities to natural plant defence mechanisms. For example, Eradicoat, a maltodextrin-based contact pesticide, suffocates pests by forming a coating around them, upon spraying and drying.<sup>284</sup> This mode of action closely resembles how resin ducts and trichome exudates trap and suffocate pests. Agrical Pro is another such mechanical pesticide, based on clay, which creates a white inert layer on plants that acts as a visual barrier to insects, thereby using camouflage as a defence strategy.<sup>285</sup> Dezone, a diatomaceous earth-based mechanical pesticide, dehydrates insects by sticking to their cuticle and absorbing their protective lipid layer.<sup>286</sup> This mechanism mirrors the defence strategy provided by plant epicuticular wax crystals. Given their mechanical modes of action, such innovations reduce the risk of pesticide resistance and pose minimal risks to human health and the environment.

Despite these advances, there remains a gap between the wealth of knowledge about pest control in nature and the development of bioinspired techniques, which could aid in advancing other IPM domains. While some biochemical strategies are exploited, many others remain underexplored. The primary challenge in developing practical and effective synthetic chemical-free methods is their limited suitability for commercial applications due to being overly time or labour-intensive. Most mechanical pesticides also still require further research to effectively target specific pests without adverse effects to beneficial insects. Adhesive pesticides that mimic

trichomes, for example, could potentially achieve this specificity by tuning the size and adhesive strength of the particles, much like how predatory insects navigate around trichomes in nature. It can also be inferred from our review that plant structures may play a role in shaping such pesticide innovations. While not many direct studies have explored linking plant morphology to improved adhesion or alternative delivery systems, this presents an intriguing research opportunity. For instance, thorns on the stem could potentially puncture vesicles, triggering the release of active compounds. We believe there lies an opportunity to draw inspiration from nature and introduce biomimetic approaches to enhance IPM strategies further.

Moving forward, efforts to address this challenge should focus on bridging the gap between plant biologists, agricultural scientists, chemists, material scientists, farmers, and policy-makers to foster innovative, interdisciplinary solutions. Furthermore, commercialisation prospects and potential challenges must be critically assessed including the cost-effectiveness of new materials, the feasibility of large-scale manufacturing, and the long-term impact on the environment and human health. Regulatory frameworks also play a pivotal role in shaping the adoption of innovative pest control solutions. Currently, pesticides have to undergo a rigorous authorisation process in the EU before being used commercially.<sup>287</sup> Policymakers have the power to facilitate the transition to sustainable IPM by restricting the usage of non-biodegradable chemicals while supporting research initiatives, streamlining approval processes for safer alternatives, and promoting farmer education programmes to encourage widespread adoption. For example, Switzerland's IP Suisse initiative introduced a voluntary, pesticide-free production scheme for cereals, like wheat, spelt, and rye. It combines both private market incentives such as a 30% price-mark up by bakeries, with government support such as direct payments to farmers for adopting pesticide-free practices. This programme is part of Switzerland's broader efforts to balance environmental and economic interests in farming.<sup>288</sup>

Ultimately, the future of IPM may be in creating non-toxic strategies to human health, specific to target pests that cause no harm to non-target organisms, do not contribute to pesticide resistance over time, and are both environmentally friendly and cost-effective. They should complement and be easily incorporated into existing IPM strategies. By embracing collaboration, innovation, and a commitment to sustainability, we can pave the way for a future where agricultural pest control harmonises with nature and contributes to a healthier and more resilient food system.

## Abbreviations

Bt	<i>Bacillus thuringiensis</i>
Cat	Catechol
CO	Castor oil
Cry protein	Crystal protein



Cyt protein	Cytolytic protein
DDAB	Didecyltrimethylammonium bromide
DDT	Dichloro-diphenyl-trichloroethane
DHBA	2,3-Dihydroxybenzoic acid
dsRNA	Double-stranded RNA
EPA	U.S. Environmental Protection Agency
Glyphosate IPA	Glyphosate-isopropylammonium
GM	Genetically modified
HIGS	Host-induced gene silencing
HSCs	Hat-shaped carriers
ICM	Integrated crop management
IPM	Integrated pest management
LC	Lambda-cyhalothrin
MCC	Microvilli of the columnar cells
MOF	Metal-organic framework
mRNA	Messenger RNA
O-CMCS	O-Carboxymethyl chitosan
PEO	Polyethylene oxide
pGPMA	Poly-[N-(3-guanidinopropyl)methacrylamide]
PIPs	Plant incorporated protectants
PTFE	Polytetrafluoroethylene
PU	Polyurethane
RISC	RNA-induced silencing complex
RNAi	RNA interference
SEM	Scanning electron microscopy
SIGS	Spray-induced gene silencing
VIGS	Virus-induced gene silencing

## Author contributions

Abinaya Arunachalam: conceptualisation, visualisation, writing – original draft, writing – review & editing; Maria Perraki: writing – original draft; Bram Knegt: writing – review & editing; Mirka Macel: writing – review & editing; Dagmar Voigt: writing – original draft, writing – review & editing; Marleen Kamperman: conceptualisation, visualisation, writing – review & editing, supervision, funding acquisition. All authors have given approval to the final version of the manuscript.

## Data availability

No primary research results, software or code have been included and no new data were generated or analysed as part of this review. Any cited data can be found in the relevant citations.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

The authors would like to thank the Dutch Research Council (NWA.1160.18.071) for their financial support. Dagmar Voigt's

contribution was funded by the German BMEL project LEADER (FKZ 28A8706B19). The authors also thank Katarzyna Heilman for immense support in creating the graphical abstract and Fig. 1, 7 and 12. Special thanks to Diederik Rep for his editorial support.

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